SUPPLEMENT | EXTENDED ABSTRACT
https://doi.org/10.1071/AJ22084

The APPEA Journal

Modelling of hydrogen gas generation from overmature organic matter in the Cooper Basin, Australia

Christopher J. Boreham[A,*], Dianne S. Edwards[A], Andrew J. Feitz[A], Andrew P. Murray[B], Nicolaj Mahlstedt[C] and Brian Horsfield[C]

For full list of author affiliations and declarations see end of paper

***Correspondence to:**
Christopher J. Boreham
Geoscience Australia, GPO Box 378, Canberra, ACT 2601, Australia
Email: chris.boreham@ga.gov.au

Accepted: 10 February 2023
Published: 11 May 2023

Cite this:
Boreham CJ *et al.* (2023)
The APPEA Journal
63(S1), S351–S356. doi:10.1071/AJ22084

ABSTRACT

A significant portion of planned energy and mineral resource investment into Australia is now for hydrogen (H_2). Whether from fossil fuels with carbon capture and storage or from electrolysis of water using renewable energy, there is a price premium for manufactured hydrogen. The production of H_2 from geological sources (geologic H_2) could be more cost-effective. The majority of sources for geologic H_2 are abiotic and their resource potential is largely unknown. Biogenic (microbial and thermogenic) sources also exist. The focus for this study is on a thermogenic source where chemical kinetics of H_2 generation from the thermal breakdown of land-plant-derived organic matter has been applied within a petroleum system modelling framework for the Cooper Basin. Modelling of mid-Patchawarra Formation coals and shales, the main source rocks for petroleum, indicate that free H_2 is available at maturities >3.5% vitrinite reflectance and that a large volume of free H_2 is predicted to occur in a 'sweet spot' deep within the Nappamerri Trough. *In-situ* free H_2 concentrations deep within the Nappamerri Trough are predicted to be comparable to methane concentrations in productive unconventional shale gas plays. Nevertheless, exploration drilling within the Cooper Basin's depocentre is sparse and a deep H_2 system remains largely untested.

Keywords: chemical kinetics of hydrogen generation, Cooper Basin, geologic hydrogen, hydrogen system, natural hydrogen, coal and carbonaceous shale source rock, petroleum system modelling, thermogenic natural gas.

Introduction

Hydrogen gas (H_2) is the most energy-rich gas weight-for-weight and is considered crucial for a sustainable clean energy future (International Energy Agency 2022). The production of H_2 from geological sources (geologic H_2) is increasingly recognised as a low-cost complement to manufactured H_2 (Lapi *et al.* 2022). Although there are numerous sources of geologic H_2 within sedimentary, metamorphic and igneous rocks (Boreham *et al.* 2021), the most studied and effectively modelled are those reactions associated with fluid–rock interactions e.g. ferrous to ferric iron oxidation accompanied by water reduction and the radiolysis of water to produce H_2. Calculation of H_2 production rates, coupled with a geological understanding, enables estimation of geologic H_2 resource potential. The majority of sources for geologic H_2 are abiotic and volumetric estimates of H_2 generation are mostly qualitative. Biogenic (microbial and thermogenic) sources of H_2 also exist. In this paper, the chemical kinetics of H_2 generation from coals and carbonaceous shales containing land-plant-derived organic matter has been applied within a petroleum system modelling framework to the Cooper Basin to quantify the generation of H_2 in a free state (free H_2).

