

Geological and geochemical approach to natural hydrogen exploration in the Northern Apennines, Italy

Vivian Azor de Freitas^{a,b,*}, Alessandra Montanini^a, Isabelle Moretti^c, Andrea Artoni^a, Stefano Segadelli^d, Jean de la Paix Izerumugaba^{c,e}, Anne Battani^c, Giuseppe Etiope^{f,g}

^a Department of Chemistry, Life Science and Environmental Sustainability, University of Parma, Parco Area delle Scienze, 157/a, 43100, Parma, Italy

^b National Agency of Petroleum, Natural Gas and Biofuels (ANP), Avenida Rio Branco 65, 20090-004, Rio de Janeiro, Brazil

^c Université de Pau et des Pays de l'Adour, E2S UPPA, LFCR, Pau, France

^d Geological, Soil and Seismic Risk Emilia-Romagna Region, Viale della Fiera, 8, 40127, Bologna, Italy

^e Université de Pau et des Pays de l'Adour, E2S UPPA, IPREM, Pau, France

^f Istituto Nazionale di Geofisica e Vulcanologia, Sezione Roma 2, Rome, Italy

^g Faculty of Environmental Science and Engineering, Babes-Bolyai University, Cluj-Napoca, Romania

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ABSTRACT

The western sector of Northern Apennines, Italy, presents favorable conditions for the occurrence of natural hydrogen (H₂), hosting ophiolitic bodies, hyperalkaline waters, and deep-seated faults. A geological and geochemical investigation was conducted to evaluate the potential for subsurface H₂ accumulations. The study involved gas analyses from spring waters, bubbling gas, and soil-gas measurements, along with petrographic analyses of ultramafic rocks. Multiple springs contain dissolved H₂ at low (up to 1 μM) to moderate (1 μM–100 μM) concentrations relative to other springs in serpentinized peridotites worldwide. In the Taro Valley, H₂ occurrences (0.28 μM–0.79 μM) are associated with hyperalkaline springs in proximity to exposed peridotites. However, the limited thickness of the peridotite body at Mt. Prinzera (~250 m) suggests that the hyperalkaline water and associated H₂ likely derive from deeper unexposed ultramafic units. Petrographic analyses of spinel-peridotites reveal varying degrees of serpentinization (45 %–95 %), characterized by serpentine mesh textures with olivine relics, pyroxene converted into serpentine, and formation of magnetite and chromite. In the Bobbio Tectonic Window, springs with neutral pH waters, located away from exposed ultramafic bodies, contain higher concentrations of dissolved H₂ (0.49 μM–3.8 μM). Although the origin of this H₂ remains unclear, it may be related to hidden ultramafic bodies within the sedimentary sequence undergoing serpentinization. Notably, all the spring-related H₂ occurrences are associated with methane (CH₄), showing thermogenic isotopic signatures (δ¹³C: 58.3 ‰ to −35 ‰ and δ²H: 200 ‰ to −145 ‰). Further research should focus on the characterization of regional hydrocarbon reservoirs, which could also host natural H₂.

1. Introduction

The goal of the Paris Agreement to keep the global average temperature below 2 °C above pre-industrial levels has driven the global transition to low-carbon energy sources, with hydrogen emerging as a prominent alternative. World hydrogen demand could increase by up to 40 % by 2030 in a net zero emissions scenario, driven by the growth of new applications such as power generation, synfuels, and transportation (IEA, 2024). Similarly, hydrogen production, currently dominated by fossil fuels, may be gradually replaced by low-carbon emissions

hydrogen methods, such as electrolysis, steam methane reforming and coal gasification combined with carbon capture. In this context, natural or geological hydrogen (hereafter as natural H₂) represents a potentially cost-effective alternative energy resource compared to manufactured hydrogen, as it is naturally occurring, minimizing the amount of required energy to be produced. Natural H₂ can be generated by a variety of geochemical processes, including serpentinization of ultramafic rocks, different types of oxidations of iron-rich rocks, water radiolysis, thermal degradation of organic matter, mechanoradical reactions along faults, and other minor mechanisms (Zgonnik, 2020; Lévy et al., 2023

* Corresponding author. Department of Chemistry, Life Science and Environmental Sustainability, University of Parma, Parco Area delle Scienze, 157/a, 43100, Parma, Italy.

E-mail addresses: vivian.defreitasazor@unipr.it, vafreitas@anp.gov.br (V. Azor de Freitas).

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and references therein).

Surface geochemical investigations represent a first step in natural H_2 exploration, as the gas produced and accumulated in underground reservoirs can naturally migrate to the Earth's surface, similar to hydrocarbon seepage, whose studies have allowed the discovery of numerous gas-oil fields throughout the world since the beginning of the 20th century. However, the geological origin of H_2 in surface environments (i.e., the identification of H_2 seepage) is not always obvious, as H_2 can also be produced by non-geological mechanisms, such as modern microbial processes (e.g., fermentation) and oxidation of iron-rich sediments in wet soil layers and shallow aquifers (Etiope and Orban, 2025 and references therein). Additionally, corrosion in boreholes (e.g., Feldbusch et al., 2018) and mechanical friction during drilling or hammering for soil-gas sampling can also generate artificial H_2 (Davies et al., 2025). Several mechanisms, then, may limit H_2 seepage, especially microbial activity, which often consumes H_2 , or the water content in the soil that slows its upward transport (Myagkiy et al., 2020). These factors must be considered in surface H_2 prospection.

Natural H_2 research and exploration are still in an early stage but are rapidly evolving and fostered by the natural H_2 accumulation discovered in Mali, where the gas is extracted at a purity of 98 % (Prinzhofer et al., 2018; Maiga et al., 2023). Since this discovery, multiple studies have been carried out in diverse geological settings around the world (e.g., Guélard et al., 2017; Hao et al., 2020; Boreham et al., 2021; Moretti et al., 2021a and b; Lefevre et al., 2022; Leong et al., 2023; Freitas et al., 2024). Industrial projects, including drilling in some cases, are underway in numerous countries, such as Australia, Brazil, Canada, France, Finland, Kosovo, Mali, Oman, South Africa, and the United States (IEA, 2024).

In Italy, studies focusing on natural H_2 are still limited. In studies not specifically addressing natural H_2 , variable concentrations of H_2 were detected in a range of environments, including mud volcanoes, springs, volcanic fluids, fluid inclusions, soil, and boreholes (Etiope et al., 2002; Duchi et al., 2005; Tassi et al., 2012; Boschetti et al., 2013; Boulart et al., 2013; Sciarra et al., 2013; Martinelli et al., 2017; Vitale Brovarone et al., 2017; Etiope and Whitar, 2019; Aiuppa and Moussallam, 2024). Specific investigations on natural H_2 were carried out in the Lanzo Peridotite in the Alps, where low H_2 concentrations of unknown origin (up to 142 ppmv) were observed in the soil (Dugamin et al., 2019), in the Larderello geothermal field, where 4.5 % of H_2 was observed in fumaroles (Leila et al., 2021), and along the Pusteria and Anterselva valleys in the eastern Alps, where up to 1 vol% of H_2 in the soil revealed to be non-geological, likely produced by near-surface fermentation (Etiope et al., 2024).

Here, we studied the occurrence of H_2 in springs in the western portion of Northern Apennines in Italy, which exhibits favorable conditions for H_2 occurrences. The widespread presence of ophiolitic bodies hosting ultramafic rocks is highly promising, as these rocks can play an important role in large-scale H_2 from serpentinization. Additionally, the area is characterized by hyperalkaline waters (pH > 9), which could indicate present-day serpentinization occurring underground, deep-seated faults, and surface gas manifestations, all favorable aspects for studying H_2 occurrences. However, no dedicated study on natural H_2 exploration has been conducted in this region to date.

To evaluate the H_2 generation potential of this area, we combined geological and hydrogeological data, measurements of H_2 concentrations in springs and surrounding soil, stable C and H isotope composition of CH_4 associated with H_2 , and petrographic studies of the ultramafic rock occurrences.

2. Geological setting and site description

The Northwestern portion of the Apennines forms a NW-SE trending fold-and-thrust belt, extending across Emilia-Romagna, Liguria, and Tuscany. They are part of Mediterranean collisional belts, resulting from the closure of the northern branch of the western Tethys, known as the

Ligure-Piemontese basin. The tectonostratigraphic framework currently observed in the region started with a Mesozoic extensional phase (e.g., Marroni et al., 1998; Stampfli and Borel, 2002; Montanini et al., 2006; Schettino and Turco, 2011; Beltrando et al., 2015; Van Hiseberg et al., 2020; Ferrari et al., 2022) culminating in the Jurassic opening of the Ligure-Piemontese oceanic basin (Tribuzio et al., 2016 and references therein). Following this, the area underwent deformation associated with the convergence of the Adria subplate with the Iberian-Europe plate during the Late Cretaceous to Early Oligocene, forming the Apenninic Belt (Marroni et al., 2017; Conti et al., 2020). The Northern Apennines are primarily composed of sedimentary cover sequences of Mesozoic-Cenozoic age and remnants of the oceanic lithosphere of the Ligure-Piemontese basin, whereas exposures of the pre-Mesozoic basement are rare and mainly limited to scattered occurrences in Tuscany, and in the Punta Bianca, Cerreto and the Alpi Apuane areas (see Pandeli et al., 1994; Molli, 2008; Molli et al., 2020).

