https://doi.org/10.1144/geoenergy2024-002 | Vol. 2 | 2024 | geoenergy2024-002

Natural hydrogen: sources, systems and exploration plays

Owain Jackson[1], Steve R. Lawrence[2], Ian P. Hutchinson[2]*, Andrew E. Stocks[2], Andrew C. Barnicoat[2] and Mike Powney[1]

[1] H2Au, Global House, 1 Ashley Avenue, Epsom, Surrey KT18 5AD, UK
[2] Natural Hydrogen Study Group (NHSG), Chiltern House, 45 Station Road, Henley-on-Thames, Oxfordshire RG9 1AT, UK
OJ, 0009-0005-0259-5460; SRL, 0009-0001-3725-742X; IPH, 0000-0003-1380-1483; AES, 0009-0003-2072-580X; ACB, 0009-0006-2744-0251; MP, 0009-0003-6463-6059
* Correspondence: ian.hutchinson@nhsgconsultants.com

Abstract: Several sources of natural hydrogen are known or postulated but the process of serpentinization, the action of water on ultramafic rocks, is shown to be the most effective. Studies indicate that the rates and volumes generated by high-temperature serpentinization, (i.e. in the temperature range of 200–320°C), could feed a focused hydrogen system potentially capable of sealing and trapping gas-phase hydrogen in commercially-sized accumulations.

Natural hydrogen is generated by serpentinization wherever ultramafic rocks can be penetrated by aqueous fluids. This includes diverse geotectonic settings ranging from divergent and convergent plate margins to intra-plate orogenic belts and Precambrian cratons.

The 'hydrogen system' describes the generation, migration and sealing/trapping of hydrogen. There are two parts to the 'generic hydrogen system': the 'source-generation sub-system' requires an ultramafic protolith, usually in basement, and a supply of water penetrating basement rocks. In the 'migration-retention sub-system' migration, sealing and entrapment of gas-phase hydrogen behaves the same as for hydrocarbon gases.

The hydrogen system by serpentinization is used to develop play models to guide exploration in the accessible and exploitable geotectonic settings of continental cratons, ophiolites and convergent margins.

Thematic collection: This article is part of the Hydrogen as a future energy source collection available at: https://www.lyellcollection.org/topic/collections/hydrogen

Received 4 January 2024; **revised** 7 March 2024; **accepted** 12 March 2024

Hydrogen occurs as a free gas in nature. It is generated in large volumes at mid-oceanic ridges (Worman *et al.* 2016) and is actively seeping to surface in ophiolite terrains (Ellison *et al.* 2021; Leong *et al.* 2023). The significance of natural hydrogen (sometimes referred to as 'gold' or 'white' hydrogen) is that, if found in commercially exploitable quantities, it could ultimately replace oil and gas as a primary energy source. Hydrogen is more mobile in the subsurface than other naturally-occurring gases (with the exception of helium) and this together with its reactivity has led to the popular belief that hydrogen will not accumulate in commercial volumes (Gaucher 2020; Zgonnik 2020; Truche *et al.* 2024). At Bourakebougou in Mali up to 98% hydrogen has been discovered in shallow carbonate reservoirs (Prinzhofer *et al.* 2018; Maiga *et al.* 2023, 2024). Official reserve volumes have not been released for Bourakebougou so it remains to be proven that hydrogen can occur in sufficient volumes and reservoir pressures to constitute a commercially viable subsurface resource. Indeed, the commerciality of hydrogen resources is still to be established.

The discovery at Bourakebougou was serendipitous (a well drilled for water in 1987) but it has provided a spur to the deliberate search for exploitable natural hydrogen reserves (Gaucher 2020). As a result, exploration is currently active in Africa, South America, Australia, USA, France and Spain (Stalker *et al.* 2022; Hand 2023). Thus far exploration has mainly adopted a 'top-down' approach which involves exploring in the vicinity of known hydrogen surface or well occurrences, or searching for surface signs of hydrogen through geomorphic features (e.g. fairy circles) and soil sampling (Moretti *et al.* 2021). In this paper we describe a 'bottom-up' or 'play-based' approach which adopts concepts and methodologies used successfully in petroleum exploration. This is based on an understanding of the *hydrogen system* and the development of play-based models that can be used in the exploration for commercial hydrogen reserves. We describe exploration models for the accessible and potentially exploitable geotectonic settings of continental cratons, ophiolites and convergent margins.

Sources of natural hydrogen

Several sources of natural hydrogen are known or have been postulated (e.g. Klein *et al.* 2020; Wang *et al.* 2023). The two most ubiquitous geological processes producing hydrogen are:

- The breakdown of water by natural radioactivity (radiolysis) (Lin *et al.* 2005; Warr *et al.* 2019).
- Water-rock interactions involving the reduction of water by the oxidation of Fe^{2+}-bearing minerals (e.g. Sleep *et al.* 2004; McCollom *et al.* 2016).

For exploration to result in commercially exploitable hydrogen resources the source should be capable of generating hydrogen at rates and volumes that allow sufficient focusing of migration in time and space to charge accessible traps. For purposes of assessing relative source capability indicative rates and volumes of hydrogen produced, based on theoretical and experimental work, are presented below.

Due to the half-life of the typical radiolytic elements such as U, Th and K, radiolysis can be seen to operate over billions of years (Lin *et al.* 2005; Warr *et al.* 2019). A rate of hydrogen production by radiolysis of 1.9×10^{-9} Bcf km^{-3} yr^{-1} (Bcf per km^3 of protolith per year) at standard temperature and pressure (STP) has been calculated from figures presented by Warr *et al.* (2019) for Precambrian Shield rocks.

The best-understood water–rock interaction reaction is serpentinization where the Fe^{2+} is contained in olivine of ultramafic rocks. Ultramafic rocks contain no free quartz, and the creation of serpentine from the Mg-olivine component consumes aqueous silica while the coupled breakdown of the iron component of the olivine produces magnetite and hydrogen.

$$\begin{aligned}&Mg_2SiO_4(\text{olivine}) + SiO_2(\text{aq}) + 4H_2O\\ &\leftrightarrow 2Mg_3Si_2O_5(OH)_4(\text{serpentine})\end{aligned}$$

$$\begin{aligned}&3Fe_2SiO_4(\text{olivine}) + 2H_2O \leftrightarrow 2Fe_3O_4(\text{magnetite}) + 3SiO_2(\text{aq})\\ &\qquad + 2H_2(\text{aq/gas})\end{aligned}$$

As silica and hydrogen are on the same side of the Fe-endmember reaction, a decrease in one of them results in the other increasing if other parameters remain fixed. Silica consumption by the dominant Mg-olivine reaction thus drives the Fe-olivine subreaction to the right, generating higher hydrogen activities (Lazar 2020).

Simply put, the more silica in solution in the system the more the serpentinization reaction will be restricted, and hydrogen generation decreased. Serpentinization is therefore a very efficient hydrogen producer and is known to be generating natural hydrogen at significant rates and volumes along mid-oceanic ridges (Worman *et al.* 2016).

The rate of hydrogen production calculated for serpentinization at STP (based on McCollom *et al.*'s (2016) experimental work using crushed olivine at 300°C/35 MPa with water/rock ratios of 1.6–2.6) is 182 Bcf km^{-3} yr^{-1}. For comparison we modelled methane gas expulsion rates of 4.8×10^{-3} Bcf km^{-3} yr^{-1} for a typical hydrocarbon source rock (TOC 5%, mixed type II/III kerogen, at a temperature of 180°C, using the Kinex software).