Cooper Basin petroleum generation

The Cooper Basin is a Pennsylvanian–Middle Triassic intracratonic basin containing predominantly terrigenous sediments, which covers an area of 127 000 km^2 with sediment

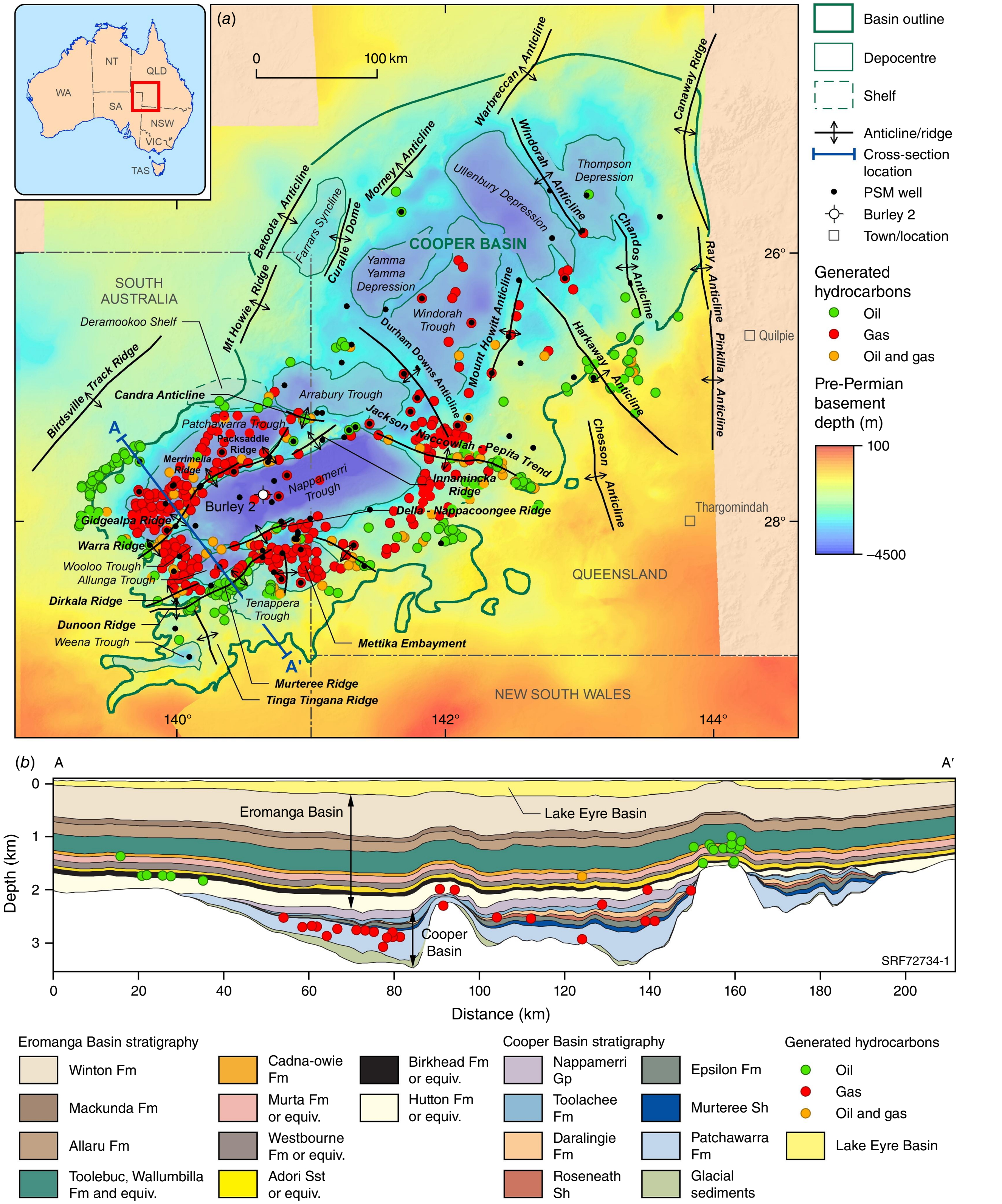

Fig. 1. (*a*) Areal extent of the Cooper Basin showing the main depocentres, troughs and ridges and the distribution of oil and gas occurrences (note: 'PSM well' identifies the location of the well used in the petroleum system model of Hall *et al.* (2019)) and (*b*) cross-section showing the distribution of the sedimentary formations of the Cooper and Eromanga basins across the Nappamerri, Patchawarra and Tenappera troughs. Modified after Hall *et al.* (2019).

thicknesses typically being up to 2500 m, although the base of the section within the deepest trough (Nappamerri) reaches over 4400 m. The overlying Jurassic–Cretaceous Eromanga Basin extends beyond the preserved depositional edge of the Cooper Basin and is over 2500 m thick. The Palaeocene to Quaternary Lake Eyre Basin overlies the Eromanga Basin (Fig. 1*a*, *b*; Hall *et al.* 2019 and references therein) but it is thin (up to 300 m) across the Cooper Basin region.