The exposed basement of the Northern Apennines consists of low-to medium-grade metamorphic rocks, including phyllites, meta-volcanics, carbonate-siliciclastic metasediments, micaschists, and amphibolites. The metamorphism was attributed to crustal thickening during the collisional phase of the Variscan orogeny locally overprinted during Tertiary Apennine orogenesis (Pandeli et al., 1994; Lo Po, D et al., 2016, 2018; Molli et al., 2002, 2020).

Three main tectonostratigraphic units are recognized in the western part of Northern Apennines, i.e., from bottom to top, Tuscan, Subligurian, and Ligurian units, which are locally overlain by the Epi-ligurian Succession (Molli et al., 2010; Conti et al., 2020, and references therein; Fig. 1).

The Tuscan units represent the former proximal portion of the Adria western continental margin, known as the Tuscan Domain (Molli, 2008; Molli et al., 2010). They consist of continental successions forming distinct thrust sheets. In particular, the Tuscan Nappe formed as a continental Triassic-Tertiary sedimentary sequence detached from its original basement and unaffected by Alpine metamorphism, while the so-called Tuscan Metamorphic units experienced pre-Alpine (Variscan) and Alpine metamorphism mostly under greenschist facies conditions (Franceschelli et al., 2004; Molli et al., 2020). The topmost portion of the Tuscan Unit is made of siliciclastic turbidites, sandstone, and carbonates deposited from the Late Oligocene to Early Miocene (Conti et al., 2020 and references therein); foredeep sequences related to the Apenninic Orogeny. Based on the age of the Early Miocene foredeep deposits, overlaying the Tuscan Metamorphic Succession, the Tuscan Unit can be subdivided into two subunits (Fig. 1): the Tuscan Succession, the youngest foredeep deposits being Aquitanian, and the Cervarola-Falterona Succession, the youngest foredeep deposits being Burdigalian.

During the Early Paleocene to Early Miocene, deep marine deposits constituted the Subligurian unit, which, from Late Eocene, were progressively superimposed by the Ligurian unit, and both overthrust the Tuscan and Cervarola-Falterona units (Ogata et al., 2012; Conti et al., 2020; Piazza et al., 2020).

The Ligurian units consist of ophiolitic sequences, which represented the oceanic lithosphere of the Ligure-Piemontese basin and sedimentary deposits formed between Late Cretaceous and Eocene in an accretionary prism (Marroni and Pandolfi, 1996; Marroni et al., 2017). They are subdivided into Internal and External Ligurian, related to distal and proximal domains of the Ligure-Piemontese oceanic basin, respectively (Sanfilippo and Tribuzio, 2011). The Internal Ligurian ophiolites are not associated with continental material and consist of gabbro-peridotite basement overlain by volcano-sedimentary sequences (Sanfilippo and Tribuzio, 2011). The Bracco-Levanto is one of the major ophiolitic bodies of Internal Ligurian units, where serpentinized peridotites, gabbros, and opphicalcites are exposed (Tribuzio et al., 1997). The External Ligurian ophiolites occur as slide-blocks in sedimentary mélanges (Marroni et al., 1998) that formed during the inception of convergence-related sedimentation in Late Cretaceous times (Marroni

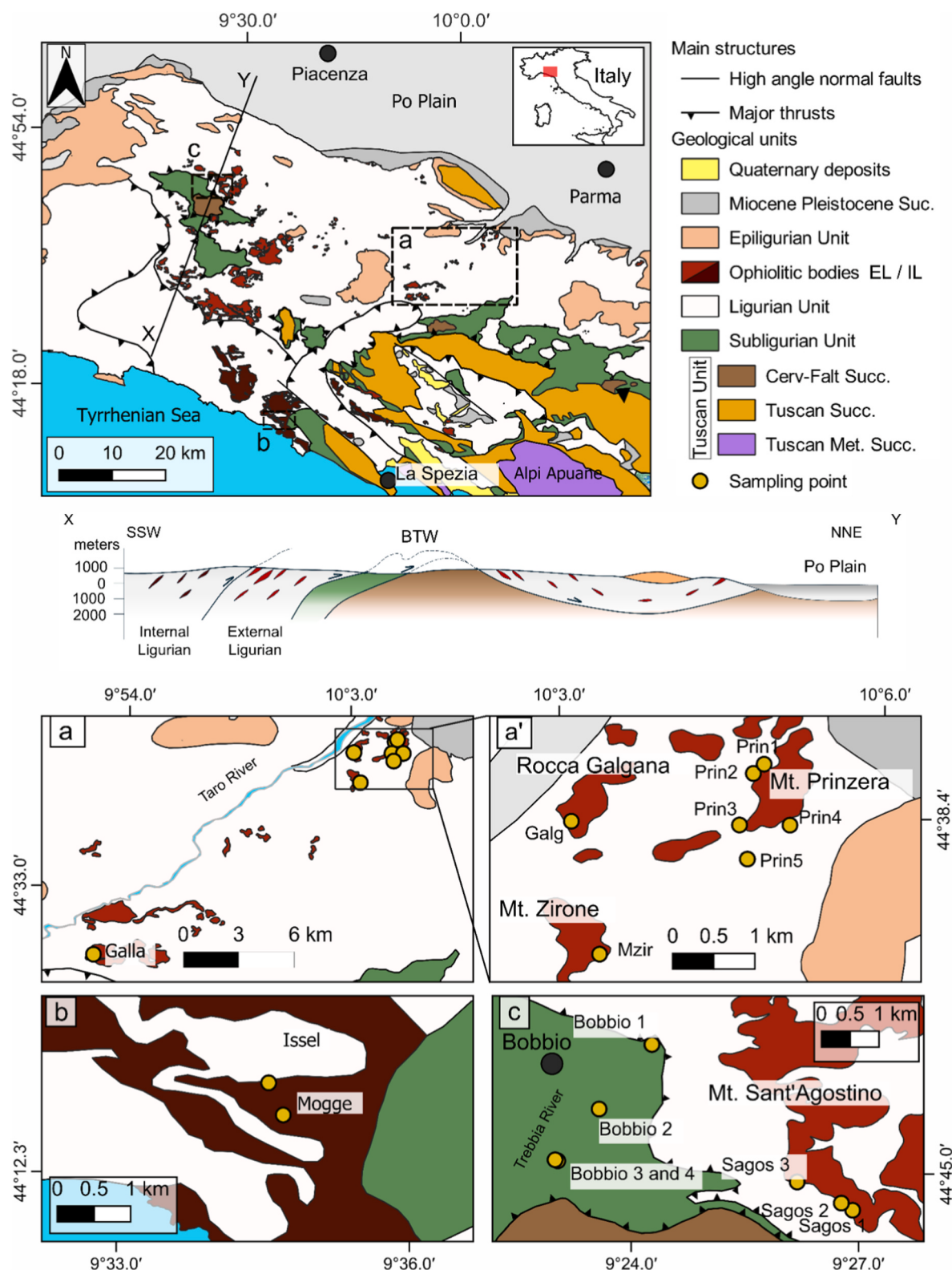


Fig. 1. Geological sketch map of Northern Apennines with emphasis on the three studied areas: a) the region along the Taro Valley (Parma Province), a') Mt. Prinzerza region in detail, b) Castagnola (La Spezia Province), and c) Bobbio (Piacenza Province). The yellow circles correspond to the 17 visited sites, the red polygons refer to the ophiolitic bodies within the External Ligurian (EL), and the dark red ones correspond to the ophiolite bodies of the Internal Ligurian (IL). Geological units were based on [Conti et al. \(2020\)](#), main structures modified from [Molli \(2008\)](#), and ophiolite bodies were based on the Geological Map of Northern Apennines ([Servizio Geologico d'Italia, 2005](#); [Servizio Geologico d'Italia, 1997](#) ; [Conti et al., 2020](#)). Tuscan Nappe, Cervarola-Falterona, and Tuscan Metamorphic Successions are comprised of the Tuscan units ([Conti et al., 2020](#)). Schematic regional cross-section extending from the Internal Ligurian Unit to the Po Plain, crossing the Bobbio Tectonic Window, adapted after [Marroni et al. \(2010, 2019\)](#). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

et al., 2017). In these ophiolites, exhumed subcontinental mantle (Montanini et al., 2006; Rampone et al., 1995) is associated with MOR-type gabbroic and basaltic rocks (Montanini et al., 2008) and, locally with continental crust material. The mantle bodies are up to a few km lateral extent and are composed of spinel-plagioclase lherzolites with pyroxenite layers (Montanini et al., 2006; Ferrari et al., 2022). The ophiolitic bodies are mainly exposed in the Piacenza area and along the Taro Valley in the Parma Province (Fig. 1; see Montanini et al., 2006; Salvioli-Mariani et al., 2020; Ferrari et al., 2022).