A total yield calculated for serpentinization of peridotite (80% olivine) at 200°C is 0.9 Bcf km^{-3} (based on Klein *et al.*'s 2013 thermodynamic modelling up to 400°C/50 MPa with a water/rock ratio of 1.0). Although the derivation of the figures for rates and yield volumes are not comparable, they serve to demonstrate the relative speed of serpentinization and the ultimate commercial hydrogen volume capacity of serpentinization as a source. In geological situations the duration of serpentinization events will be extended by the inefficiency of the water–rock interaction but they are still expected to be short-lived. Skelton *et al.* (2005) estimated the duration of a passive margin serpentinization event to be between 100 000 and one million years.

Other potential iron oxidation sources include siderite deposits, biotite and peralkaline granites, and iron formations. Rates of hydrogen formation from these sources have not been quantified but there are factors that diminish their suitability (relative to serpentinization):

- Siderite generates more CO_2 than hydrogen (McCollom 2003), undesirable both for the presence of CO_2 and the mixture's propensity to bacterial hydrogen consumption.
- Due to their quartz content, creating conditions of high silica activity relative to mafic rocks, biotite and peralkaline granites create less reducing conditions than serpentinization leading to lower hydrogen production.
- Iron formations react with water but due to buffering by haematite and magnetite the reaction conditions will be less reducing, and consequently, hydrogen yields per unit volume of source rock will be much less than those of serpentinization (Malvoisin and Brunet 2023).

The conclusion is that serpentinization is the most effective and hence important subsurface process for producing and focusing gas-phase hydrogen in potentially commercial volumes. Serpentinization is confined to ultramafic geo-bodies at the point of water interaction and effective enough to constitute a significant 'point-source' in time and space. Understanding the serpentinization 'hydrogen system' therefore, becomes the key to exploration for exploitable reserves.

The hydrogen system (serpentinization)

The 'hydrogen system' is introduced as an analogue to the 'petroleum system' used to understand petroleum generation and migration (Magoon and Dow 1994). However, two important differences are highlighted (Fig. 1):

- In the hydrogen system the source rock (or protolith) will usually be located in basement rocks and geologically-separate from the sediments it will migrate through. The petroleum source rock is within the basin and the petroleum system forms part of the basin dynamic.
- Hydrogen generation by serpentinization can be considered geologically 'instantaneous'. Hydrocarbons are generated from petroleum source rocks over a millions to 10's of million of years (Tissot and Welte 2013).

The '***Generic Hydrogen System'*** (serpentinization) is presented in the form of two linked sub-systems (Fig. 2).

Source-generation sub-system

The protolith, water supply and reaction

Serpentinization is a metamorphic reaction whereby water hydrates olivine (and/or pyroxene) contained within ultramafic rocks (the

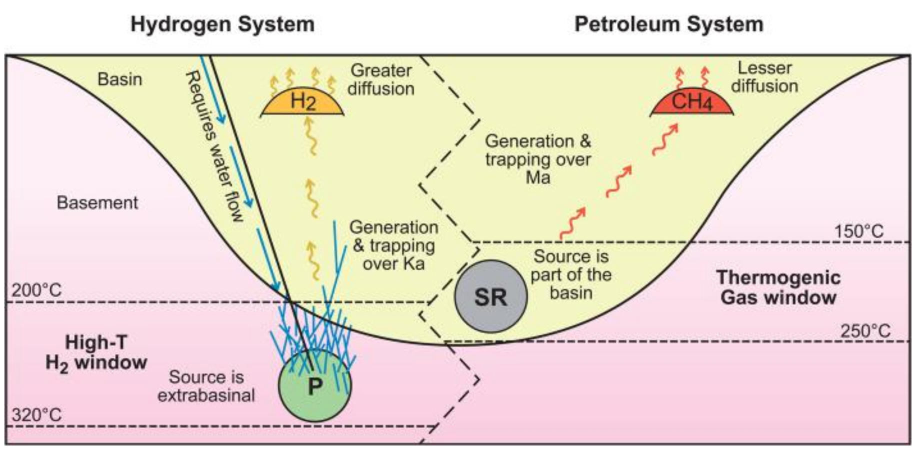

Fig. 1. Hydrogen system v. petroleum system. A comparison of fluid systems highlighting differences in the nature and location of the source with respect to the host sediments. SR, petroleum source rock; P, protolith.

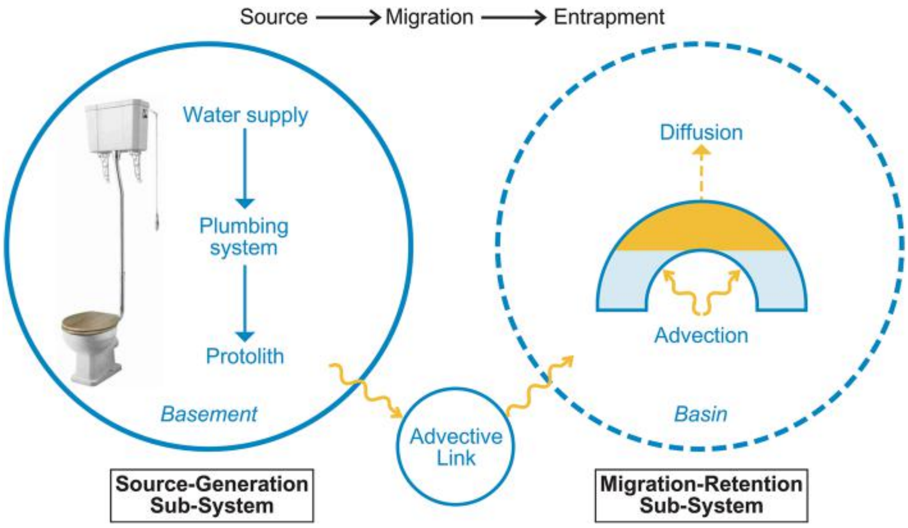

Fig. 2. The 'generic hydrogen system' (serpentinization). Showing sub-systems depicting source protolith in basement with water supply, the advective link and migration, sealing and accumulation in basin sediments.

'protolith') (Sleep *et al.* 2004; Evans *et al.* 2013). The key aspect of the reaction is the oxidation of ferrous to ferric iron by the reduction of water to hydrogen:

$$3FeO_{(silicate)} + H_2O = Fe_3O_4 + H_2$$

Geochemical modelling has shown serpentinization to be highly effective at generating low oxygen activities and high hydrogen activities (McCollom *et al.* 2016; Lazar 2020). The main controls on serpentinization, and the rates and volumes of hydrogen production, are: petrological composition of the protolith, olivine composition (Fe v. Mg), grain-size, temperature and water–rock ratio (see McCollom *et al.* 2022; Hutchinson *et al.* 2024 and references therein). Although serpentinization can take place over a broad range of temperatures, experiments have shown that the range for optimal hydrogen production is between 200 and 300°C (Klein *et al.* 2013; McCollom *et al.* 2022). Here we designate this as 'high-temperature' serpentinization.

In nature the water supply for serpentinization can be provided by seawater, meteoric (groundwater) or subduction-related aqueous fluids. Both the source and the nature of the plumbing system (allowing water access to the protolith), are specific to the geotectonic setting (see below). The rate of water supply and the degree of accessibility to the protolith (i.e. efficiency of the plumbing system) are critical for the focusing potential of the source (expressed as 'flush v. trickle'). The timing of the interaction could also be important in terms of the ultimate resource potential. If serpentinization is triggered 'late' (i.e. in the last few thousand years) there is a chance that the resource is replenishable as has been suggested in the case of Bourakebougou (Prinzhofer *et al.* 2018; Maiga *et al.* 2023).