Hydrocarbon generating source rocks are dominated by land-plant-derived organic matter with the Toolachee and Patchawarra formations being considered prospective. Both Permian formations collectively host the main commercial reservoirs for gas in the Cooper Basin (Fig. 1*b*; Hall *et al.* 2019 and references therein). Petroleum system modelling indicated that the main phase of hydrocarbon generation began in the latest Permian in the Nappamerri Trough depocentre in South Australia while the mid-Cretaceous corresponded to a time when hydrocarbons were generated in the adjacent troughs, including the Patchawarra and Windorah troughs. Source rock maturity varies between depocentres, with large areas of the Nappamerri, Patchawarra and Windorah troughs being gas mature to overmature at present day (Hall *et al.* 2016).

Modelling free H_2 generation

Modelling of gas generation employed the Zetaware software suite (Kinex version 4.94, Genesis Version 5.68b and Trinity T3 version 6.61). Input parameters from Hall *et al.* (2019) were used, including basin history (burial, thermal and pressure), source characterisation (net thickness, richness and quality) and the primary methane, late methane and free H_2 generation kinetics of Mahlstedt *et al.* (2022). The maturation history model is shown for Burley 2 (Fig. 2*a*) because it is a deep well located in the centre of the Nappamerri Trough (Fig. 1*a*) where the Patchawarra Formation source rocks are overmature (measured vitrinite reflectance (Ro) >2%) with predominantly dry gas generation. The modelled Ro is displayed in Fig. 2*a*, which also highlights the variation in the vitrinite reflectance kinetic models available in the literature and employed within the Zetaware software suite; for modelling vitrinite reflectance in Fig. 2*a*, *b*, this paper uses the ARCO vitrinite reflectance kinetic model (see Falvey and Middleton 1981). Additionally, well histories of Hall *et al.* (2019) were slightly modified for those wells where measured Ro was >2% to best honour the fit between the modelled and measured Ro profiles over this high-maturity region.

Utilising primary methane, late methane and free H_2 generation kinetics (Mahlstedt *et al.* 2022), the cumulative transformation history (i.e. transformation ratio (TR) from 0 to 1) of a source rock positioned in the middle of the Patchawarra Formation in Burley 2 is modelled and displayed in Fig. 2*b*. Methane generation is exhausted at the hydrocarbon deadline where TR >0.9, which occurs at the time of maximum paleotemperature, in this case ~250°C and a