The Epiligurian Succession originated from a piggy-back basin with sedimentary units deposited unconformably on the Ligurian units between the Middle Eocene and Late Miocene/Early Pliocene (Piazza et al., 2016; Conti et al., 2020).

2.1. Description of the studied sites and field relations

In the western Northern Apennines, three areas were chosen as study sites: the region along the Taro Valley (Parma Province), Castagnola (La Spezia Province), and Bobbio (Piacenza Province) (Fig. 1).

Along the Taro Valley, two hyperalkaline springs associated with ophiolitic bodies were investigated (Fig. 1a): Galla (pH 10.3) in Gropo di Gorro locality and Prin2 in Mt. Prinzerà, showing pH of 11.2 and dissolved H_2 previously reported by Boschetti et al. (2013). Additional springs with neutral to slightly alkaline pH (7.5–8.8) have also been investigated (Prin1, Prin3, Prin4, Prin5, Galg), including a groundwater sample from about 13 m deep in a borehole in the Mt. Zirone (Mzir).

Prin2 and Galla springs correspond, respectively, to sodium-sulfate and sodium-hydroxide waters, with high pH (10.3–11.2), low Eh (up to -103 mV) and high B/Cl ratios (higher than 13000 mg/L) (Boschetti and Toscani, 2008). The other springs studied in the Mt. Prinzerà region exhibit a $Mg-HCO_3$ composition, with intermediate pH values ranging from 7.5 to 8.8, fresh salinity (228 mg/L), and positive redox potential (from 90 to 565 mV) (Segadelli et al., 2017a).

In the Castagnola area, we investigated a hyperalkaline spring water (Issel) and a managed spring with pH 8.6 (Mogge), both situated in the Bracco-Levanto ophiolitic massif (Fig. 1b). Issel corresponds to a sulfide-bearing spring (Fantoni et al., 2002) with high pH (>10) and negative Eh (-220.4 mV).

In the Bobbio region, two areas were tested: springs in the ultramafic body of Mt. Sant' Agostino and additional springs in the sedimentary successions of Bobbio Tectonic Window (BTW) along the Trebbia River (Fig. 1c). The last area was selected due to the presence of deep faults and gaseous manifestations previously reported (Scicli, 1972; Martinelli et al., 2012), including bubbling springs in the old thermal baths of Bobbio (Bobbio3 and Bobbio4). These baths, closed over 20 years ago, still preserve the ruins of the original building.

Along the Trebbia River (Bobbio1 to 4), the springs are thermal (20 °C– 30 °C) and contain chlorine-sodic waters as a result of mixing with Cl-rich fossil marine waters, possibly originated by the dissolution of Triassic evaporites, which remained trapped in sedimentary layers during the Apennine orogeny (Duchi et al., 2005; Boschetti et al., 2011). In Mt. Sant' Agostino, the springs (Sagos1, Sagos2, and Sagos3) have slightly alkaline waters (pH 8.2 to 8.5) and a $Mg-HCO_3$ composition (data provided by the water management company IRETI S.p.a.).

2.1.1. Ultramafic bodies

The km-sized mantle bodies of Mt. Prinzerà-Mt. Zirone and Mt. Sant' Agostino (Fig. 1c) are composed of variably serpentinized spinel-plagioclase foliated peridotites. Their textures vary from porphyroclastic to mylonitic and ultramylonitic. The most preserved outcrops are characterized by relatively large (up to 1 cm across) pyroxene porphyroclasts. Pyroxenite layers concordant with the foliation of the host peridotite, mainly ranging in thickness from a few millimeters to 8–10 cm, are widespread. At Mt. Prinzerà, brittle deformation with multiple stages of veining, hydration, and local formation of tectonic breccias is common (see Montanini et al., 2006; Segadelli et al., 2017b for a

detailed description).

The Gropo di Gorro body forms a km-sized outcrop with a thickness of 150–200 m (see Salvioli-Mariani et al., 2020 and quoted references). Here, the original mantle rocks have undergone extensive serpentinization and are now composed of massive to intensely fractured serpentinites. Pyroxene porphyroclasts and Cr-spinels with whitish rims of altered plagioclase have been locally preserved. Cataclastic texture and complex serpentine-carbonate veining patterns may occur along the margins of the body.

The Bracco-Levanto ophiolite consists of a gabbroic pluton intruded into mantle peridotites (Sanfilippo et al., 2014). In the Issel spring area (Fig. 1b), the exposed mantle rocks are dark gray, massive serpentinites with rare relics of orthopyroxene porphyroclasts.

2.1.2. Bobbio Tectonic Window

In the westernmost part of the Northern Apennines, the Bobbio Tectonic Window exposes the Cervarola-Falterona Succession, and it is surrounded by the Ligurian and Subligurian units (Servizio Geologico d'Italia, 1997; Ogata et al., 2012).

The Cervarola-Falterona units are represented by siliciclastic turbidites of the Bobbio Formation, slumped deposits of Marsaglia Complex, both Miocene in age, overthrust by the Late Eocene-Early Miocene hemipelagites and turbidites of the Salsominore Formation and fine-grained turbidites of the Rio Fuino Sandstone (Labaume, 2011).

The Subligurian units bordering the BTW correspond to Val D'Aveto Formation, an Oligocene turbiditic complex that also includes conglomerates with volcanic clasts (basalt, andesite, and rhyolite, Mattioli et al., 2002) and calcareous and siliciclastic turbidites of Paleocene-Eocene Canetolo Unit.

The Ligurian units comprise deep marine mass and gravitational flow deposits of the Monte Ragola and Monte Veri Cretaceous complex (i.e., External Ligurian ophiolites), which are associated with ultramafic olistoliths (Servizio Geologico d'Italia, 1997; Labaume, 2011). The ultramafic bodies of Monte Sant' Agostino and Monte Gavi, north-eastwards, and Monte Ragola, south-eastwards, are some mantle bodies exposed around the BTW (Ferrari et al., 2022).

3. Material and methods

H_2 occurrence was investigated in 16 springs and one borehole (Fig. 2), located in the three areas indicated in Fig. 1. The presence of H_2 was also checked in the soil around some springs, and mineralogical analysis of exposing ultramafic rocks was carried out, as described below.

3.1. Sampling and laboratory analysis of dissolved gas in spring water

Water samples from 16 springs (Fig. 2a–d) and one borehole (Fig. 2e) were collected in 2019, 2023, and 2024 in 500 mL Duran borosilicate glass bottles capped with bromobutyl rubber stopper. In the laboratory, the dissolved gas was extracted using the equilibrium headspace method (Capasso and Inguaggiato, 1998), and the concentrations of H_2 , CH_4 , and CO_2 were measured. H_2 was quantified using a semiconductor + pellistor sensor (Huberg Metrex 2, Italy; lower detection limit 5 ppmv; range 0–5 vol%; accuracy ≤ 2 % at 1000 ppmv, and ≤ 1 % at 10,000 ppmv; measurements checked with 100 and 1000 ppmv H_2 standards), while CH_4 and CO_2 were analyzed using a Tunable Diode Laser Adsorption Spectrometry (TDLAS) detector (Gazomat, France; uncertainty 0.1 ppmv, lower detection limit 0.1 ppmv; range 0–100 vol%) and a Licor non-dispersive infrared sensor (Licor LI-820; accuracy < 3 % of reading; range 0–20,000 ppmv). To prevent seal damage and possible H_2 leakage from the bottles, the interval from sampling to gas analysis — regardless of the collection date — ranged from one to eight weeks. During this period, the bottles were stored in a refrigerator at 4 °C until analysis.

Stable carbon and hydrogen isotope compositions of CH_4 ($\delta^{13}C$ vs.



Fig. 2. Photographs illustrating various sampling methods and spring water types: a) natural spring water, exhibiting a white track in the wall (Bobbio1); b) hyperalkaline spring water coming out of ophiolitic rocks (Issel), c) tapped spring water sampling (Sagos3); d) bubbling spring water forming a pond close to the Trebbia River's margin (Bobbio4); e) borehole water sampling (Mzir), and f) bubbling spring gas sampling (Bobbio3).

