

POTENTIAL SOURCES AND GEOLOGICAL SETTING OF “WHITE” HYDROGEN FOR FUTURE EXPLORATION IN BULGARIA

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ABSTRACT. This study provides a preliminary assessment of the geological potential for natural hydrogen (also known as white, or geological hydrogen) exploration in Bulgaria by integrating published datasets, well information, and regional geological analysis. The evaluation targets a variety of geological settings in which hydrogen-rich gases may occur, including ophiolites, rift zones, faults, geysers, hot springs, etc. These settings, which are characterised by deep-rooted fault systems, tectonic boundaries, and elevated geothermal gradients, are recognised as first-order controls on crustal fluid circulation and gas transport. Serpentinised ultramafic rocks are highlighted as a potential source of hydrogen, which is produced through serpentinisation. Structurally focused zones may support vertical migration of fluids from deep hydrogen sources. Uranium mineralisation and clay-hosted deposits indicate sustained fluid flow, as radiolysis in crystalline rocks is considered a major hydrogen generation mechanism. Both hydrogen (H₂) and helium (He) gases are released during water radiolysis. Hydrogeochemical evidence indicates the presence of dissolved H₂ (3–4%) and He (0.8–1.2%) in several regions, supporting the presence of active deep fluid systems. The findings indicate that Bulgaria has promising geological conditions for natural hydrogen exploration, especially in fault-controlled hydrothermal systems and serpentinised complexes. Further work should integrate gas geochemistry, isotopic analyses, and advanced geophysical methods to identify and rank white hydrogen prospects.

Key words: natural hydrogen, geological settings, Bulgaria.

ПОТЕНЦИАЛНИ ИЗТОЧНИЦИ НА „БЯЛ“ ВОДОРОД И ГЕОЛОЖКИ ПРЕДПОСТАВКИ ЗА ПРОУЧВАНЕ В БЪЛГАРИЯ

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РЕЗЮМЕ. Настоящото изследване представя предварителна оценка на геоложкия потенциал за проучване на естествен (известен също като бял, или геоложки) водород в България чрез интегриране на публикувани литературни данни, информация от сондажи и регионален геоложки анализ. Оценката е насочена към различни геоложки условия, където могат да бъдат открити богати на водород газове, като офиолити, рифтови зони, разломи, гейзери, горещи извори и т.н. Тези условия, които се характеризират с дълбокозаложени разломни системи, тектонски граници и повишени геотермални градиенти, се считат за фактори от първи ред относно циркулацията на флуидите в земната кора и придвижването на газ. Серпентинизирани ултрамафични скали са доказани като потенциален източник на водород (H₂) чрез серпентинизация. Структурно фокусираните зони могат да поддържат вертикална миграция на флуиди от дълбочинни източници. Урановата минерализация и глинестите находища показват устойчив флуиден поток, тъй като се смята, че радиолизата в кристалините скали е основен механизъм за генериране на водород. Като H₂, така и хелиеви (He) газове се отделят по време на процесите на радиолиза. Хидрогеохимичните данни показват разтворен H₂ (до 3–4%) и He (0.8–1.2%) в няколко региона, което се интерпретира като белег за активни дълбочинни флуидни системи. Резултатите показват, че България притежава благоприятни геоложки условия за проучване на естествен водород, особено в контролирани от разломните хидротермални системи и серпентинизирани комплекси. По-нататъшната работа трябва да съчетава газо-геохимични и изотопни анализи, хидрогеоложки проучвания и съвременни геофизични методи за идентифициране и класиране на перспективни зони за бял водород.

Ключови думи: бял водород, геоложки условия, България.

Introduction

The increasing worldwide energy demand and global efforts to transition from fossil fuels to renewable energy sources can be addressed by hydrogen gas as a key solution. Natural hydrogen (H₂), also called geological, or “white” hydrogen, compared to the existing black, grey, blue, pink, and green hydrogen, is seen as a potentially cheaper alternative with a minimal carbon footprint.