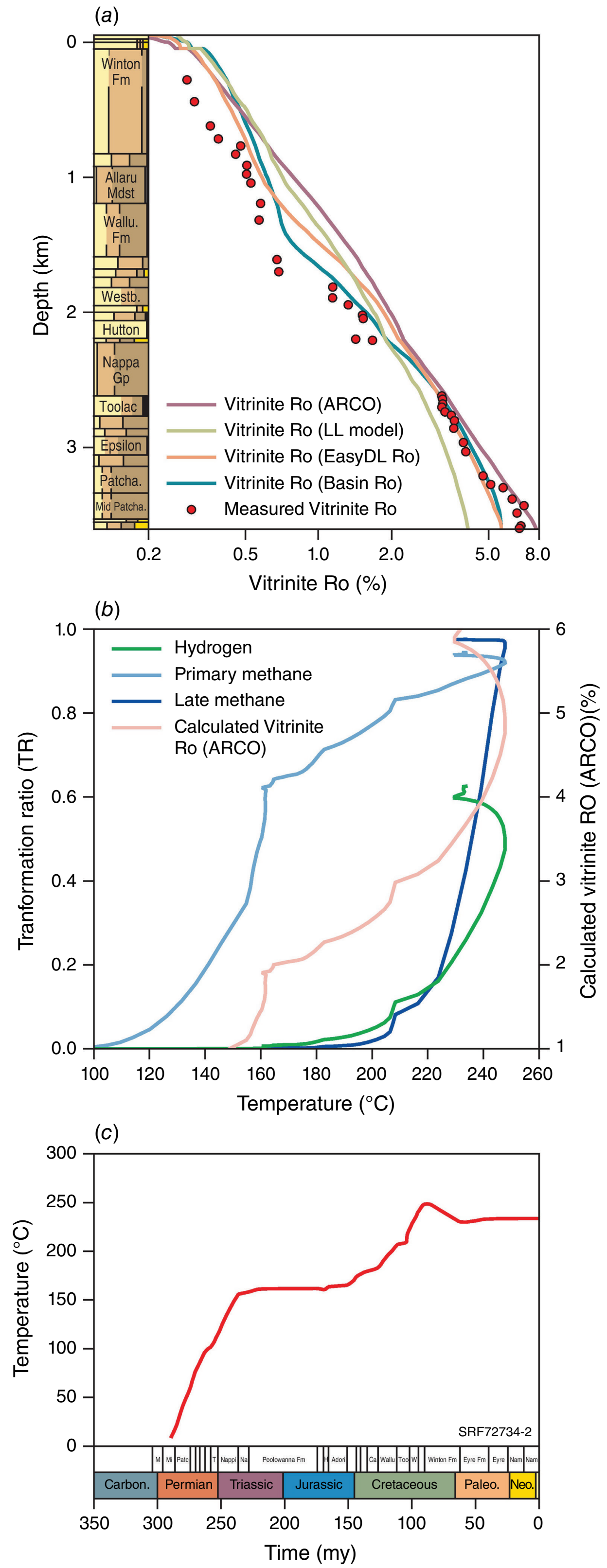

Fig. 2. For Burley 2 well (*a*) modelled and measured vitrinite reflectance (Vitrinite Ro) versus depth, (*b*) transformation ratio for primary methane, late methane and free H_2, and modelled vitrinite reflectance versus modelled temperature and (*c*) modelled temperature history versus age.