VPDB and $\delta^2\text{H}$ vs. VSMOW), extracted from Bobbio1 and Bobbio2, were analyzed using, respectively, an Agilent 6890N GC coupled to a Finnigan Delta S Isotope Ratio Mass Spectrometer (IRMS) via a GC-Isolink or a Finnigan GC-C III interface from Thermo (uncertainty of $<0.2\text{‰}$), and an Agilent 7890A GC coupled to a MAT 253 IRMS via a GC-isolink interface from Thermo (uncertainty of $<1\text{‰}$).

The isotopic composition of CH_4 , extracted from Bobbio3 and Bobbio4 water samples, was analyzed on an automated IRMS system (Brass and Röckmann, 2010; Röckmann et al., 2016) with a typical uncertainty of $<0.1\text{‰}$ for $\delta^{13}\text{C}_{\text{CH}_4}$ and $<2\text{‰}$ for $\delta^2\text{H}_{\text{CH}_4}$. The system has been validated in international intercomparison programs (Umezawa et al., 2018). The stable carbon isotopic compositions of CH_4 and CO_2 ($\delta^{13}\text{C}$ vs. VPDB), extracted from water samples of Prin1, Prin2b, and Galla, were analyzed by Cavity Ring-Down Spectroscopy (CRDS) using a Picarro G2201-I C isotope analyzer (Picarro Inc., USA; uncertainty $<0.4\text{‰}$ for $\delta^{13}\text{C}_{\text{CH}_4}$ and $<0.12\text{‰}$ for $\delta^{13}\text{C}_{\text{CO}_2}$). The measurements were also checked and confirmed using two certified isotope standards ($\delta^{13}\text{C}_{\text{CH}_4}$: 39.4‰ and $+19.4\text{‰}$ VPDB) from the Biogeochemical Laboratories of Indiana University.

3.2. Sampling and laboratory analysis of free gas

Three gas samples were collected as bubbles from the springs

Bobbio1, Bobbio3 (Fig. 2f), using a multi-layer foil bag, and Bobbio4, using the classic inverted funnel system and sampling into a copper tube, which was tightly clamped at both ends to ensure no leakage or contamination.

For Bobbio1 and Bobbio3, the stable carbon isotopic composition of CH_4 and CO_2 ($\delta^{13}\text{C}$ vs. VPDB) was analyzed by CRDS using the same methodology for dissolved gas samples Prin1, Prin2b, and Galla described in section 3.1.

The Bobbio4 bubble gas sample was analyzed with an Agilent 6890N/7890A/7890B gas chromatograph (GC). The H_2 , O_2+Ar , N_2 , and CH_4 were measured on the cited GC equipped with a 12 m, 0.32 mm molsieve column (Agilent), a heated injection valve and a TCD detector. Hydrocarbons and CO_2 were analyzed on the GC equipped with a 50 m, 0.32 mm Porabond-Q column (Agilent), a heated injection valve, a heated backflush valve (for C_{6+}), a TCD detector (for CO_2) and an FID detector (for hydrocarbons). Stable carbon and hydrogen isotopes of methane and carbon dioxide were analyzed using the same methodology applied for dissolved gas samples.

3.3. Measurements of pH

The water pH was measured in the field using a portable instrument HQ Series multi-meter equipped with a PHC101 sensor (measure range:

2–14 pH, accuracy of ± 0.02 pH) for Issel and Mogge springs, and using a Hanna HI991300 pH meter (measure range: 2 to 16 pH, accuracy of ± 0.1 pH) for Galg, Bobbio1, 2, 3 and 4 springs. In the case of Prin3, 4 and 5, the pH was measured in the laboratory four weeks after sampling using an XS PC70 (measurement range: 2 to 16 pH, accuracy of ± 0.02 pH). For Prin1, Prin2a, b, and c and Galla pH data are from [Boschetti et al. \(2013\)](#), in which the springs are referred to as PR01, PR10, and UM15, respectively. For the borehole water from Mt. Zirone (Mzir), the mean pH values reported in Regione [Emilia-Romagna, Regione \(2016\)](#) were considered. The pH data for the springs Sagos1, 2, and 3 were provided by the company IRETI S.p.a., which manages the springs as drinking water sources.

3.4. On-site measurements of H_2 in soils

Twelve measurements of H_2 in soil gas were carried out around the six selected springs, Prin2, Prin3, Galg, Bobbio4, Sagos1, and Sagos2, to check possible H_2 concentrations in the soil. The measurements were performed in July 2023 using the portable instrument BIOGAS5000 from Geotech®. The distance between the soil-gas measurements and the springs is approximately a few meters for all sites except for Prin3, which is about 80 m away. The sensor measurement's range is 0–1000 ppmv (± 10.0 %FS) for H_2 . At each site, a hole 80 cm deep and 1 cm wide was drilled in the soil using a portable drilling machine from Bosch® in percussion mode.

3.5. Rock investigations

Ultramafic rock samples from the studied ophiolitic bodies, i.e., Mt. Prinzerà, Mt. Zirone, Rocca Galgana, Mt. Sant' Agostino, Groppo di Gorro, and Bracco-Levanto, were selected for petrographic analyses. Their thin sections were examined under transmitted light using a Leitz optical microscope. Given that serpentinization of ultramafic rocks is a well-known process for natural H_2 generation in the subsurface, the petrographic study focused on identifying the primary minerals involved in this process and their textural relationships. For this purpose, the serpentinization degree and concentrations of olivine and pyroxene were estimated, and we searched for accessory minerals such as brucite and magnetite.

Table 1

Concentrations of CH_4 , H_2 , and CO_2 (μM) dissolved in the groundwater and stable carbon ($\delta^{13}C$ ‰, VPDB) and hydrogen (δ^2H ‰, VSMOW) isotope composition of CH_4 for the three investigated areas. All sites correspond to water springs, except for the water sample Mzir collected from a borehole at a depth of 13 m.

Sample	Site	Latitude	Longitude	pH	CH_4	H_2	CO_2	$\delta^{13}C_{CH_4}$	$\delta^2H_{CH_4}$
a) Taro Valley									
Prin1	Mt. Prinzerà	44°38'54.54"	10°4'53.33"	8.8	1.13	b.d.l.	nm	−44.0	nm
Prin2a	Mt. Prinzerà	44°38'48.92"	10°4'46.55"	11.2	42.44	0.33	<ASW	nm	nm
Prin2b	Mt. Prinzerà	44°38'48.92"	10°4'46.55"	11.2	83.75	0.79	nm	−55.0	nm
Prin2c ^a	Mt. Prinzerà	44°38'48.92"	10°4'46.55"	11.2	73.13	0.28	<ASW	−58.3	−200
Prin3	Mt. Prinzerà	44°38'54.54"	10°4'53.33"	7.7	0.57	0.44	<ASW	nm	nm
Prin4	Mt. Prinzerà	44°38'20.92"	10°5'7.57"	7.7	0.00	b.d.l.	70.2	nm	nm
Prin5	South of the Mt. Prinzerà	44°38'2.23"	10°4'44.09"	7.5	0.01	b.d.l.	126.1	nm	nm
Galg	Rocca Galgana	44°38'23.08"	10°3'06.75"	8.0	0.02	b.d.l.	52.2	nm	nm
Galla	Groppo di Gorro	44°30'10.44"	9°52'29.79"	10.3	5.63	0.67	nm	−39	nm
Mzir	Mt. Zirone	44°37'10.21"	10°3'22.70"	8.0	0.05	b.d.l.	19.1	nm	nm
b) Castagnola area									
Issel	Bracco-Levanto	44°13'12.27"	9°34'33.72"	11.1	1.13	b.d.l.	<ASW	nm	nm
Mogge	Bracco-Levanto	44°12'52.55"	9°34'42.67"	8.61	0.09	b.d.l.	26.8	nm	nm
c) Bobbio area									
Bobbio1	Piancasale	44°46'42.48"	9°24'16.37"	8.0	47.63	0.49	287.3	−35.0	−157.0
Bobbio2	Rio Foio	44°45'51.43"	9°23'34.46"	7.2	361.25	b.d.l.	237.6	−35.1	−145.0
Bobbio3	Old thermal baths	44°45'9.78"	9°23'1.77"	7.2	89.56	3.86	428.2	−25.8	−46.5
Bobbio4	Old thermal baths	44°45'11.53"	9°22'59.05"	7.6	174.00	0.90	496.2	−26.7	−50.2
Sagos1	Sant' Agostino	44°44'31.29"	9°26'55.10"	8.2	0.00	b.d.l.	62.6	nm	nm
Sagos2	Scabiazza	44°44'36.89"	9°26'46.71"	8.5	0.07	b.d.l.	<ASW	nm	nm
Sagos3	Monte1 and 2	44°44'52.72"	9°26'8.62"	8.2	0.07	b.d.l.	36.4	nm	nm
Air Saturated Water (ASW) at 20 °C					0.0025	0.0004	14.5		

^a Data from [Boschetti et al. \(2013\)](#) b.d.l.: below the detection limit (corresponding to 5 ppmv H_2 in the extracted gas phase), nm: not measured.