Generation and expulsion

Given the depths envisaged for high-temperature serpentinization and the solubility of hydrogen, the hydrogen escaping the protolith is more likely to be in aqueous solution. In a detailed study, Lazar (2020, figure 12) shows that while hydrogen activities will not exceed its solubility at higher temperatures, gas-phase hydrogen is expected to form at temperatures below about 250°C. Therefore, depending on the temperature (and depth) of serpentinization, hydrogen may be generated *in situ* as a gas-phase ($T < 250$°C) or in solution in an aqueous phase. Lazar (2020) demonstrates that dissolved gas can be expected to exsolve when the temperature drops below 250°C at 2 kbar. The impact of pressure on these equilibria is not well understood, but Lazar's work suggests that hydrogen activities controlled by serpentinization decrease (relatively slowly) with increasing pressure which implies that lower temperatures would be required at greater depths to form a hydrogen-rich gas phase.

The effectiveness of the serpentinization reaction as a producer of hydrogen, v. other iron oxidation sources is driven by the higher hydrogen activities of serpentinization reactions. Higher hydrogen activities mean more hydrogen in solution at depth, and therefore less water to both drive the reaction, and to transport the hydrogen produced away from the reaction site. This effectiveness is due to higher saturations and a greater likelihood of gas-phase production in, or close to, the protolith.

In whatever phase, hydrogen expulsion from the protolith will be assisted by reaction-induced fracturing (Zhang *et al.* 2019; Renard 2021). The initial stages of serpentinization are accompanied by a volume increase leading to the development of a mesh-like vein network (Cannat *et al.* 2019). Fracturing may also occur after the earlier, mesh-textured serpentinization (Rouméjon *et al.* 2015). It is speculated that hydrogen expulsion may also be assisted by tectonic fracturing related to faulting. Often this will be the same fault-fracture system that allowed the water to get to the protolith. Some hydrogen may be expelled in solution in convection cells which can form within permeable fault zones linking basin and basement (Yang 2006). The 'advective link' (see Fig. 2) is formed by hydrogen moving with water in solution along fault-zones as described, and/or by gas-phase migration through basement fracture networks, where it could be trapped, or move into adjacent sediments.

Migration-retention sub-system

Migration

Once the hydrogen has gained access to sediments via the 'advective link', it will migrate through the porous medium by the same mechanisms as any gas (e.g. methane). These are:

- Advection in the gas-phase driven by pressure (buoyancy) and described by Darcy's Law.
- Advection in solution also driven by pressure gradients.
- Diffusion in solution at the molecular level, driven by concentration gradients and described by Fick's Law.

Gas advecting of diffusing in solution will exsolve and become gas-phase as maximum solubility levels are breached at lower temperatures and pressures (i.e. at shallower depths). Driven by buoyancy, advection in the gas-phase is the most efficient migration process and hydrogen is more mobile than methane (by a factor of two according to Lodhia and Clark 2022). Migration in the gas-phase is the important mechanism because migration in solution and subsequent exsolution at shallow levels, (as may be happening at Bourakebougou, see Maiga *et al.* 2023), could potentially limit the ultimate size of any accumulation due to low solubility of hydrogen and low reservoir pressures.

Sealing/trapping

As with methane, advective flow of gas-phase hydrogen will dominate up to the point where the capillary forces in the pores in low-permeability rocks become too strong to be overcome by the buoyancy pressure. Despite its greater buoyancy, hydrogen column heights, comparable to those of methane, can be retained by capillary forces beneath lithologies that typically form effective sealing formations (or aquicludes) for methane (Hutchinson *et al.* 2024). To reduce the risk of dilution by hydrocarbons during migration and accumulation it is preferable that the sediments are not hydrocarbon-saturated or mature for petroleum generation.

When advection ceases due to pore-throat size restriction (i.e. the gas can be considered sealed), molecular diffusion of dissolved hydrogen will take over as the migration mechanism. Diffusion coefficients for gases in pure water indicate that hydrogen is approximately 2.8 times more diffusive than methane at 25°C (Muhammed *et al.* 2022). The magnitude of diffusive loss (diffusion flux) is a function of the concentration gradients of the dissolved gases. The relatively low solubility of hydrogen compared to methane (methane is about 14 times more soluble than hydrogen at surface conditions, see Kaye and Laby 1986), will act to constrain diffusive losses of hydrogen and counter the impact of its high diffusion coefficient. There is therefore little risk of significant diffusive losses relative to the potential size of a commercial accumulation in a static (closed) system or to the rate of hydrogen influx in a dynamic (open) system (Monge and Vayssaire 2022), especially where thick and/or well indurated sealing formations are present.

In any gas accumulation, the seal can be breached if the buoyancy pressure overcomes the mechanical sealing strength of the rock. Hutchinson *et al.* (2024) show that maximum column lengths for hydrogen are only marginally shorter than those for methane (for a given contact depth).

Geotectonic settings of hydrogen production

Serpentinization of ultramafic rocks constitutes the most effective source of natural hydrogen for commercial accumulations. The protolith is an olivine-rich ultramafic rock, formed by elements of either lithospheric mantle or crust. A ready supply of water is required which, depending on the geotectonic setting, can be provided by seawater, meteoric water or subduction-related aqueous fluids. Active hydrogen production is observed at mid-oceanic ridges and in ophiolites, and can be postulated wherever serpentinization of ultramafic rocks can take place – note terrestrial olivine is always at least partially serpentinized. The dynamics of geotectonic evolution (Fig. 3) demonstrate that, with varying water sources, lithospheric rocks have been, and are, copious and continuous producers of hydrogen.