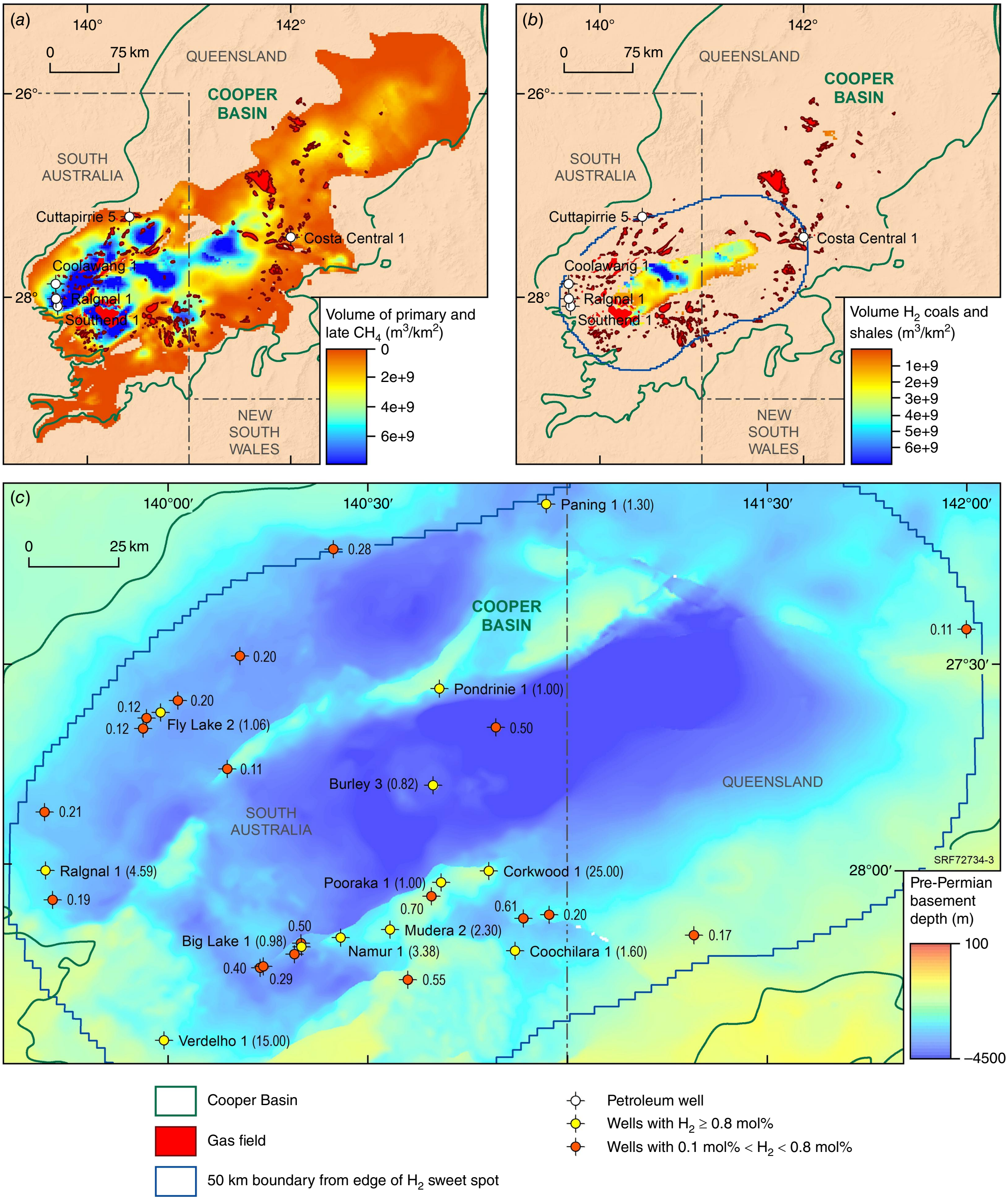

Fig. 3. Areal distribution of modelled cumulative gas generation volumes m^3/km^2 from a mid-Patchawarra Formation source rock for (*a*) methane (primary + late) and (*b*) free H_2 (the enclosed black line marks the 50 km boundary from the edge of the H_2 'sweet spot'. Note: initial primary methane potential = 40 mg/g TOC (total organic content), initial late methane potential = 50 mg/g TOC, initial free H_2 potential = 20 mg/g TOC (Mahlstedt *et al.* 2022)) and (*c*) well location with reported maximum H_2 mol% where H_2 >0.1 mol% (Supplementary Table S1 lists data from WCRs and five well gases in Boreham *et al.* (2021). Note: well names for maximum H_2 ≥0.8 mol%; Burley 3 with a maximum H_2 = 0.82 mol% is for pre-well-fire gas whereas post-well-fire gas has a maximum H_2 = 40 mol%). Note: Apply structural elements in Fig. 1 to Fig. 3.

modelled Ro of ~3.5%, in the Late Cretaceous just prior to the Winton Formation uplift and erosion (Fig. 2*b, c*). Importantly, at this same time, the transformation of the initial free H_2 potential is only ~50% completed (TR ~0.5). Thus, where the Patchawarra Formation source rock experienced higher maturity and temperature, methane-free H_2 would be generated.