4. Results

4.1. Dissolved gas in the investigated groundwaters

In the Taro Valley, three springs (Prin2, Prin3, and Galla; [Fig. 1a](#)) exhibit variable amounts of dissolved H_2 (from 0.28 μM to 0.79 μM ; [Table 1](#)), while H_2 was below the detection limit in the remaining spring waters from Mt. Prinzerà and the nearby ophiolitic bodies (Rocca Galgana and Mt. Zirone). In Mt. Prinzerà, the hyperalkaline spring water Prin2, which contains significant amounts of CH_4 (42.44–83.75 μM) and CO_2 below the Air Saturated Water (ASW) level, was sampled at three different times: during the fall-winter of 2010/2011 (Prin2c, [Boschetti et al., 2013](#)), in summer-autumn of 2019 (Prin2b) and during the summer of 2023 (Prin2a). H_2 was found dissolved in the water during all sampling campaigns, regardless of the season and the difference of more than 12-year gap between sampling events. The Prin2b sample displays the highest amounts of dissolved H_2 (0.79 μM). Dissolved H_2 was also detected in Prin3 (0.44 μM), a neutral spring (pH 7.7), which, like Prin2, is located on the western side of Mt. Prinzerà. In the Groppo di Gorro ophiolitic body, located 22 km southwest of Mt. Prinzerà, the Galla hyperalkaline spring contains 0.67 μM of dissolved H_2 , similar to the Prin2b sample. However, it exhibits lower amounts of CH_4 (5.63 μM). The stable carbon isotopic composition of CH_4 , $\delta^{13}C_{CH_4}$, measured in Prin1, Prin2, and Galla samples, ranges from −58.3 ‰ to −39 ‰.

In the Castagnola area (Bracco-Levanto ophiolitic body; [Fig. 1b](#)), H_2 concentration is below the detection limit both in the hyperalkaline spring water of Issel and in the Mogge spring, characterized by a pH of 8.6. The CH_4 concentration is higher (1.13 μM) in the hyperalkaline spring (with CO_2 below the ASW level) compared to the Mogge spring (0.09 μM of CH_4 with 26.8 μM of CO_2).

In the Bobbio region ([Fig. 1c](#)), along the Trebbia River, dissolved H_2 was detected in three different springs (Bobbio1, 3, and 4), ranging from 0.49 μM to 3.86 μM . Here, H_2 is associated with variable amounts of CH_4 (47.6 μM –361.3 μM) and CO_2 (237.6 μM –496.2 μM). In Bobbio1 and Bobbio2 springs, the $\delta^{13}C_{CH_4}$ values range from −35.1 ‰ to −35 ‰, and the $\delta^2H_{CH_4}$ values are from −157 ‰ to −145 ‰. Bobbio3 and 4 exhibit higher $\delta^{13}C$ and δ^2H values ranging from −26.7 ‰ to −25.8 ‰ and −50.2 ‰ and −46.5 ‰, respectively. In three springs at the base of the ophiolitic massif of Mt. Sant' Agostino (Sagos1, 2 and 3), dissolved H_2 is

below the detection limit, CH₄ concentrations were up to 0.07 μM, and CO₂ levels up to 62.6 μM.

4.2. Free gas in bubbling springs

The free gas samples (Bobbio1, Bobbio3, and Bobbio4) correspond to numerous discontinuous bubble gas flows, each lasting a few seconds. The bubbling gas from Bobbio4 was sampled during the summer of 2023, while Bobbio1 and Bobbio3 sampling was conducted during the autumn of 2024.

The bubbling gas in Bobbio4 is mainly composed of CH₄ (97.4 %) and CO₂ (1.8 %; Table 2). The H₂ level was below the GC detection limit (400 ppmv).

The stable carbon isotopic compositions (δ¹³C) of CH₄ and CO₂ measured in these free gas samples range from −35.8 ‰ to −35.7 ‰ and from −27 ‰ to −21.4 ‰, respectively, while δ²H_{CH4} in Bobbio4 was −152 ‰ (Table 3).

4.3. Gas concentration in the soil

Soil-gas measurements detected some levels of H₂ across all analyzed sites (Table 4), but the values remain low. H₂ concentrations ranged from 4 ppmv to 17 ppmv, with the lowest values observed in the Mt. Prinzerà springs (Prin2 and Prin3), where dissolved H₂ was detected. The highest soil-gas concentrations were found in the Rocca Galgana spring (Galg), where dissolved H₂ was below the detection limit.

4.4. Petrographic characterization of ultramafic rocks

The peridotites from Mt. Prinzerà and nearby bodies (Rocca Galgana, Mt. Zirone) display similar petrographic features. They have foliated textures, ranging from porphyroclastic to mylonitic. They have undergone variable degrees of serpentinization (45 %–95 %). Porphyroclastic texture prevails, showing porphyroclasts of olivine, clinopyroxene, and orthopyroxene (up to 10 mm) embedded in a fine-grained matrix (Fig. 3a). This matrix is mainly formed by serpentine and olivine in a mesh texture and by recrystallized pyroxenes and minor spinel. Only pseudomorphs after olivine and pyroxene are discernible in the most serpentinized samples. Cr-spinel may also occur as porphyroclasts, sometimes with plagioclase rims (Fig. 3a). Disseminated brown amphibole may occur as an accessory phase. Magnetite (Fig. 3b) occurs in some samples associated with serpentine. Brucite was not identified in the analyzed thin sections.

In the Gropo di Gorro ultramafic body, the degree of serpentinization is generally high (mostly from 80 % to 100 %), but relatively fresh samples (serpentinization ca. 50 %) have been locally found. They display an isotropic, coarse-grained granular texture with large porphyroclasts of exsolved ortho- and clinopyroxenes and olivine (as relics in a mesh-texture, Fig. 3c). Dark brown Cr-spinel is mantled by altered plagioclase, which also occurs as disseminated patches. More frequently, olivine was entirely replaced by serpentine with a mesh texture, which was subsequently replaced by chlorite. Orthopyroxenes were typically converted into fibrous gray serpentine (bastite), while spinel is transformed into opaque Mg-chromite (±chlorite) with altered plagioclase rims.

The peridotites outcropping in the Castagnola locality, belonging to the Levanto-Bonassola ophiolite (Sanfilippo et al., 2014), are massive rocks, extensively serpentinized. Olivine was replaced by mesh-texture

Table 2
Gas concentrations of the bubbling spring Bobbio4.

Sample	CH ₄	C ₂ H ₆	N ₂	CO ₂	H ₂	H ₂ S	CO	O ₂ +Ar	Air correction %
Bobbio4	97.4	0.017	0	1.8	nd	nd	nd	0.72	40.3

Gas composition is in vol% corrected for air. The air correction was based on the original N₂, O₂ and Ar concentrations. nd: not detected. Ethene and C₃₊ hydrocarbons are present in total concentrations of less than 0.004 vol%.

Table 3
Isotopic data of the bubbling springs in the Bobbio region.

Sample	δ ¹³ C _{CH4}	δ ¹³ C _{CO2}	δ ² H _{CH4}
Bobbio1	−35.8	−27	nm
Bobbio3	−35.7	nm	nm
Bobbio4	−37.5	−21.4	−152

Isotopic data: δ¹³C_{CH4} and δ¹³C_{CO2} in permil (‰), VPDB; δ²H_{CH4} permil (‰), VSMOW. nm: not measured.

Table 4
Soil-gas H₂ concentrations around six springs.

Sample	Site	H ₂ ppmv
Prin2	Monte Prinzerà	4
		5
Prin3	Boschi di Bardone	4
Galg	Rocca Galgana	9
		15
		17
Bobbio4	Bubbling spring old thermal baths	8
		10
Sagos1	Sant'Agostino Sanctuary	5
		7
Sagos2	Spring water Scabiazza	9
		11

serpentine, pyroxenes were replaced by fibrous, bastite-like serpentine with rare relics, and spinel was transformed into opaque Mg-chromite.

