

Isotope fingerprinting of produced hydrogen and its potential regulatory applications

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Summary

Stable isotopes of hydrogen ($^2\text{H}/^1\text{H}$) carry natural fingerprints of produced molecular hydrogen by mechanism of origin which are difficult or costly to adulterate. A newly compiled database of 5677 measurements reveals that green hydrogen (electrolytic or biological hydrogen, e.g., nitrogenase, hydrogenase) is readily distinguished by its considerable depletion in heavy isotopic species, ranging from -831 to -555 ‰ in $\delta^2\text{H}$ relative to V-SMOW, as compared to -377 to +196 ‰ for fossil fuel sources (grey/turquoise hydrogen), and -379 to 0 ‰ for wood/biomass burning (brown hydrogen), compared to analytical uncertainty of close to ± 1 ‰. White hydrogen, naturally produced in a variety of geologic settings, ranges from -996 to -49 ‰, reflecting diverse overlapping origins. Potential applications of fingerprinting include tracking of produced hydrogen by source, process and distribution control, grading and regulation of low carbon intensity (CI) products, and leakage detection for carbon capture and storage (CCUS) operations.

Theory / Method

A total of 230 peer-reviewed papers reporting on hydrogen produced in nature, experimental investigations, or arising from unintended or anthropogenic causes were reviewed. Those containing relevant hydrogen isotope measurements were extracted and results were compiled in a database. The most interesting results were gleaned from studies on global atmospheric inventories or budgets that apportioned atmospheric H_2 according to its sources, which ably demonstrated isotopic differentiation. The overall data compilation also contains related data inventories of reactants, intermediates, as well as source water and ambient atmospheric data for the troposphere and stratosphere. Meteoric water data were obtained from the International Atomic Energy Agency's Global Network for Isotopes in Precipitation available online from IAEA (2024). Estimates of $\delta^2\text{H}$ in atmospheric water vapour for GNIP stations was obtained from Gibson et al. (2008).

Several experiments were conducted to compliment the literature review and to provide better understanding of the stability, repeatability and robustness of isotopic labelling of hydrogen production sources. Initial trials of various commercially available benchtop hydrogen production lines were operated and sampled including both alkaline and proton exchange membrane (PEM) electrolysis systems, and a methane pyrolysis line, the latter similar to that of Dolgikh et al. (2022).

Results, Observations, Conclusions

Results from the literature review combined with new experimental results provide a robust perspective of distinct labelling of produced hydrogen according to the process associated with its formation (Fig. 1). Note that hydrogen isotope data for reactants, intermediates and ambient environmental hydrogen was also collected to assess the isotopic composition of hydrogen-bearing compounds in the precursors and, hence, to allow estimation of the isotopic separation

between specific reactants and produced hydrogen product, which is important for evaluating and understanding individual fractionation processes in detail. As a first illustration of the hydrogen fingerprinting effects we will first describe the broad-scale differences observed in the signatures of produced hydrogen and then we will proceed to discuss some of the specific fractionation mechanisms to the degree they are understood or can be predicted based on existing evidence.