In recent decades, H₂ has been actively explored in North America, Asia, Africa, and Australia (Tian et al., 2022), with significant quantities found in Mali's Baurakebougou field, Albania's Bulqize chromite mine, France's Lorraine mining basin, and Turkey's Chimaera, and the data and experience have only been increasing. After decades of focusing on natural hydrogen as an exploration target, most publications indicate that data collection methods, interpretation techniques, and workflows—primarily developed by the hydrocarbon industry over the past century—could be effectively adapted to locate natural hydrogen in the subsurface (Levy et al., 2023; Jackson et al., 2024; Elis, 2025).

The main goal of the study is to provide a preliminary assessment of the geological potential for natural hydrogen exploration in Bulgaria by integrating published datasets, well information, and regional geological analysis.

Methods

After a fairly detailed literature review of recent publications and articles, and based on the global experience of H₂ exploration in many regions of the world, the methodology adopted and undertaken in this research is based on what was suggested in the workflow of previous studies (Levy et al., 2023) to efficiently explore this new resource, starting with pre-fieldwork consisting of identifying H₂ hotspots.

This pre-fieldwork includes a comprehensive review and analysis of all available data that could indicate the presence of H₂, such as seepage or H₂ measurements in water sources or wells, typically collected for other purposes. It also involves identifying hydrogen source rocks at different scales, like country or basin levels, to select and define promising exploration areas.

Geological setting of the natural hydrogen sources and occurrences

A play-based approach, which adopts concepts and methods proven in petroleum exploration, is proposed for broad application in H_2 resource exploration (Elis, 2025).

Consequently, this adaptation to a hydrogen system, involving presumed elements and processes such as source rocks, reservoirs, seals, traps, and migration pathways (Fig. 1), requires careful analysis. To target locations where H_2 can be abundant, it is important to first define the processes that generate it.