5. Discussion

5.1. Evaluation of H₂ concentration data

Hyperalkaline springs associated with serpentinized ophiolitic rocks frequently (but not always) contain measurable amounts of H₂ (e.g., Boulart et al., 2013; Etiope et al., 2013; Pasquet et al., 2025). However, this amount is not constant and may vary over time. For instance, at the same spring in the Semail ophiolites, the H₂ content varied from below the detection limit (i.e., 400 ppmv) to 44.6 % (after air correction) over five months (Pasquet et al., 2025). The paucity of H₂ in some CH₄-bearing hyperalkaline waters may result from complete microbial or abiotic H₂ consumption through CO₂ reduction in a limited H₂ production system.

Dissolved H₂ was observed in the hyperalkaline springs of Prin2 and Galla, whereas it was below the detection limits in Issel. Among ophiolite-related sites with lower pH values (7.5–8.8), the only site where dissolved H₂ was detected corresponds to the Prin3 spring, which is located at the base of Mt. Prinzerà, about 900 m southwest of Prin2.

In Prin2b, Prin3, and Galla, H₂ concentrations are of the same order of magnitude or slightly higher than the level of H₂ that, according to literature (Etiope and Orban, 2025), can be attributed to near-surface microbial origin (up to 0.426 μM). Two of the three H₂ measurements in Prin2 (Prin2a and Prin2c) showed levels below the microbial range, suggesting either variability in the geological H₂ input or partial or complete microbial H₂ consumption.

Most of the springs in the Bobbio area contain higher amounts of dissolved H₂ than the ophiolite-related hyperalkaline springs studied here. The exception is the Bobbio2 spring, which exhibits dissolved H₂ concentration below the detection limit and a higher concentration of

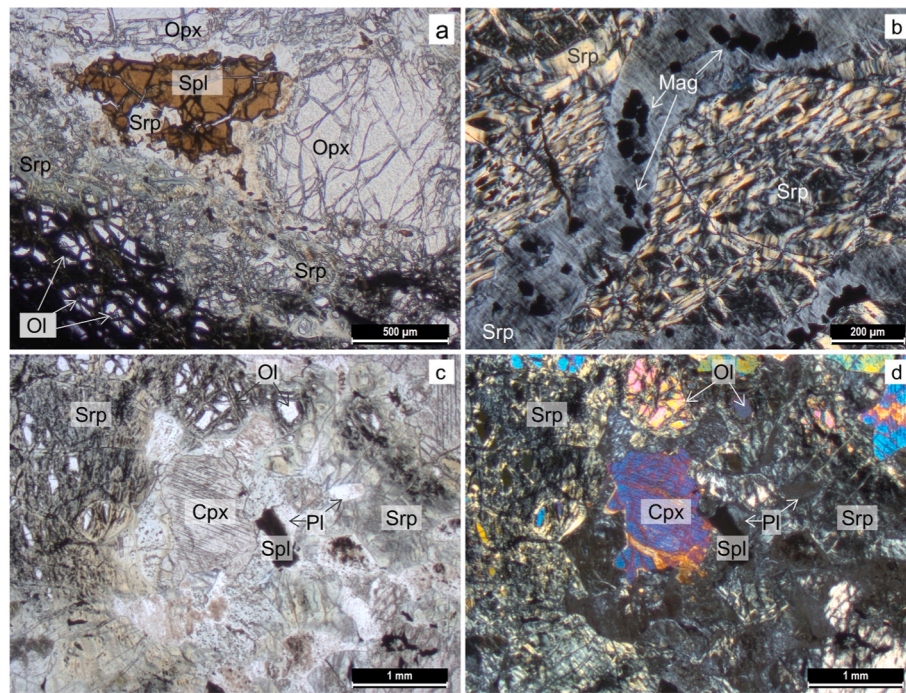


Fig. 3. Thin section photographs of peridotite samples from Taro Valley. a) Coarse olivine and porphyroclasts of orthopyroxene and spinel bordered by serpentine in peridotite sample from Mt. Prinzera (parallel nicols). b) Serpentine in a mesh texture with hourglass core cut by serpentine vein containing magnetite in peridotite sample from Mt. Prinzera (crossed nicols). c) and d) parallel and crossed nicols, respectively, coarse-grained peridotite of Gruppo di Gorro, exhibiting porphyroclasts of exsolved ortho- and clinopyroxenes, olivine as relics in a mesh-texture; dark brown Cr-spinel bordered by altered plagioclase, which also occurs as disseminated patches. Mag: magnetite; Ol: olivine; Cpx: clinopyroxene; Opx: orthopyroxene; Pl: plagioclase; Srp: serpentine; Spl: spinel. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

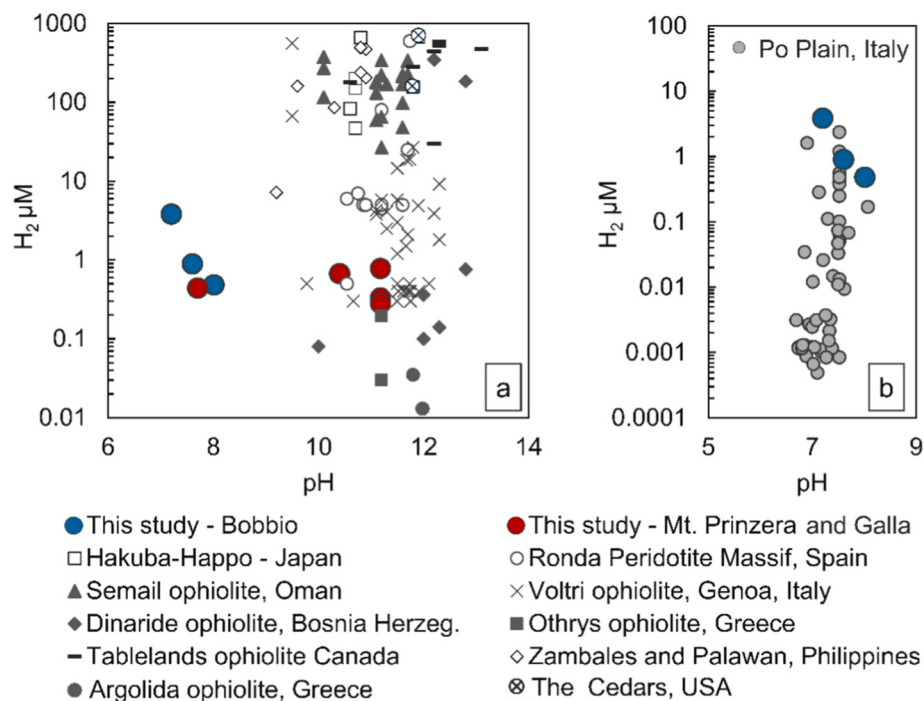


Fig. 4. Binary diagram exhibiting dissolved H_2 concentrations versus pH from different springs and wells. a) Dissolved H_2 concentrations in hyperalkaline springs worldwide compared with the results obtained in this study. World data from Schwarzenbach (2011), Boulart et al. (2013), Etiope et al. (2013), Szponar et al. (2013), Suda et al. (2014), Cardace et al. (2015), Etiope et al. (2016), Brazelton et al. (2017), Etiope et al. (2017), D'Alessandro et al. (2018), Cook et al. (2021), Ojeda et al. (2023). b) Dissolved H_2 levels versus pH for the Bobbio samples compared to Po plain well data (Italy), located in Northern Italy and showing similar pH values (Sciarra et al., 2013; Martinelli et al., 2017).

dissolved CH_4 compared to the other springs in the same region. The occurrence of dissolved H_2 along Trebbia River in Bobbio was unexpected, as it lies within a structural window, with ophiolitic bodies exposed several km away at a higher structural position. The springs exhibit neutral pH values (7.2–8.0), initially not suggesting ongoing serpentinization in the subsurface.

The concentrations of dissolved H_2 observed in this study are relatively low (up to $1 \mu\text{M}$), whereas one sample (Bobbio3) exhibits intermediate levels ($1 \mu\text{M}$ – $100 \mu\text{M}$) compared to hyperalkaline springs associated with ultramafic rocks worldwide (Fig. 4a). Consistently higher concentrations were found in Semail (Oman), The Cedars (USA), Tablelands (Canada), Zambales and Palawan (Philippines) ophiolites, and Hakuba-Happo (Japan) hot springs related to serpentinites. In the ophiolites of Voltri (Italy), Ronda (Spain), and Dinaride (Bosnia and

Herzegovina), a few springs exhibit very high concentrations of dissolved H_2 ($>100 \mu\text{M}$), although most sites displayed low to intermediate levels. Dissolved H_2 concentrations in Greece's Othrys and Argolide ophiolites are lower than those measured in this study.