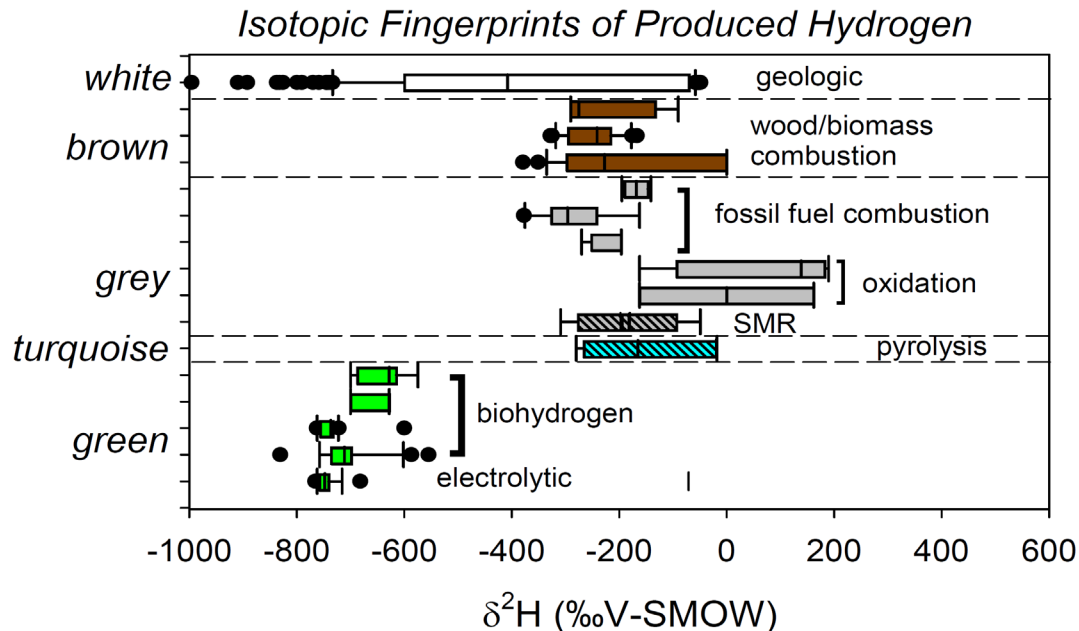


Figure 1. Range of isotope signatures of molecular hydrogen from peer-reviewed literature and new experimental data illustrating distinct fingerprinting. Hydrogen colour spectrum is also shown on y-axis.

Novel/Additive Information

The most striking feature of the survey is that green hydrogen products, i.e. H_2 produced by nitrogen fixation, nitrogenase/hydrogenase enzymes, from biohydrogen, and from water-splitting reactions such as electrolysis, are distinctly more depleted in deuterium as compared to grey hydrogen produced by fossil fuel conversion, including methane pyrolysis and methane steam reformation, as well as hydrogen produced unintentionally or anthropogenically through the relatively inefficient processes of incomplete combustion (i.e., fossil fuel burning, biomass burning, wood burning, and car exhaust). Hydrogen produced naturally in the atmosphere through methane oxidation and VOC oxidation, which might be considered as useful low-pressure analogues for reforming by partial oxidation, are also shown to be distinct from green hydrogen, and are found to be enriched relative to other fossil fuel derived hydrogen products. White hydrogen, because it occurs naturally in a range of geologic settings, expectedly spans a wide range of sources and broadly overlaps both green and grey/turquoise hydrogen sources. White hydrogen has been found to occur in relation to mantle sources, hydrothermal activity, radiolytic alteration and serpentinization, fault-zones, mid-ocean ridge spreading, continental volcanic activity, kimberlites and bacterial activity (Boreham et al. 2021). The range observed for white hydrogen is largely consistent with the known range of deuterium content between the oceans ($\delta^2\text{H} \sim 0$ ‰) and the mantle ($\delta^2\text{H} = < -218$ ‰) (Hallis 2016), and in primary minerals formed within

the early solar system ($\delta^2\text{H} \sim -850 \text{‰}$; Aleon et al. 2022). The fact that white hydrogen overlaps with green hydrogen may be evidence of bacterially mediated geological processes in some settings. Furthermore, overlap with green hydrogen is not likely to pose a dilemma for fingerprinting as white hydrogen is also essentially “green” as it does not contribute to anthropogenic greenhouse gas (GHG) emissions.

This compilation contributes to the explanation and better understanding of systematic differences in the hydrogen isotopic composition of produced hydrogen according to mode of production and other controls including the isotopic composition of precursors and whether or not the hydrogen is produced through carbon-bound hydrogen reactions or water splitting reactions. Given the significant distinction noted between green hydrogen and grey hydrogen, and sensitivity to factors controlling the conversion process to hydrogen, we can postulate several potential applications to the hydrogen economy.

- We anticipate that isotope fingerprinting may be useful for tracing the source and mode of formation of produced hydrogen including identification and grading of low carbon intensity (CI) products, which could be applied as a regulatory tool. Identification and certification of green hydrogen products that might be preferred for some users or by some political jurisdictions could support higher pricing for such low CI products.
- It is likely that isotope signatures could be applied to monitor hydrogen production processes to detect changes in efficiency, catalytic performance or other operating conditions. For regulatory purposes, individual operators could be monitored to ensure that licensed production methods are adhered to, and that feedstocks and production conditions remain consistent over time within specified thresholds.
- Mixing of specific hydrogen sources could be monitored within distribution networks to permit mass balance of various sources including leakages and degradation due to interaction with pipeline or storage infrastructure.
- Isotopic characterisation of production sources and distribution would also allow for robust tracking and mass balance of leakage impacts on the atmospheric H_2 cycle.
- Isotopic fingerprints could be used to track interactions between produced hydrogen in underground storage including hydrogeochemical interactions with geologic strata and leakage detection.
- Similar use of carbon, oxygen, nitrogen and sulfur isotope signatures would aid in monitoring and understanding the fate of carbon materials during production of aqua, blue and turquoise hydrogen.

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