Employing a 2D surface of a mid-Patchawarra Formation source rock (coal and carbonaceous shale), the cumulative gas generation (m^3 gas/m^2 rock) for methane (primary + late) and free H_2 is mapped in Fig. 3*a, b*, respectively. Methane generation is prevalent across much of the Cooper Basin, while free H_2 generation is predominantly restricted to a 'sweet spot' in the central Nappamerri Trough. Interestingly, both methane and free H_2 have similar maximum 'm^3 gas/m^2 rock' generation rates. With consideration of rock thickness and a conservative H_2 expulsion efficiency of 90%, Mahlstedt *et al.* (2022) estimated 86 Tcf free H_2 gas is still retained, much more must have expelled from the overmature Patchawarra Formation source rocks.

The H_2 system

The concentration of H_2 in Australian natural gas is typically low with ~80% of the dataset having $H_2 < 0.1$ mol%. Nevertheless, natural gases with H_2 concentration >1 mol% are found in all Australian states and the Northern Territory (Boreham *et al.* 2021). In the Cooper Basin, the areal extent of those gases reported in Boreham *et al.* (2021) shows that the five gases with $H_2 > 0.1$ mol% (Table S1) fall either on or within a 50 km boundary extended from the outline of the H_2 'sweet spot' in the Nappamerri Trough (Fig. 3*b*). While the migration and fate of H_2 gas is beyond the scope of this paper, if the source of H_2 is from the thermal decomposition of organic matter then this may define the extent of the H_2 system, consistent with the critical elements of a petroleum system defined by Magoon and Dow (1994).

In order to further constrain and have confidence in the areal extent of an inferred H_2 system, well completion reports (WCRs) were consulted for petroleum wells drilled in the Cooper and Eromanga basins. WCRs from 3346 wells were examined with a low proportion (557 wells) containing gas data and a limited number (35 wells and 108 gas analyses) containing H_2 mol% values. Of these, 26 wells have gases with $H_2 > 0.1$ mol% and 9 of these wells having gases with $H_2 > 1.0$ mol% (Fig. 3*c*) (Table S1). The southwest margin of the Nappamerri Trough hosts H_2-rich (>10 mol% H_2) natural gases in South Australia where migration of H_2 may be up to ~40 km from the edge of the thermogenic H_2 generation 'sweet spot' (kitchen) (Fig. 3*b, c*). Natural gases with much lower H_2 contents typify the northern extent over the Patchawarra Trough in South Australia where source rock maturities are lower. The lack of wells both fewer in number and without H_2 mol% data lends to an uncertain and unconstrained H_2 system in Queensland (Fig. 3*c*).

Summary and conclusions

The need for a reliable and volumetrically significant supply of H_2 at the right price is a challenge for the future low-carbon economy. Experience gained over more than a century by petroleum and mineral explorationists guarantee the right tools are now available for the exploration for geologic hydrogen. Geologic hydrogen gas has the advantage over petroleum since it has around 10 times more sub-surface sources and hence greater opportunities, compared to sources of petroleum. Thermogenic hydrogen is seen as a viable candidate in the hydrogen 'mix' because an organic-rich, highly overmature rock can be modelled to determine where geologic hydrogen is generated, in this case the central Nappamerri Trough in the Cooper Basin, and hence influence future exploration opportunities and activities.

Supplementary material

Supplementary material is available online.

References

Boreham CJ, Edwards DS, Czado K, Rollet N, Wang L, van der Wielen S, Champion D, Blewett R, Feitz A, Henson PA (2021) Hydrogen in Australian natural gas: occurrences, sources and resources. *The APPEA Journal* **61**, 163–191. doi:10.1071/AJ20044

Falvey DA, Middleton MF (1981) Passive continental margins: evidence for a prebreakup deep crustal metamorphic subsidence mechanism. In 'Oceanologica Acta', 1981. pp. 103–114. Special Issue open access version. Available at https://archimer.ifremer.fr/doc/00246/35699

Hall LS, Palu TJ, Murray AP Boreham CJ, Edwards DS, Hill AJ, Troup A (2016) 'Cooper Basin Petroleum Systems Modelling: Regional Hydrocarbon Prospectivity of the Cooper Basin: Part 3'. Record 2016/029. (Geoscience Australia: Canberra) doi:10.11636/Record.2016.029