The dissolved H_2 concentrations from Bobbio were also compared with dissolved gas from Po Plain wells (Fig. 4b; Sciarra et al., 2013; Martinelli et al., 2017), located in northern Italy, approximately 125 km–160 km to the east of Bobbio. Notably, the dissolved H_2 concentrations in the Bobbio region are higher than most wells observed in Po Plain, which also exhibits neutral pH values and is not linked directly to ophiolitic formations.

Nonetheless, while comparisons between worldwide values are informative, it is important to consider that other factors can influence H_2 solubility, such as temperature, pressure, and salinity. In particular,

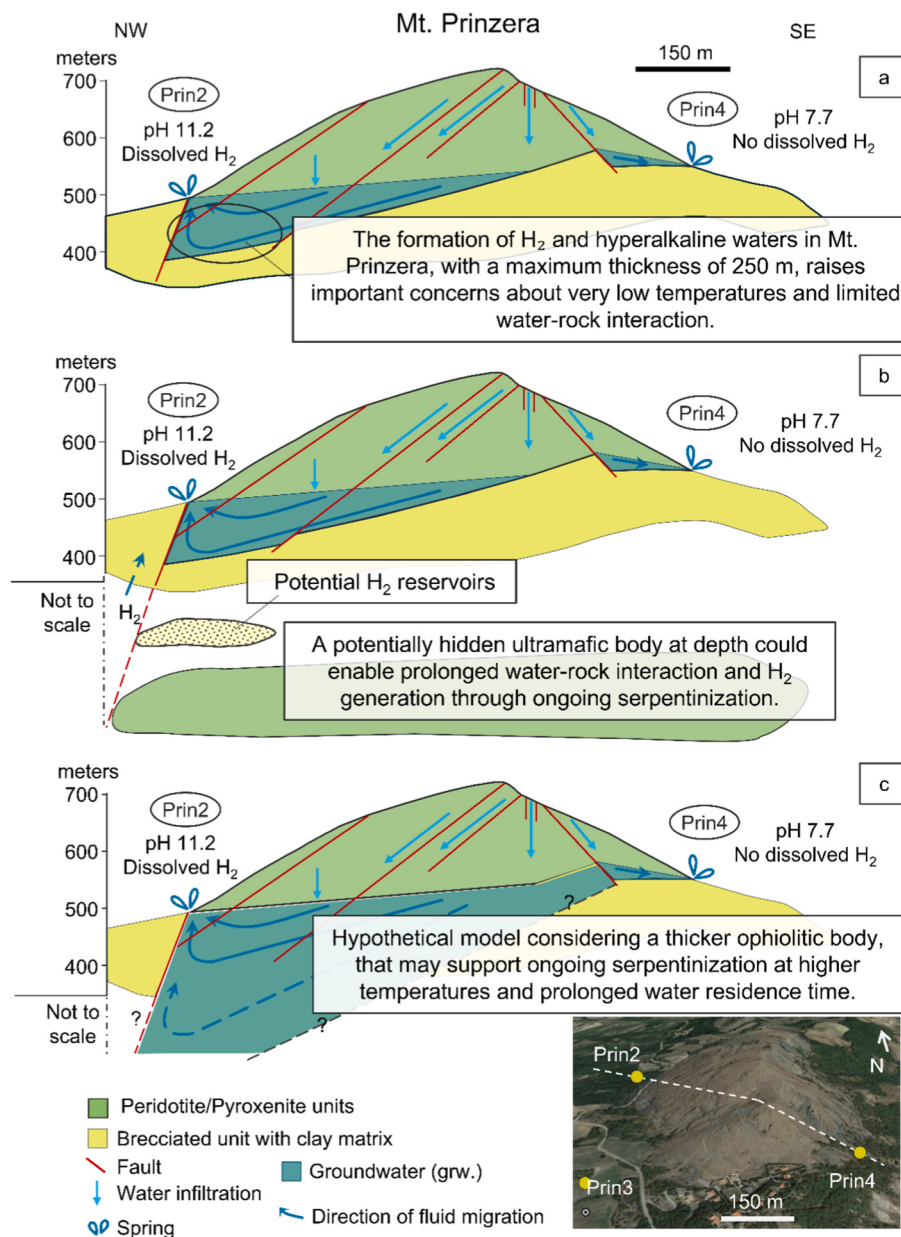


Fig. 5. Hypothetical H_2 generation models through water-rock interaction within the peridotite units in Mt. Prinzer (modified from the high-flow hydrogeological model proposed by Segadelli et al., 2017a). a) The H_2 generation model is based on water-rock interaction within the peridotite units in Mt. Prinzer, considering a maximum thickness of 250 m. b) The model considers the presence of a hidden ultramafic body beneath the boundaries of Mt. Prinzer, generating H_2 through ongoing serpentinization at greater depths. c) This model assumes a deeper root for the ultramafic body of Mt. Prinzer than previously estimated by (Segadelli et al., 2017a), allowing ongoing serpentinization and H_2 generation due to increased depth and temperature and considering a longer water residence time. Dashed lines indicate hypothetical traces. Satellite image from Google Earth Pro (2025), image date 9/18/2022. The vertical scale corresponds to meters above sea level (m.a.s.l.).

NaCl brine waters, such as those found in the Bobbio region, exhibit significantly lower H_2 solubility than pure water (Lopez-Lazaro et al., 2019).

H_2 in the bubbling gas at Bobbio has only been investigated using GC, with a detection limit of 400 ppmv. Further analyses should be conducted using more sensitive instruments.

The very low concentrations of H_2 observed in the soil cannot confirm a geological H_2 seepage, as these levels could be artificially generated during the drilling process or may result from microbial H_2 production in wet ground layers adjacent to the springs (Davies et al., 2025; Etiope and Orban, 2025). Nevertheless, it is important to emphasize that the soil-gas study conducted was preliminary to check H_2 occurrence around the selected springs. A more extensive soil-gas survey is needed, as previous studies reported significant spatial and temporal variability of H_2 values from soil-gas measurements (e.g., Zgonnik et al., 2015; Moretti et al., 2021b; Lévy et al., 2023; Loiseau et al., 2024). Soil-gas measurements, particularly along faults in the Prinzerà and Bobbio areas, should be carried out to verify the existence of natural H_2 seepage potentially related to subsurface H_2 -enriched accumulations.

5.2. Potential of H_2 generation in subsurface rocks

5.2.1. Sites associated with ophiolites

According to Segadelli et al. (2017a and b), brecciated and serpentinized peridotites in Mt. Prinzerà, originally exhibiting very low permeability, are extensively fractured, resulting in significant vertical hydrogeological heterogeneity. Multiple deformation phases affected the entire massif. Notably, Quaternary extensional tectonic events resulted in high-angle faults predominantly oriented WNW-ESE. These structures control groundwater flow, with perennial springs primarily sustained by deep groundwater sources (Segadelli et al., 2017a; and b). In the western sector, within the hyperalkaline spring zone, groundwater is likely to circulate deeply and for extended periods along the fault network, emerging with high pH and with dissolved CH_4 and H_2 (Fig. 5a). In contrast, in the eastern part, the water flows over shorter and shallower paths, resulting in neutral pH and negligible CH_4 and H_2 content.

The presence of H_2 , associated with a hyperalkaline spring within the ultramafic rock body at Mt. Prinzerà, suggests that serpentinization is the main H_2 -generating process. Nonetheless, possible maximum thickness of the Mt. Prinzerà body, approximately 250 m, as estimated by Segadelli et al. (2017a), would imply very low-temperature serpentinization and would not be compatible with deep water circulation models required to form high pH waters (e.g., Barnes et al., 1972; Cipolli et al., 2004). At such shallow depths, the expected maximum temperature is approximately 30 °C, assuming an average regional geothermal gradient of 21.2 °C/km (Acosta et al., 2024) and a surface temperature of 25 °C. Several studies have demonstrated that oxido-reduction reactions can generate H_2 at low temperatures (below 150 °C, e.g., Geymond et al., 2023; Leong et al., 2023; Carlin et al., 2024; Templeton et al., 2024). Additionally, experimental models have demonstrated that H_2 can be produced from ultramafic protoliths even at very low temperatures (between 30 °C and 70 °C, Neubeck et al., 2011).

Even considering H_2 generation at such low temperatures plausible, the origin of the hyperalkaline water at Prin2 is still puzzling. Sodium-rich hyperalkaline waters, such as Prin2, require a relatively long residence time and deep circulation within a closed system for CO_2 to evolve from $Mg-HCO_3$ waters, like those found in the non-hyperalkaline springs in Prinzerà (Barnes et al., 1972; Bruni et al., 2002; Cipolli et al., 2004). Based on geochemical thermodynamic modeling, prolonged water-rock interaction at depth for Prin2 is supported by Boschetti and Toscani (2008, which included Galla) and Segadelli et al. (2017a). However, none of these studies discussed how such prolonged residence time could occur within an ophiolitic body estimated to be only a few hundred meters thick.