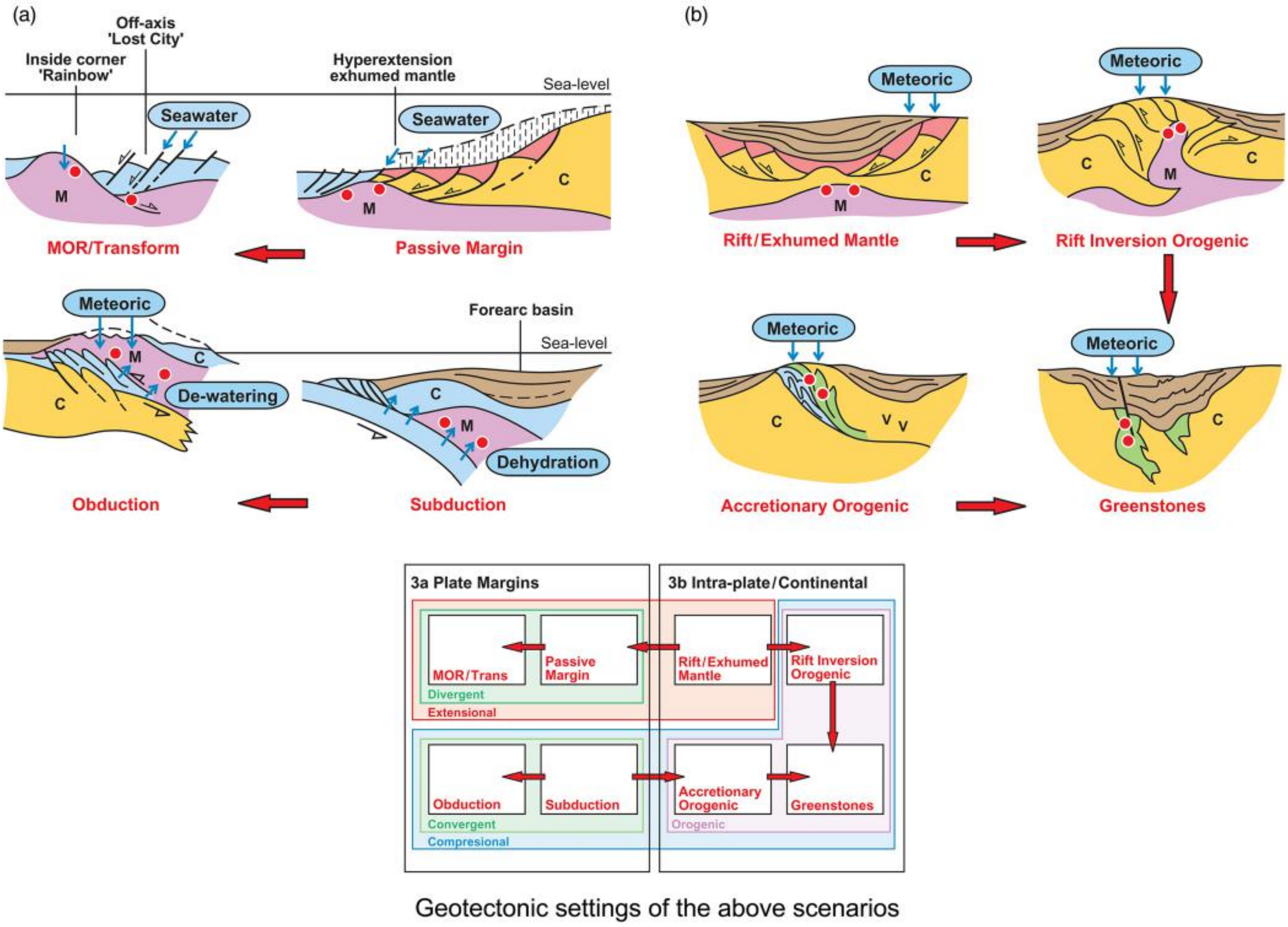

Fig. 3. Geotectonic settings of hydrogen production. Shows geotectonic settings of serpentinization and hydrogen generation. (**a**) Plate margin settings including divergent and convergent margins (ophiolites). (**b**) Intra-plate continental settings including intra-cratonic rifts, orogenic belts and greenstones. M, mantle; C, crust; red circles, serpentinization; blue arrows, water supply.

Plate margins

- Mid-oceanic ridges/transforms: serpentinization occurs at the axis of mid-oceanic ridges where mantle is directly exposed to seawater (e.g. inside corners of transform intersections) or where seawater can percolate down axial faults (Fig. 3a) (see Worman *et al.* 2016). Serpentinization also occurs along transform faults/fracture zones where faulting allows seawater access to the mantle (Rüpke and Hasenclever 2017).
- Passive margins: serpentinization of exhumed mantle can occur along hyper-extended passive margins (Fig. 3a). This is demonstrated by ODP drilling along the Iberian Margin (see Leg 103 Site 637) where mantle is at relatively shallow depths in the continent–ocean transition zone and rift faulting has allowed seawater access for serpentinization to take place (Albers *et al.* 2021).
- 'Cordilleran' ophiolites (subduction): in this scenario ophiolites are emplaced at convergent margins where the oceanic crust of the subducting plate is accreted to the upper plate (Fig. 3a). Along the Pacific margin of Central America ODP drilling has encountered serpentinized peridotites along the trench-slope (see Leg 84, Sites 566C, 567 and 570). In this case the protolith could either be accreted oceanic tholeiites (e.g. Nicoya Complex), or an upper-plate mantle wedge (e.g. Santa Elena Peridotite Nappe) as exposed onshore Costa Rica. Aqueous fluids are derived from the subducting slab by de-watering and metamorphic de-hydration in the subduction zone (see Vitale Brovarone *et al.* 2020).
- 'Tethyan' ophiolites (obduction): in this case oceanic crust-lithosphere, formed in a fore-arc or back-arc, (supra-subduction zone, SSZ), setting, has been obducted over a continental passive margin that has failed (or is failing) to subduct (Fig. 3a). Examples include Oman Mountains and New Caledonia where the ophiolite is exposed or at shallow depths and serpentinization is currently active due to the action of meteoric water (Mayhew *et al.* 2013; Ulrich *et al.* 2020; Ellison *et al.* 2021). Earlier, higher-temperature phases of serpentinization will have taken place during oceanic spreading and subsequent subduction/obduction.

Intra-plate – oceanic

- Deformed oceanic crust – lithosphere: serpentinization can occur where fault-structures (axial faults and fracture zones) in oceanic crust are reactivated by later deformation and allow seawater penetration to the lower crust/mantle. An example is provided by the actively deforming Central Indian Ocean where evidence for serpentinization includes low-velocity zones, crustal diapirs and elevated heat-flow (Delescluse and Chamot-Rooke 2008).

Intra-plate – continental

- Rift/exhumed mantle: in this scenario, hyperextended, intra-cratonic rifting brings continental lithospheric mantle closer to the surface (Fig. 3b). Such rifting usually represents incipient continental break-up and are strongly volcanic (e.g. the East African Rift System). Meteoric water can gain access to mantle rocks through rift faults extending close to the surface and rift-fill sediments provide a suitable host for hydrogen.
- Rift inversion orogenic ('Pyrenean'): this is an evolution of the rift setting where subsequent collisional tectonics has incorporated the exhumed mantle into an orogenic belt (Fig. 3b). The Pyrenees provides the archetype where meteoric water is accessing lherzolites at the surface or shallow depths (Lefeuvre *et al.* 2021). The generated hydrogen can access foreland basin sediments via long-range thrust faults on either side of the orogenic belt.
- Accretionary orogenic (ophiolites): these are formed where 'tethyan' or 'cordilleran' margins and their ophiolites are consolidated into an orogenic belt by continent–continent or arc–continent collisions (Fig. 3b). In this way, orogenic ophiolites are located along major tectonic suture zones. An example is presented by the Bou Azzer ophiolite situated along the northern margin of the West African Craton in the Anti-Atlas of Morocco (see Bousquet *et al.* 2008). Mountain belt precipitation can penetrate uplifted ophiolites and released hydrogen can access sediments occupying syn- or post-orogenic basins.
- Greenstones: greenstone belts are mega-scale components of the granite-greenstone terrains that make up Archean and Paleo–Proterozoic cratons (Anhaeusser 2014). They occur in cratons on every continent and often form the basement to younger cratonic basins. The igneous rocks of greenstones can be broadly equated to the oceanic mantle-crust sequences of Phanerozoic ophiolites (Furnes *et al.* 2015) and include peridotites, dunites and olivine-rich volcanic rocks called komatiites. Early phases of serpentinization are likely to have taken place during formation/deformation but many contain sufficient remnant olivine to activate later

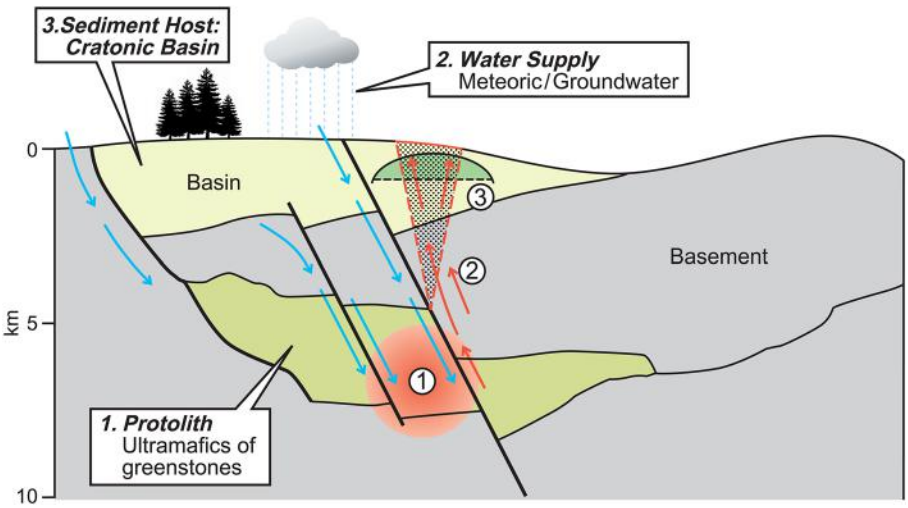

Fig. 4. Cratonic greenstone exploration model. Depicts serpentinization in greenstone protolith triggered by meteoric water supply and overlying host sediments of cratonic basin. (1) Zone of serpentinization reaction and hydrogen generation; (2) Advection and solution flow of hydrogen; (3) Sealing and trapping of gas-phase hydrogen (modified from Hutchinson *et al.* 2024). Blue arrows: groundwater; gold arrows: hydrogen.