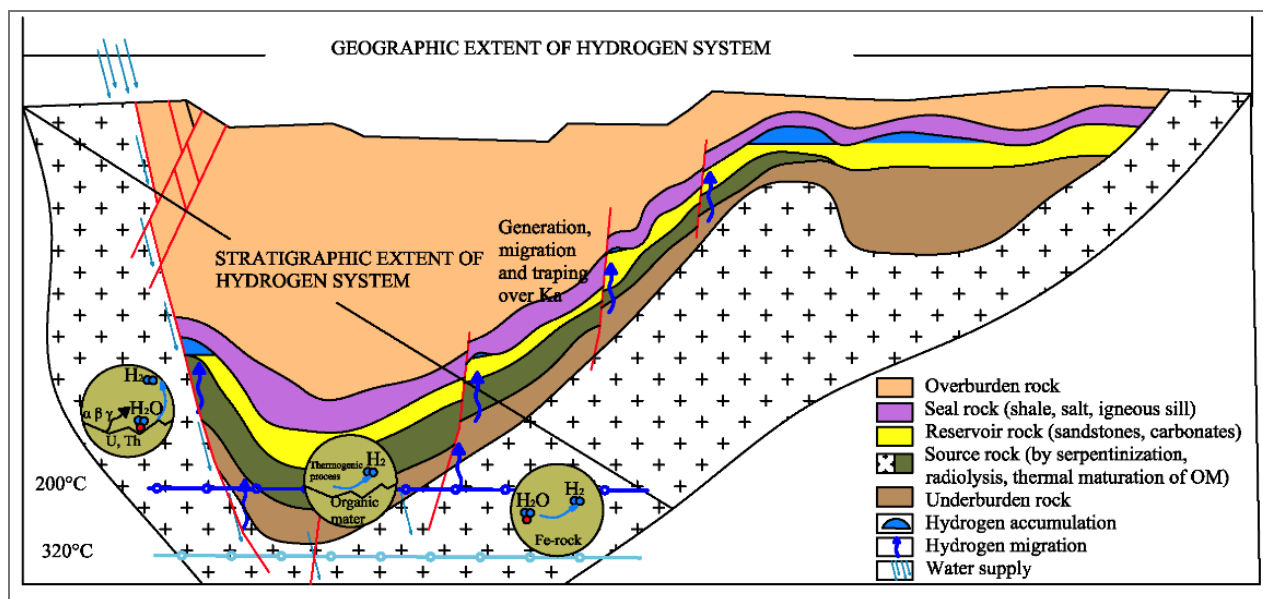


Fig. 1. Hydrogen system approach

Various hypotheses exist regarding the origin of H_2 (Zgonnik, 2020; Shestopalov, 2020), but it is generally believed to originate from either abiotic or biotic sources. Abiotic hydrogen production in the Earth's crust happens over a wide temperature range, above 600 °C, whereas biotic processes are limited to cooler environments that support life. It is assumed that there are several mechanisms for hydrogen generation:

1) Deep-seated hydrogen—either primordial from the core or mantle, or produced in the lower crust by degassing processes;

2) Water-rock reactions, such as the reduction of water during the oxidation of iron-rich minerals, with processes like serpentinisation of ultramafic rocks thought to produce substantial hydrogen amounts. This process occurs mainly at mid-oceanic ridges at temperatures between 150 °C and 350 °C, and onshore in ophiolites at lower temperatures. Other sources include siderite deposits, biotite, peralkaline granites, and banded iron formations, although their hydrogen-generating potential is constrained by certain factors;

3) Radiolysis or water breakdown through natural radioactivity, involving elements like uranium, thorium, and potassium present in the Earth's crust;

4) Thermal maturation of high-rank organic matter in organic-rich rocks. Mechanoradical processes and geothermal areas could also contribute to the generation and exploration of natural hydrogen.

Results and discussions

The study begins with an overview of lithologies conducive to H_2 production to identify key regions of interest in Bulgaria. The tracers are then presented, indicating the presence of H_2 .

Natural hydrogen generated by the water-rock reaction

The analysis suggests that the primary sites for H_2 exploration are likely to be those connected with ophiolite associations. The geological environments and geotectonic settings of the Balkan Peninsula are essential for understanding the region's behaviour and evolution. Previous studies (Schmid et al., 2008; Spiridonov, 2020) highlight notable similarities in emplacement mechanisms and characteristics typical of the Tethyan ophiolites (obduction) type of geotectonic settings (Jackson et al., 2024), which occur when oceanic lithosphere, formed in a fore-arc or back-arc, known as a supra-subduction zone (SSZ) setting, is obducted over a continental passive margin that has failed or is failing to subduct (Fig. 2A). The Tethyan obduction type highlights promising ophiolite associations for H_2 exploration on the Balkan Peninsula, shaped by the subduction-collision dynamics between the Eurasian and Apulian plates and the extensive Vardar-Izmir-Ankara suture (Spiridonov, 2020). Several ophiolite complexes extending from west to east have been identified, sharing similar features (Fig. 2B) and spanning the territories of Albania, Kosovo, Bosnia and Herzegovina, Serbia, Greece, Turkey, and Bulgaria. Ophiolites occur in the Dinarides, the Vardar zone, the Circum-Rhodope belt, around the periphery of the Rhodope massif, and to the south of the Rhodopes. To the east, they extend into the Tavshanli zone, south of the Vardar-Izmir-Ankara suture.

Based on this geological data, in the study, specific regions within Bulgarian territory are identified where the spatial surface distribution of H_2 -producing rocks – comprising slices of oceanic lithosphere onto the continent known as ophiolites – could undergo serpentinisation. Even if the ophiolites occupy small areas on the land scale compared to mid-oceanic ridges, they have a huge potential for serpentinisation and therefore H_2 generation.