Hall LS, Palu TJ, Murray AP, Boreham CJ, Edwards DS, Hill AJ, Troup A (2019) Hydrocarbon prospectivity of the Cooper Basin, Australia. *AAPG Bulletin* **103**(1), 31–63. doi:10.1306/05111817249

International Energy Agency (2022) Hydrogen. Available at https://www.iea.org/fuels-and-technologies/hydrogen

Lapi T, Chatzimpiros P, Raineau L, Prinzhofer A (2022) System approach to natural versus manufactured hydrogen: an interdisciplinary perspective on a new primary energy source. *International Journal of Hydrogen Energy* **47**, 21701–21712. doi:10.1016/j.ijhydene.2022.05.039

Magoon LB, Dow WG (1994) 'The Petroleum System—From Source to Trap'. AAPG Memoir 60. (The American Association of Petroleum Geologists: Tulsa, OK, USA) doi:10.1306/M60585

Mahlstedt N, Horsfield B, Weniger P, Misch D, Shi X, Noah M, Boreham C (2022) Molecular hydrogen from organic sources in geological systems. *Journal of Natural Gas Science and Engineering* **105**, 104704. doi:10.1016/j.jngse.2022.104704

Data availability. Burial history and maturation model for Burley 2 in Zetaware format is available on request to the corresponding author.

Conflicts of interest. The authors declare that no conflicts of interest exist.

Declaration of funding. This study was funded by Geoscience Australia's Exploring for the Future program. No funding from external organisations was received for this research.

Acknowledgements. Marita Bradshaw and Tehani Palu are thanked for their reviews of a pre-submission version of the manuscript. Chris Evenden and Silvio Mezzomo provided assistance in drafting the figures. We would like to acknowledge Minerals, Energy and Groundwater Information Services for data compilation. C. J. B., D. S. E. and A. F. publish with the permission of the CEO, Geoscience Australia.

Author affiliations

[A]Geoscience Australia, GPO Box 378, Canberra, ACT 2601, Australia.

[B]Murray Partners PPSA Pty. Ltd., Perth, Australia.

[C]GEOS4 GmbH, D-14552 Michendorf, Germany.

The authors

Christopher J. Boreham is a Principal Organic Geochemist at Geoscience Australia working in the Minerals, Energy and Groundwater Division. He obtained a Ph.D. in Chemistry at the Australian National University. Chris applies his skills to understand the evolution of petroleum and abiogenic gas in Australian basins. Chris is a member of PESA and AAPG.

Dianne S. Edwards is a Principal Organic Geochemist at Geoscience Australia working in the Minerals, Energy and Groundwater Division. She received her Ph.D. from the University of Adelaide in 1996. Dianne's focus is on building databases and web services to release geochemical information that underpins Australia's petroleum systems. Dianne is a member of PESA.

Andrew J. Feitz is an Environmental Engineer and Director of Low Carbon Geoscience and Advice at Geoscience Australia. He holds a Ph.D. from UNSW and worked as a senior researcher at The University of New South Wales (UNSW) and the Karlsruhe Institute of Technology (Germany). Andrew leads GA's efforts supporting implementation of the National Hydrogen Strategy.

Andrew Murray is a director of Murray Partners PPSA and provides training and consulting in petroleum system analysis. He holds M.Sc. and Ph.D. degrees in Petroleum Geochemistry and was head of the discipline at Woodside Energy for 18 years.

Nicolaj Mahlstedt is a Petroleum System Analyst at GEOS4 GmbH and holds a Ph.D. in Organic Geochemistry from the Technical University (TU) of Berlin. He has 10+ years' experience in upstream research and development. His major interests include petroleum system analysis in conventional as well as unconventional settings, and compositional kinetic modelling.

Brian Horsfield is CEO and Managing Director of GEOS4, a geochemistry research and service provider for the upstream energy sector. He is an elected member of the German Academy of Science and Technology, and is Emeritus Professor of Organic Geochemistry and Hydrocarbon Systems at TU Berlin.