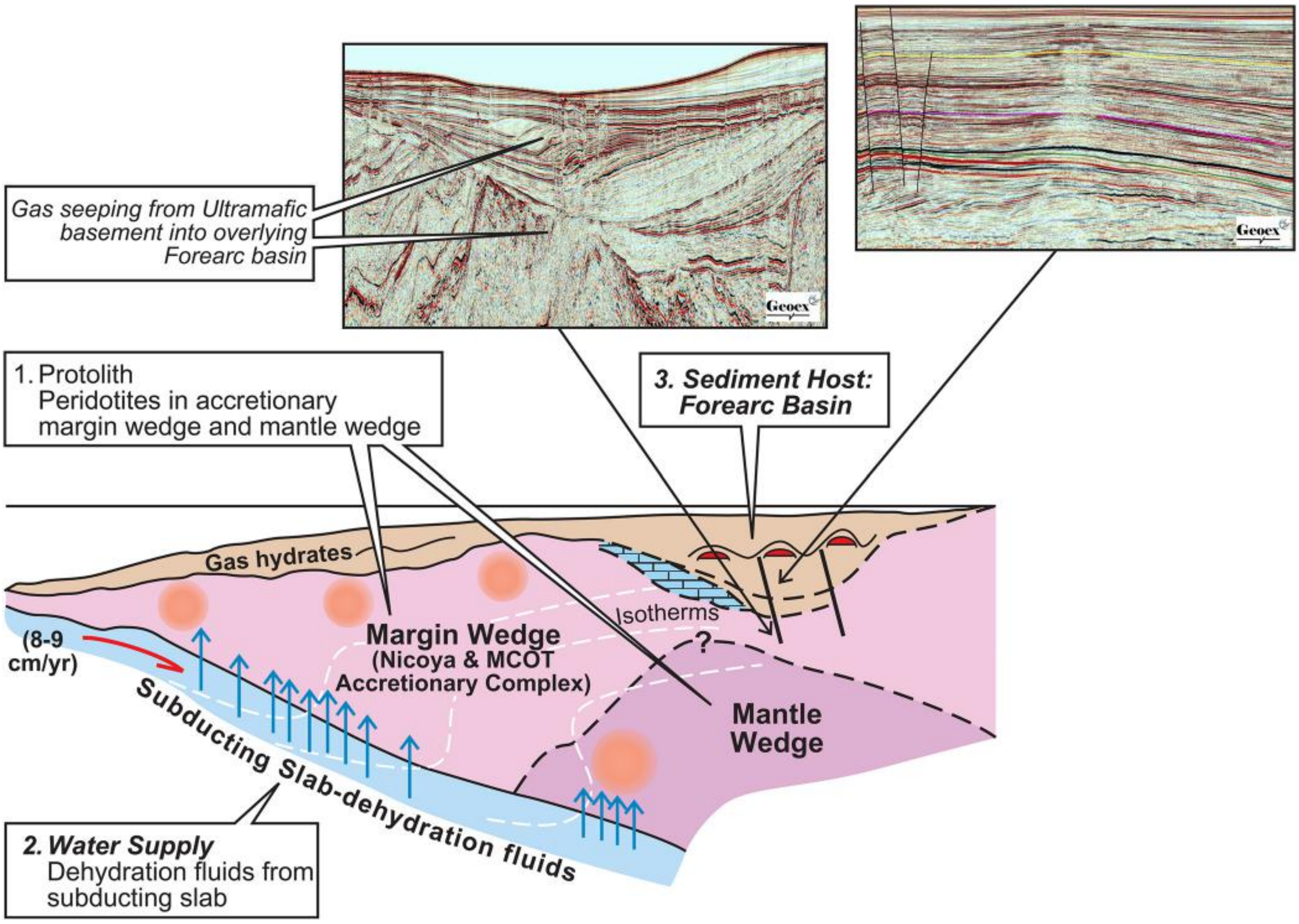

Fig. 5. 'Cordilleran' fore-arc basin exploration model. Protolith in supra-subduction zone with aqueous fluids derived from subduction zone. Based on Pacific margin of Central America and Sandino Fore-arc basin (modified from Sallarès *et al.* 2013). Seismic images from Nicaragua courtesy of Geox MCG.

phases of serpentinization by meteoric water penetration along re-activated faults.

Play-based exploration

The petroleum system provides information on the source-migration part of the 'source-migration-trap' paradigm and has been used to guide petroleum exploration since the 1970s/80s. The other useful, but older, concept is that of the 'exploration play' which recognizes the combination of geological conditions controlling the accumulation of petroleum in a particular province or cluster of oil/gas-fields (Allen and Allen 2005).

The hydrogen 'migration-retention sub-system' works in the same way as a gas-prone petroleum system. Although hydrogen is more mobile than methane it will be sealed by similar impermeable lithologies and can be retained in traps over geological time-frames. In addition, hydrogen has the potential for trap recharge where the serpentinization reaction is ongoing or recent. Trapping scenarios will be formed by the reservoir–seal (or aquitard-aquiclude) having a suitable structural or stratigraphic trapping configuration. In this regard hydrogen exploration can benefit from the knowledge gained from >100 years of petroleum exploration.

Investigation of the 'source-generation sub-system' requires knowledge from a range of geological disciplines including metamorphic and igneous geology, minerals/ore deposits geology and hydrogeology. This also presents opportunities in that a new set of diagnostic criteria become available for establishing first-order play elements. Here we use this approach to develop play-based exploration models for geotectonic settings deemed to be the most accessible for exploration and potential future exploitation.

Cratonic greenstone exploration model

In this model hydrogen is generated by the serpentinization of ultramafic rocks contained within Precambrian 'greenstones' (Hutchinson *et al.* 2024). It requires a supply of water (from groundwater), connecting faults to act as a plumbing system and a cratonic basin sediment cover to host hydrogen accumulations (Fig. 4). This model is based on the Bourakebougou discovery in Southern Mali (Prinzhofer *et al.* 2018; Maiga *et al.* 2023, 2024). Hutchinson *et al.* (2024) postulate a source protolith in Birimian greenstones below the Taoudeni Basin and serpentinization triggered by a water supply from groundwater percolating down neo-tectonically-active, basement-penetrating faults.

Greenstone belts have a recognizable outcrop pattern in the map domain but the key to protolith discrimination lies in the analysis of the available geological/petrological information to identify olivine-rich rock units. Where greenstones are located on the edge of cratonic basin cover, they can be extrapolated along strike under sedimentary cover using available geophysical data. With a high mafic/ultramafic rock content the dominant signature of greenstones will be a positive gravity response although this may be negated by the presence of associated less dense sediments and serpentinized igneous rocks (see e.g. Ranganai 2012). An additional diagnostic feature may be provided by the magnetic response of magnetite content produced by high-temperature serpentinization (Toft *et al.* 1990).