The Balkan-Carpathian ophiolite segment. The Balkan-Carpathian segment (Haydoutov, 1991) comprises a complex assemblage of lower-grade ophiolite massifs across Romania, Serbia, and Bulgaria, formed in a mid-ocean ridge setting, with the protolith dated to 563 million years ago. Key ophiolite massifs within this segment include Tcherni Vrach, Zaglavac, Deli Jovan, and South Banat, which feature structures, such as pillow lavas, pyroxenites, and gabbro-porphyrite dikes. These ophiolites, shaped by ocean-floor metamorphism and obduction

alongside an island-arc association in the subduction zone, highlight intricate geological processes. Stratigraphically, the ophiolite formations in NW Turkey are similar to those in the Balkan-Carpathian region. The South Banat ophiolite massif, located at the northwestern edge of the Carpathian-Balkan segment, is thought to predate the Early Caledonian period and comprises two main rock types: ultramafic tectonites and cumulative gabbros mingled with ultramafic rocks throughout the ophiolite profile.

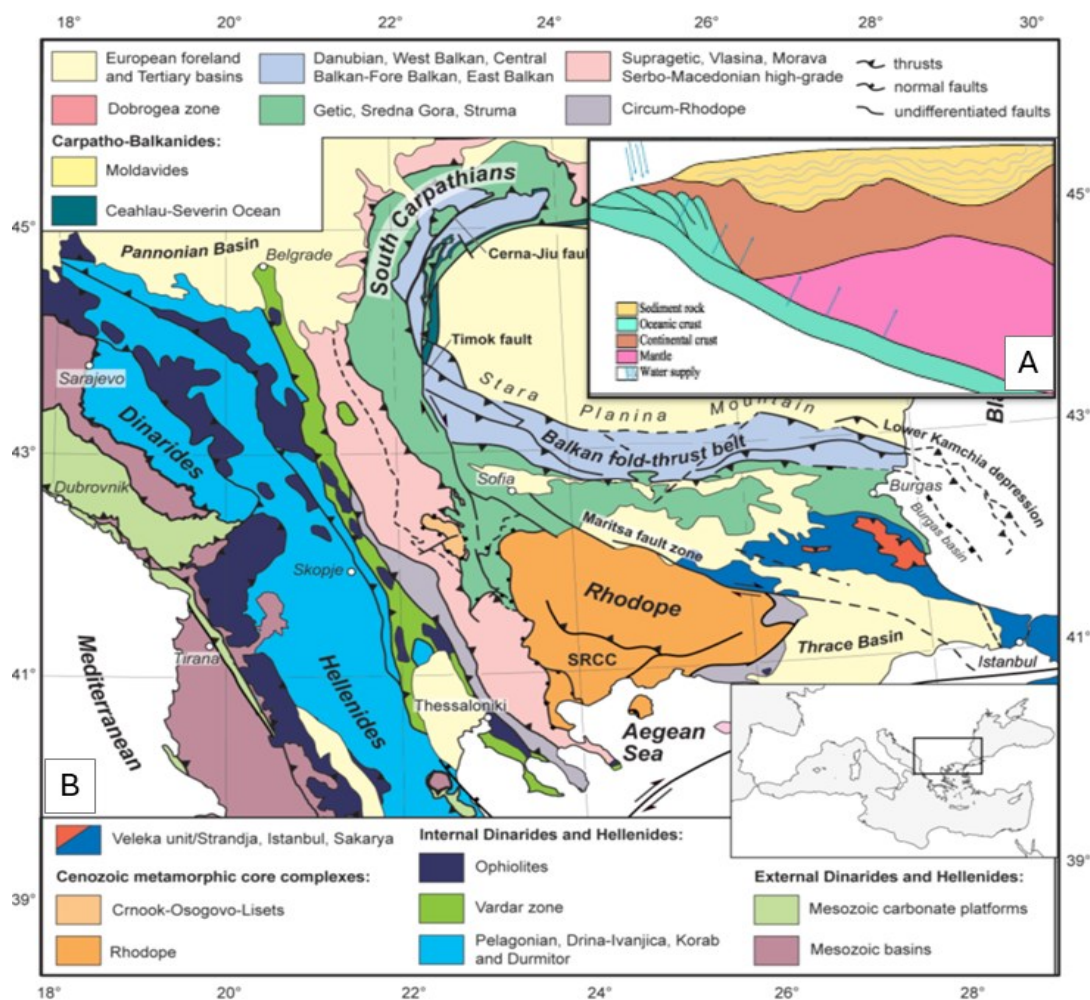


Fig. 2. Natural hydrogen potential ophiolite complexes in the Balkan Peninsula: A) Tethyan ophiolite obduction zone type geotectonic setting (modified after Jackson et al., 2024), B) Tectonic map (modified after Schmid et al., 2008)