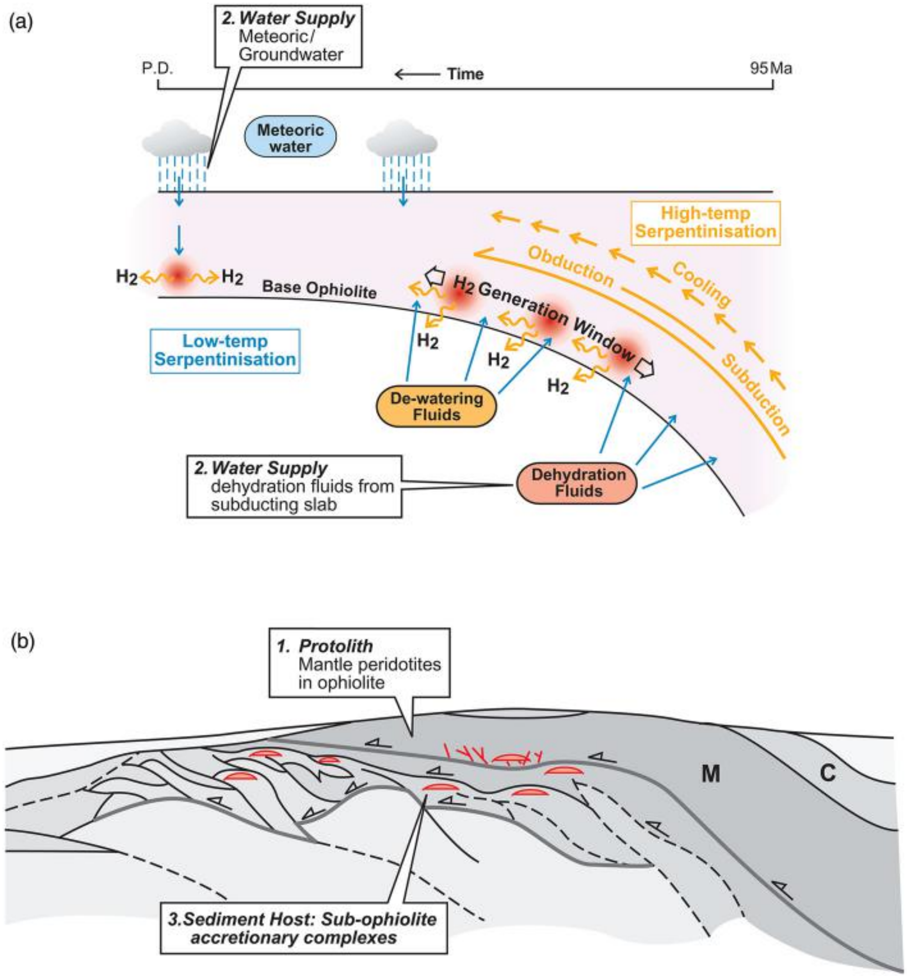

Fig. 6. 'Tethyan' ophiolite exploration model. (**a**) Time aspect showing 'early' and 'late' phases of serpentinization. (**b**) cross-section based on Oman Mountain ophiolites (after Tarapoanca *et al.* 2010) showing ophiolite and sub-ophiolite plays.

'Cordilleran' forearc basin exploration model

This model is based on the Sandino fore-arc basin offshore Nicaragua (Fig. 5). It is proposed that a hydrogen system is produced by subduction-related dehydration fluids interacting with ultramafic rocks underlying the basin. The supra-subduction basement has been shown to be dense rocks of accreted oceanic crustal rocks or 'mantle wedge' (Walther *et al.* 2000; Sallarès *et al.* 2013). Serpentinized peridotites have been encountered by ODP drilling along the trench-slope suggesting that the 'source-generation sub-system' has been effective below the fore-arc basin (von Huene *et al.* 2007). Seismic data show the effects of gas emanating from basement into the overlying fore-arc basin sediments (Fig. 5).

The basement terrain can be investigated by geophysics (seismic and potential field) for delineation of protolith geo-bodies. In the basin, exploration will follow a petroleum workflow but the risk of dilution by hydrocarbon gases generated within the basin has also to be assessed.

'Tethyan' ophiolite exploration model

The Semail Ophiolite was obducted during the Late Cretaceous and now occupies a large part of the surface outcrop of the Oman-UAE Mountains. Hydrogen gas is actively seeping at the surface either as a free gas or exsolving from spring-water (Leong *et al.* 2023). Hydrogen is shown to be largely the product of 'low-temperature' serpentinization by the action of groundwater (Ellison *et al.* 2021). However two ways of generating hydrogen by 'high-temperature' serpentinization are envisaged (Fig. 6):

'Late'-phase serpentinization

In this scenario hydrogen is generated in recent history by the action of circulating groundwater (Ellison *et al.* 2021). High-temperature serpentinization will depend on a major rock volume of mantle ophiolite reaching depths of >6 km (assuming a geothermal gradient of 30°C per km). Hydrogen generation would be dependent on meteoric water penetrating via faults or shear zones to the deeper parts of the ophiolite. Geophysically-constrained structural models are therefore important in determining the depth of the base ophiolites as well as the internal structure. With the recent generation it is likely that some of the hydrogen generated is trapped in sheared/mylonitised and serpentinized zones in the ophiolite (such as the basal 'Banded Ultramafic Unit' of Oman, see Searle *et al.* 2022), unless it is lost to the groundwater system (Leong *et al.* 2023).

'Early'-phase serpentinization

In this scenario, serpentinization and hydrogen generation is activated in the lower part of the ophiolite by water derived from de-hydration/metamorphism of subducting oceanic crust and/or de-watering of accretionary sub-ophiolite sediments (e.g. Hayti Complex and Hawasina of Oman) during obduction. Hydrogen generation would have been during the high-temperature conditions of subduction and/or obduction in the Late Cretaceous. It is expected that to be preserved over this time-scale hydrogen needs to have migrated into and sealed in sub-ophiolite rock units. In Oman Zgonnik *et al.* (2019) interpret the results of gas sampling and analysis in terms of a sub-ophiolite source of hydrogen. An alternative interpretation is that hydrogen has migrated 'downwards' into sub-ophiolite rock units from the ophiolite protolith. Some of the hydrogen sampled at surface in ophiolites in Oman, New Caledonia, Philippines and Turkey is interpreted by Vacquand *et al.* (2018) to have originated in earlier, hotter serpentinization episodes.

Conclusions

Serpentinization is a fast and effective metamorphic reaction triggered by water interacting with olivine-rich ultramafic rocks. It is a ubiquitous geological process known to occur in a range of geotectonic settings.

With modest water–rock ratios, high-temperature serpentinization (200–320°C) will generate gas-phase hydrogen in sufficient volumes and rates to constitute a prolific source.

The rate of hydrogen generation will depend on a variety of factors including the rate of water delivery ('trickle or flush') and the effective surface area of water–rock interaction ('grain-size'/permeability).

Serpentinization can be described as a 'point source' since ultramafic geo-bodies tend to be spatially confined and hydrogen generation will be concentrated at the site of water-protolith interaction.

The focusing of hydrogen generation in time and space is sufficient to feed a hydrogen system capable of concentrating gas-phase migration in potentially commercial volumes.

Depending on PT conditions (i.e. depth) hydrogen will be expelled from the protolith in the gas-phase or in solution. Dissolved hydrogen will exsolve to gas-phase when the PT decreases at shallower depths.

Despite its greater mobility, gas-phase hydrogen migration will be checked by impermeable formations and significant column heights can build under suitable seal/trapping conditions.

There will be some diffusive loss of hydrogen from trapped accumulations but, as with methane, this is not expected to be volumetrically significant. Hydrogen can therefore be retained in traps over geological time-scales.

If hydrogen generation is recent or current there is the possibility that traps are being actively charged resulting in a potentially replenishable resource.

Hydrogen can be explored for and exploited in the same way as hydrocarbon gases. Play elements are based on the protolith-water interaction regime specific to each geotectonic setting as illustrated in models for hydrogen exploration in the accessible geotectonic settings of continental cratons, ophiolites and convergent margins.

Acknowledgements The authors thank Geoex MCG for allowing the use of 2D seismic data from offshore Nicaragua. RAK Gas and Metatek are also thanked for workshop discussions on the hydrogen potential of the Semail Ophiolite of Oman/UAE. Jon Gluyas (University of Durham) and an anonymous reviewer are thanked for their useful and constructive comments.

This work was first presented as part of the Natural Hydrogen: A New Frontier for Energy Geoscience conference at the Geological Society, London, 4–5 July 2023.

Author contributions **OJ**: conceptualization (equal), formal analysis (equal), investigation (equal), resources (equal), validation (equal), writing – original draft (equal); **SRL**: conceptualization (equal), formal analysis (equal), investigation (equal), methodology (equal), resources (equal), validation (equal), writing – original draft (equal); **IPH**: conceptualization (equal), formal analysis (equal), investigation (equal), resources (equal), validation (equal), writing – review & editing (equal); **AES**: conceptualization (equal), formal analysis (equal), investigation (equal), methodology (equal), resources (equal), validation (equal), writing – original draft (equal); **ACB**: conceptualization (equal), formal analysis (equal), investigation (equal), resources (equal), validation (equal), writing – original draft (equal); **MP**: conceptualization (equal), formal analysis (equal), investigation (equal), resources (equal), validation (equal), writing – original draft (equal).

Funding This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

Competing interests The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability Data sharing is not applicable to this article as no datasets were generated or analysed during the current study.

References

Albers, E., Bach, W., Perez-Gussinye, M., McCammon, C. and Frederichs, T. 2021. Serpentinization driven H_2 production from continental break-up to mid-oceanic ridge spreading: unexpected high rates at the West Iberia Margin. *Frontiers in Earth Science*, **9**, https://doi.org/10.3389/feart.2021.673063

Allen, P.A. and Allen, J.R. 2005. *The Petroleum Play Basin Analysis: Principles and Applications*. Blackwell, Oxford, 405–493.

Anhaeusser, C.R. 2014. Archaean greenstone belts and associated granitic rocks – a review. *Journal of African Earth Sciences*, **100**, 684–732, https://doi.org/10.1016/j.jafrearsci.2014.07.019

Bousquet, R., El Mamoun, R., Saddiqi, O., Goffé, B., Möller, A. and Madi, A. 2008. Mélanges and ophiolites during the Pan-African orogeny: the case of the Bou-Azzer ophiolite suite (Morocco). *In:* Ennih, N. and Liegeois, J.-P. (eds) *The Boundaries of the West African Craton*. *Geological Society, London, Special Publications*, **297**, 233–247, https://doi.org/doi:10.1144/SP297.11

Cannat, M., Rouméjon, S., Momoh, E. and Leroy, S. 2019. Tectonic and magmatic controls on serpentinization at slow spreading mid-ocean ridges. *Geophysical Research Abstracts*, **21**, https://meetingorganizer.copernicus.org/EGU2019/EGU2019-12381.pdf

Delescluse, M. and Chamot-Rooke, N. 2008. Serpentinization pulse in the actively deforming Central Indian Basin. *Earth and Planetary Science Letters*, **276**, 140–151, https://doi.org/10.1016/j.epsl.2008.09.017

Ellison, E.T., Templeton, A.S., Zeigler, S.D., Mayhew, L.E., Kelemen, P.B. and Matter, J.M. 2021. Low-temperature hydrogen formation during aqueous alteration of serpentinized peridotite in the samail ophiolite. *Journal of Geophysical Research: Solid Earth*, **126**, https://doi.org/10.1029/2021jb021981

Evans, B.W., Hattori, K. and Baronnet, A. 2013. Serpentinite: what, why, where? *Elements*, **9**, 99–106, https://doi.org/10.2113/gselements.9.2.99

Furnes, H., Dilek, Y. and de Wit, M. 2015. Precambrian greenstone sequences represent different ophiolite types. *Gondwana Research*, **27**, 649–685, https://doi.org/10.1016/j.gr.2013.06.004

Gaucher, E.C. 2020. New perspectives in the industrial exploration of native hydrogen. *Elements*, **16**, 8–9, https://doi.org/10.2138/gselements.16.1.8

Hand, E. 2023. Hidden hydrogen. *Science*, **379**, 630–636, https://doi.org/10.1126/science.adh1477

Hutchinson, I.P., Jackson, O., Stocks, A.E., Barnicoat, A.C. and Lawrence, S.R. 2024. Greenstones as a source of hydrogen in cratonic sedimentary basins. *Geological Society London, Special Publication*, **547**, https://doi.org/10.1144/SP547-2023-39

Kaye, G.W.C. and Laby, T.H. 1986. *Tables of Physical and Chemical Constants and Some Mathematical Functions*. 15th edn. Longman & Co., New York.

Klein, F., Bach, W. and McCollom, T.M. 2013. Compositional controls on hydrogen generation during serpentinization of ultramafic rocks. *Lithos*, **178**, 55–69, https://doi.org/10.1016/j.lithos.2013.03.008

Klein, F., Tarnas, J.D. and Bach, W. 2020. Abiotic sources of molecular hydrogen on earth. *Elements*, **16**, 19–24, https://doi.org/10.2138/gselements.16.1.19

Lazar, C. 2020. Using silica activity to model redox-dependent fluid compositions in serpentinites from 100 to 700°C and from 1 to 20 kbar. *Journal of Petrology*, **61**, 461–499, https://doi.org/10.1093/petrology/egaa101

Lefeuvre, N., Truche, L. *et al.* 2021. Native H_2 exploration in the western Pyrenean Foothills. *Geochemistry, Geophysics, Geosystems*, **22**, e2021GC009917, https://doi.org/10.1029/2021GC009917

Leong, J.A., Nielsen, M. *et al.* 2023. H_2 and CH_4 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

Lin, L.-H., Slater, G.F., Sherwood Lollar, B., Lacrampe-Couloume, G. and Onstott, T.C. 2005. 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

Lodhia, B.H. and Clark, S.R. 2022. Computation of vertical fluid mobility of CO_2, methane, hydrogen and hydrocarbons through sandstones and carbonates. *Scientific Reports*, **12**, https://doi.org/10.1038/s41598-022-14234-6

Magoon, L.B. and Dow, W.G. (eds) 1994. The petroleum system. *The Petroleum System - From Source to Trap*. *AAPG Memoir*, **60**. American Association of Petroleum Geologists, Tulsa, Oklahoma, 3–24.

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

Maiga, O., Deville, E., Laval, J., Prinzhofer, A. and Diallo, A.B. 2024. Trapping processes of large volumes of natural hydrogen in the subsurface: the emblematic case of the Bourakebougou H_2 field in Mali. *International Journal of Hydrogen Energy*, **50**, 640–647, https://doi.org/10.1016/j.ijhydene.2023.10.131

Malvoisin, B. and Brunet, F. 2023. Barren ground depressions, natural H2 and orogenic gold deposits: spatial link and geochemical model. *Science of The Total Environment*, **856**, 158969, https://doi.org/10.1016/j.scitotenv.2022.158969

Mayhew, L.E., Ellison, E.T., McCollom, T.M., Trainor, T.P. and Templeton, A.S. 2013. Hydrogen generation from low-temperature water–rock reactions. *Nature Geoscience*, **6**, 478–484, https://doi.org/10.1038/ngeo1825

McCollom, T.M. 2003. Formation of meteorite hydrocarbons from thermal decomposition of siderite (FeCO3). *Geochimica et Cosmochimica Acta*, **67**, 311–317, https://doi.org/10.1016/S0016-7037(02)00945-6

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

McCollom, T.M., Klein, F. and Ramba, M. 2022. Hydrogen generation from serpentinization of iron-rich olivine on Mars, icy moons, and other planetary bodies. *Icarus*, **372**, 114754, https://doi.org/10.1016/j.icarus.2021.114754