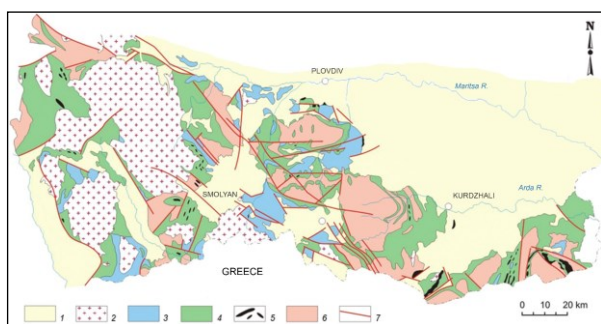


Fig. 3. Geological map of the metamorphic complex in the Rhodope Massif (modified after Kozhoukharova, 2021)

1, Cenozoic; 2, granites; 3-5, Rhodopian Group (3, marbles, 4, variegated formation with ophiolites, 5, serpentinites); 6, Prarhodopian group (gneisses, granite-gneisses, migmatites); 7, faults

The Rhodope ophiolite association. Tectonically, this area encompasses the eastern part of the Rhodope Massif, which is part of the Moravian-Rhodope tectonic unit (Fig. 3). Within the Rhodope Massif, the Proterozoic metamorphic complex, which is part of the general stratigraphic sequence of the crystalline basement, is included. The latter represents a single stratigraphic unit comprising two rock complexes of different ages and lithologies: the lower, the Prarhodopian Supergroup (PRS), and the upper, the Rhodope Supergroup (RS). The Rhodope Ophiolite Association has formed in a Neoproterozoic supra-subduction zone (SSZ) in three stages (Kozhoukharova, 2021):

- serpentinisation at the ocean floor;
- obduction of serpentinite fragments, scraped from a soft and plastic hydrated coat of the sliding ultramafic plate;

c. SSZ-type autochthonous Neoproterozoic basic volcanism, including and covering serpentinite bodies. This determines the heterogeneous nature of the ophiolite association, elements of which are the serpentinites (Fig. 3).

The Proterozoic metamorphic complexes of the Rhodope Massif include many serpentinite bodies that vary in size, from small lenses of several metres to huge lenticular bodies up to 10–12 km long and 300–500 m wide. The largest outcrops are found in the Eastern Rhodopes and are composed of lizardite, chrysotile, and antigorite, which are highly hydrated and contain relics of olivine and bastite. This preserved paragenesis (Kozhoukharova, 2021) indicates that low-temperature metamorphic processes occurred in an SSZ, during which serpentinisation (hydration) of primary peridotites took place. Hence, the source/protolith of these serpentinites has been ultramafic rocks – peridotites.

Natural hydrogen generated by the radiolysis of water

The radiolysis of water within the lithosphere is another key process for generating natural hydrogen. Many radioactive elements, such as uranium, thorium, and potassium, in the Earth's crust can release alpha, beta, and gamma rays during radioactive decay, and the energy released decomposes water molecules into oxygen and hydrogen. Notably, brine can generate more hydrogen than pure water. This process might occur everywhere, but at different intensities. Considering that rocks capable of producing H_2 through water radiolysis are associated with uranium provinces, the study briefly synthesises the U deposits in Bulgaria. Uranium mining in Bulgaria was a major industry in the past, with 48 primary mines and over 30 exploration sites, heavily concentrated in Southern Bulgaria, the Rhodopes, and near Sofia. Key areas include the Buhovo-Seslavtsi region (near Sofia), the Central Rhodopes (Narechen, Smolyan), and deposits along the Maritsa, Tundzha, and Struma rivers.

Based on the geological background and the distribution characteristics of various uranium deposit types in Europe, Wang et al. (2024) describe several uranium metallogenic provinces, including the Balkan-Rhodope uranium metallogenic belt. The metallogenic belt in Bulgaria is distributed across various regions, with uranium mineralisation mainly found in the West Balkan Mountains, central and western Rhodope Massifs, and the Thrace Basin. The area's basement comprises Precambrian and Cambrian metamorphic rocks and Variscan granite, while the basin consists of Paleogene volcanic sediments overlaying Neogene sediments. The structures are complex, with the ancient basement heavily reworked during the Variscan orogeny and intruded by numerous granitic rocks. The later Alpine movements further restructured the belt, creating small intermountain basins and a significant volcanic-sedimentary activity. There are three main types of uranium mineralisation:

1) Sandstone type, mainly in Cenozoic intermontane basins, where volcanic tuffaceous sediments provide sufficient uranium to sustain mineralisation. At the same time, the formation of some uranium mineralisation was modified by hydrothermal activity during the later stage of volcanic activity, which further activated and remobilised uranium in the stratum, accompanied by the formation of green altered rock and a large number of clay minerals (chlorite and montmorillonite).

2) Granite-related or metamorphic type, found near contact zones of Variscan granitic rocks, with mineralisation developing from the late Jurassic to the late Early Cretaceous. High-grade

mineralisation formed by hydrothermal remobilisation of early rocks, and in some deposits with black schist as the host rock (such as Buhovo), uranium precipitation may be related to the high organic matter content of these schists.

3) Volcanic-related mineralisation occurs in Cenozoic volcanic rocks, such as the Smolyan deposit on the southwestern Rhodope Massif, with mineralisation in rhyolite, tuff, and other volcanic rocks. The Rosen deposit in Eastern Bulgaria is associated with volcanic rocks of the monzonite-gabbro-syenite intrusion, dating to the late Cretaceous-Palaeocene. Additionally, uranium mineralisation occurs in Upper Eocene to Lower Oligocene volcanic sediments within Cenozoic basins.

Natural hydrogen generated by the maturation of organic matter

It is suggested (Hanson and Hanson, 2024) that an overlapping set of thermo-catalytic processes produces hydrocarbons (HC) and H_2 . Initially, clay reacts with kerogen, producing HC, H_2 , and amorphous carbon. The alteration of clays releases hydronium. During the late catagenic phase, thermo-catalysis of HC by amorphous carbon yields shorter-chained HC and H_2 , whilst amorphous carbon degrades to carbon black. During the expulsion of HC and H_2 , the permeability of the source rock becomes more heterogeneous, thereby isolating some reactants and creating pyrobitumens and other carbonaceous materials. At higher temperatures during metagenesis, isolated pyrobitumens and other carbonaceous materials in shales are converted to graphite, releasing gaseous HC and, in a second phase, diatomic H_2 via thermo-catalytic reactions with carbon black. This matches the temperatures and results observed in laboratory experiments and petrochemical processes used to generate H_2 . The current conclusion of the HC generation story at the methane preservation limit should be recognised as the start of H_2 generation, with graphitisation marking the end of the process (Fig. 4a).

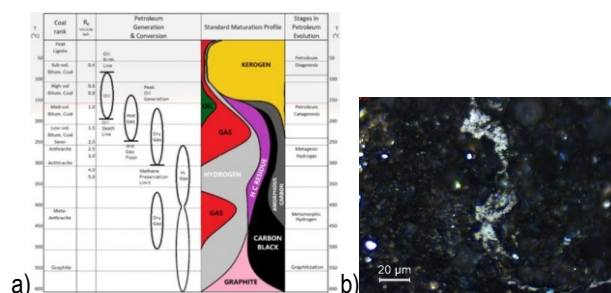


Fig. 4 a) Hydrocarbon model with addition of hydrogen (Hanson & Hanson, 2024); **b) Photomicrographs of pyrobitumen from shale samples with Silurian age in NE Bulgaria**