Monge, A.M. and Vayssaire, A. 2022. A review of some aspects of the molecular hydrogen transport behavior in the subsurface. EAGE Annual 83rd Conference and Exhibition, Madrid, Spain, 1–5, https://doi.org/10.3997/2214-4609.202210914

Moretti, I., Brouilly, E., Loiseau, K., Prinzhofer, A. and Deville, E. 2021. Hydrogen emanations in intracratonic areas: new guide lines for early exploration basin screening. *Geosciences*, **11**, 145, https://doi.org/10.3390/geosciences11030145

Muhammed, N.S., Haq, B., Al Shehri, D., Al-Ahmed, A., Rahman, M.M. and Zaman, E. 2022. A review on underground hydrogen storage: insight into geological sites, influencing factors and future outlook. *Energy Reports*, **8**, 461–499, https://doi.org/10.1016/j.egyr.2021.12.002

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

Ranganai, R.T. 2012. Gravity and aeromagnetic studies of the Filabusi Greenstone Belt, Zimbabwe Craton: regional and geotectonic implications. *International Journal of Geosciences*, **3**, 1048–1064, https://doi.org/10.4236/ijg.2012.35106

Renard, F. 2021. Reaction-induced fracturing: when chemistry breaks rocks. *Journal of Geophysical Research: Solid Earth*, **126**, e2020JB021451, https://doi.org/10.1029/2020JB021451

Rouméjon, S., Cannat, M., Agrinier, P., Godard, M. and Andreani, M. 2015. Serpentinization and fluid pathways in tectonically exhumed peridotites from the Southwest Indian Ridge (62–65°E). *Journal of Petrology*, **56**, 703–734, https://doi.org/10.1093/petrology/egv014

Rüpke, L.H. and Hasenclever, J. 2017. Global rates of mantle serpentinization and H_2 production at oceanic transform faults in 3-D geodynamic models. *Geophysical Research Letters*, **44**, 6726–6734, https://doi.org/10.1002/2017GL072893

Sallarès, V., Meléndez, A., Prada, M., Ranero, C.R., McIntosh, K. and Grevemeyer, I. 2013. Overriding plate structure of the Nicaragua convergent margin: relationship to the seismogenic zone of the 1992 tsunami earthquake. *Geochemistry, Geophysics, Geosystems*, **14**, 3436–3461, https://doi.org/10.1002/ggge.20214

Searle, M., Rioux, M. and Garber, J.M. 2022. One line on the map: a review of the geological history of the Semail Thrust, Oman-UAE mountains. *Journal of Structural Geology*, **158**, 104594, https://doi.org/10.1016/j.jsg.2022.104594

Skelton, A., Whitmarsh, R., Arghe, F., Crill, P. and Koyi, H. 2005. Constraining the rate and extent of mantle serpentinization from seismic and petrological data: implications for chemosynthesis and tectonic processes. *Geofluids*, **5**, 153–164, https://doi.org/10.1111/j.1468-8123.2005.00111.x

Sleep, N.H., Meibom, A., Fridriksson, T., Coleman, R.G. and Bird, D.K. 2004. H_2-rich fluids from serpentinization: geochemical and biotic implications. *Proceedings of the National Academy of Science*, **101**, 12818–12823, https://doi.org/10.1073/pnas.0405289101

Stalker, L., Talukder, A., Strand, J., Josh, M. and Faiz, M. 2022. Gold (hydrogen) rush: risks and uncertainties in exploring for naturally occurring hydrogen. *The APPEA Journal*, **62**, 361–380, https://doi.org/10.1071/AJ21130

Tarapoanca, M., Andriessen, P. *et al.* 2010. Forward kinematic modelling of a regional transect in the Northern Emirates using geological and apatite fission track age constraints on paleo-burial history. *Arabian Journal of Geosciences*, **3**, 395–411, https://doi.org/10.1007/s12517-010-0213-3

Tissot, B.P. and Welte, D.H. 2013. *Petroleum Formation and Occurrence*. Springer, Berlin.

Toft, P.B., Arkani-Hamed, J. and Haggerty, S.E. 1990. The effects of serpentinization on density and magnetic susceptibility: a petrophysical model. *Physics of the Earth and Planetary Interiors*, **65**, 137–157, https://doi.org/10.1016/0031-9201(90)90082-9

Truche, L., Donzé, F.-V. *et al.* 2024. A deep reservoir for hydrogen drives intense degassing in the Bulqizë ophiolite. *Science*, **383**, 618–621, https://doi.org/10.1126/science.adk9099

Ulrich, M., Muñoz, M., Boulvais, P., Cathelineau, M., Cluzel, D., Guillot, S. and Picard, C. 2020. Serpentinization of New Caledonia peridotites: from depth to (sub-)surface. *Contributions to Mineralogy and Petrology*, **175**, https://doi.org/10.1007/s00410-020-01713-0

Vacquand, C., Deville, E. *et al.* 2018. Reduced gas seepages in ophiolitic complexes: evidences for multiple origins of the H_2-CH_4-N_2 gas mixtures. *Geochimica et Cosmochimica Acta*, **223**, 437–461, https://doi.org/10.1016/j.gca.2017.12.018

Vitale Brovarone, A., Sverjensky, D.A., Piccoli, F., Ressico, F., Giovannelli, D. and Daniel, I. 2020. Subduction hides high-pressure sources of energy that may feed the deep subsurface biosphere. *Nature Communications*, **11**, https://doi.org/10.1038/s41467-020-17342-x

von Huene, R., Aubouin, J. *et al.* 2007. *In:* Orlofsky, S. (ed.) *Initial Reports of the Deep Sea Drilling Project, Leg 84*. U.S. Government Printing Office, Washington D.C., 967, https://doi.org/10.2973/dsdp.proc.84.143.1985

Walther, C.H.E., Flueh, E.R., Ranero, C.R., von Huene, R. and Strauch, W. 2000. Crustal structure across the Pacific margin of Nicaragua: evidence for ophiolitic basement and a shallow mantle sliver. *Geophysical Journal International*, **141**, 759–777, https://doi.org/10.1046/j.1365-246x.2000.00134.x

Wang, L., Jin, Z., Chen, X., Su, Y. and Huang, X. 2023. The origin and occurrence of natural hydrogen. *Energies*, **16**, 2400, https://doi.org/10.3390/en16052400

Warr, O., Giunta, T., Ballentine, C.J. and Sherwood Lollar, B. 2019. Mechanisms and rates of ^{4}He, ^{40}Ar, and H_2 production and accumulation in fracture fluids in Precambrian Shield environments. *Chemical Geology*, **530**, 119322, https://doi.org/10.1016/j.chemgeo.2019.119322

Worman, S.L., Pratson, L.F., Karson, J.A. and Klein, E.M. 2016. Global rate and distribution of H_2 gas produced by serpentinization within oceanic lithosphere. *Geophysical Research Letters*, **43**, 6435–6443, https://doi.org/10.1002/2016GL069066

Yang, J. 2006. Full 3-D numerical simulation of hydrothermal fluid flow in faulted sedimentary basins: example of the McArthur Basin, Northern Australia. *Journal of Geochemical Exploration*, **89**, 440–444, https://doi.org/10.1016/j.gexplo.2005.11.080

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

Zgonnik, V., Beaumont, V., Larin, N., Pillot, D. and Deville, E. 2019. Diffused flow of molecular hydrogen through the Western Hajar mountains, Northern Oman. *Arabian Journal of Geosciences*, **12**, 71, https://doi.org/10.1007/s12517-019-4242-2

Zhang, L., Nasika, C., Donzé, F.-V., Zheng, X., Renard, F. and Scholtès, L. 2019. Modeling porosity evolution throughout reaction-induced fracturing in rocks with implications for serpentinization. *Journal of Geophysical Research: Solid Earth*, **124**, 5708–5733, https://doi.org/10.1029/2018JB016872