Based on the results of our previous studies in Eastern Bulgaria, where geochemical and petrographic methods are combined to determine thermal maturity, we have established that most shale rocks in the Silurian sequence are mature or overmature. On the polished section of a few representative samples from these shale rocks, dark-coloured organic matter and pyrobitumen are observed (Fig. 4b). In this context, pyrobitumen formation is considered to correspond to the exact maturity range over which late dry gas generation occurs. It is considered that the exclusive generation of molecular hydrogen from overmature organic matter occurs after late gas generation has ceased. This gives us reason to assume that these areas

also appear promising for assessing the potential for H₂ generation.

Natural hydrogen generated by other processes

In addition to the three key abiotic processes for hydrogen generation mentioned above—serpentinisation, water radiolysis, and reactions involving dissolved magmatic gases—the fourth is mechanical and occurs in geological fault zones. This process occurs whenever silicate rocks are crushed. During cataclasis, hydromechanical reactions break chemical bonds, generating radicals that interact with groundwater to produce hydrogen. Based on an analysis of geological settings, attention should be directed to regions characterised by extensive fault systems and tectonic contact zones, which may serve as conduits that facilitate the migration of deep-seated fluids and gases.

Indicators of the natural hydrogen presence

After identifying potential zones of interest for H₂ generation, attention is focused on those that are targets for H₂ production, and data from the available literature are analysed. Some interesting findings indicate the direct presence of H₂ in hydrocarbon exploration wells, and different dissolved gas emissions are observed across several boreholes. Besides seeking rocks rich in uranium and thorium minerals, the most effective way to detect radiolysis might be to search for helium, since crustal helium can only originate from radioactive activity.

According to the reviewed literature, a wide area in Northeast Bulgaria, within the broader structural zone at the junction between the Fore-Balkan and the Moesian Platform, contains elevated concentrations of dissolved and free gases (Bokov and Chamberski, 1987), including a significant helium component. In selected intervals from wells in adjacent structural zones, helium contents of approximately 0.8–1.2% have been reported. According to the literature, transition zones commonly act as preferential pathways for the upward migration of deep-seated fluids and gases. These values clearly suggest a significant involvement of deep gas sources and an active link between subsurface geological environments and surface fluid systems. Likewise, hydrogen has been detected in dissolved gases in brine waters at concentrations of around 3–4%, and traces of H₂ are found in all analysed samples. This is a particularly important result, as it suggests that hydrogen is not an isolated local anomaly but a recurring feature of the investigated fluid system. The simultaneous presence of helium and hydrogen, whether free or dissolved, is highly significant, as it suggests a broader deep-fluid circulation system rather than a single, localised gas manifestation. It is found that the measured free hydrogen content varies widely across different areas within the same geological setting and at different depths, with the minimum content being only a few digits and the maximum exceeding 90%. Natural hydrogen as a dissolved gas in groundwater has been observed in many cases. The results show that the hydrogen content in groundwater ranges from trace to tens of per cent, with higher values in areas associated with deep faults and rift zones.

Conclusion

In conclusion, this preliminary assessment indicates that Bulgaria has favourable geological conditions for the generation and potential accumulation of natural hydrogen. The most

promising settings include ophiolite and serpentinite-bearing zones where water–rock reactions may occur, uranium-rich provinces where radiolysis can contribute to hydrogen production, mature organic-rich formations, and major fault systems that can support both generation and migration. The reviewed geological, geochemical, and well data suggest that hydrogen occurrences in Bulgaria are not isolated anomalies but part of broader subsurface fluid systems with real exploration significance. Although no confirmed reserves can yet be defined, the results provide a strong basis for future work and support the development of an integrated exploration workflow that combines geological analysis, subsurface data, gas measurements, and remote-sensing methods to identify and prioritise the most prospective target areas.

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