Alternative models involving higher serpentinization temperatures, exceeding 50 °C, and longer residence pathways inside the ultramafic body can also be hypothesized. One model assumes the presence of a hidden ultramafic body beneath Mt. Prinzerà, generating H_2 -rich fluids through serpentinization at greater depths and longer residence time. These fluids could then ascend along faults, reaching potential reservoirs and the surface (Fig. 5b). The widespread presence of ultramafic slide-blocks in the External Ligurian, especially in the study area, supports the possibility of ultramafic bodies under Mt. Prinzerà. It can also be hypothesized that the thickness of the Mt. Prinzerà body is greater than previously estimated. If this is the case, the base of the ultramafic body could extend deeper, providing longer water circulation and facilitating H_2 generating and the existence of hyperalkaline waters (Fig. 5c).

These speculative models (Fig. 5) require further investigation to understand the origin of the hyperalkaline waters at Prinzerà and their associated hydrogen content.

Regardless of the hypothetical scenario, the mineral assemblage of peridotites may offer valuable insights into the temperature conditions during serpentinization. According to thermodynamic models and considering the general serpentinization reaction — Olivine + H_2O → Serpentine + Brucite + Magnetite + H_2 — the formation of specific minerals varies depending on the protolith composition and temperature (Klein et al., 2013). The absence of brucite in petrographic studies is notable when considering low-temperature serpentinization as the mechanism for H_2 generation at Mt. Prinzerà since brucite typically forms during the serpentinization of olivine at low temperatures. However, its formation is not predicted in models where at least 50 % of pyroxene undergoes serpentinization along with olivine (Klein et al., 2013), which is the case at Mt. Prinzerà (Fig. 3). Magnetite formation during serpentinization is generally associated with temperatures exceeding 200 °C (Klein et al., 2013), but minor amounts may still form at lower temperatures (Klein et al., 2020). Thus, the small amounts of magnetite observed in a few thin sections of Mt. Prinzerà peridotites align with low-temperature serpentinization. Considering the serpentinization of olivine Fo₈₉ (Montanini et al., 2006) at low temperatures (<200 °C), thermodynamic models predict limited H_2 production, below 200 mmol/kg (Klein et al., 2013), which could explain the low H_2 concentration measured at Mt. Prinzerà. However, the petrographic studies alone were not conclusive in constraining the serpentinization conditions. Additional mineral and rock studies should be carried out on the peridotite rocks to investigate the possible serpentinization at Mt. Prinzerà properly.

It is noteworthy that, despite its relatively low concentrations, H_2 has been consistently detected at the Prin2 spring over multiple years (2011, 2019, and 2023) and during both summer and winter. This constant detection suggests the presence of a persistent migration of H_2 , likely from underground H_2 -rich aquifers or reservoirs or prolific generating rocks crossed by the hyperalkaline waters. The variation in dissolved H_2 concentrations over time indicates that H_2 input into the groundwater changes, possibly due to variable groundwater flow pathways and/or interaction with H_2 -bearing rock, and/or biotic or abiotic H_2 consumption.

Notably, the Prin3 spring, located in the southwestern part of the massif (Figs. 1 and 5, satellite image), has neutral pH and low CH_4 levels, but exhibits dissolved H_2 concentrations similar to those of the hyperalkaline springs. The presence of H_2 in Prin3 may result from mixing deeper water, related to the serpentinization process with shallower recharge waters.

At Galla (Fig. 1a), no previous studies have been carried out to evaluate hydrogeological aspects. However, the presence of hyperalkaline water suggests favorable water-rock interaction under appropriate conditions that may have generated H_2 . Nevertheless, CH_4 concentrations are significantly lower than those at Mt. Prinzerà, likely due to the reduced potential for thermogenic methane generation in the sedimentary rocks of the region.

In the hyperalkaline Issel Spring (Fig. 1b), the concentration of

dissolved H_2 below the detection limit suggests that the serpentinization process in the subsurface, evidenced by the high pH, is incapable of producing H_2 in detectable quantities or that biotic or abiotic processes totally consume any produced H_2 . The limited H_2 production during the serpentinization may be due to insufficient water supply or circulation within the ultramafic massif, which can reduce the water/rock ratio and fails to provide the necessary conditions for H_2 generation. Moreover, the absence of dissolved H_2 in other springs associated with ultramafic bodies, such as Mt. Sant'Agostino, Mt. Zirone, Rocca Galgana, and Mogge Alta (Fig. 1a and c), aligns with their approximately neutral pH, suggesting that no active serpentinization is taking place in the subsurface.

5.2.2. Sites lacking exposed ultramafic rocks

The notable concentration of dissolved H_2 in the Bobbio Tectonic Window (3.86 μM in Bobbio3 spring, Table 1) represents the highest measured value in the western sector of Northern Apennines and was unexpected, as the water is not hyperalkaline. The measured concentration (Table 1) is one order of magnitude higher than the level attributed to microbial processes (0.426 μM ; Etiope and Orban, 2025, Table 1). Additionally, it is comparable to levels observed in hyperalkaline springs associated with ultramafic bodies like the Ronda Peridotite in Spain and Voltri in Italy (Fig. 4a). Thus, there may be a geological source of H_2 within the Bobbio Structural Window. Thrust faults related to the Apenninic Belt, along with younger normal faults, both predominantly NW-SE oriented, may act as migration pathways. These structural features could connect deep H_2 generation sites to the surface, even at considerable depth.

The chloride-rich fossil marine waters in the Bobbio area (Duchi et al., 2005; Boschetti et al., 2011) exhibit neutral pH and do not seem to have passed through active serpentinization zones, as might occur in Mt. Prinzera. Consequently, H_2 generation does not appear to be associated with this relatively shallow process, especially considering the absence of ultramafic outcrops nearby. An alternative process may, therefore, be responsible for H_2 generation within the subsurface.

The isotopic composition of CH_4 can provide insights into the process occurring in the subsurface. The $\delta^2H_{CH_4}$, $\delta^{13}C_{CH_4}$ and $\delta^{13}C_{CO_2}$ values

suggest a thermogenic origin for the dissolved methane in the Bobbio1 and Bobbio2 springs, as well as for the free gas from Bobbio4 (Fig. 6). These results are consistent with the broader classification of light hydrocarbons in the western part of the Northern Apennines (Borgia et al., 1988; Duchi et al., 2005; Martinelli et al., 2012). The dissolved methanes in Bobbio3 and Bobbio4 are enriched in both deuterium and ^{13}C relative to the other springs (Fig. 6a), suggesting methane oxidation near the surface. Coleman et al. (1981) reported isotopic enrichment of δ^2H and $\delta^{13}C$ in experiments on microbial methane oxidation. They observed a variation in δ^2H (ΔH) relative to $\delta^{13}C$ (ΔC), with the $\Delta H/\Delta C$ ratio ranging from 8 to 14 times higher depending on the temperature. The lowest $\Delta H/\Delta C$ ratio was noted at approximately 11.5 °C, while the highest ratio occurred near 26 °C. The data from Bobbio3 and Bobbio4 show a $\Delta H/\Delta C$ ratio of approximately 10.3, suggesting microbial oxidation of thermogenic gas, whose original isotopic signature is maintained in other Bobbio springs (Bobbio1 and Bobbio2; Fig. 6a). Regarding a possible abiotic origin of methane, although dissolved H_2 is present, which could contribute to Fischer-Tropsch-type reactions, the isotopic data of methane does not provide clear evidence for an abiotic origin. However, the combination of $\delta^{13}C_{CH_4}$ and $\delta^{13}C_{CO_2}$ does not clearly distinguish between abiotic and thermogenic origin (Fig. 6b). Therefore, a minor abiotic contribution cannot be ruled out.

A potential origin of H_2 in the Bobbio zone through serpentinization of ultramafic rocks can be hypothesized, even within a structural window dominated by sedimentary rocks. The complex tectonic setting of the Northern Apennines, marked by imbricated thrust stacks, allows the presence of ophiolitic slices from the Ligurian Unit intercalated with the sedimentary succession of Tuscan units. This structural configuration was confirmed during drilling of the Pontremoli well, located 55 km to the southeast of Bobbio, where the Subligurian and Ligurian units were encountered beneath the Tuscan units at depths >1 km (Agip, 1971, 1971; Artani et al., 1992). The neutral pH, chloride-rich waters could be responsible for transporting H_2 in dissolved form. In this scenario, H_2 could have been generated through serpentinization at greater depths, possibly in the past, with the gas trapped in reservoirs. Over time, the trapped H_2 could have migrated along deep-seated faults toward the surface, eventually released and dissolved in water. H_2 as free gas could

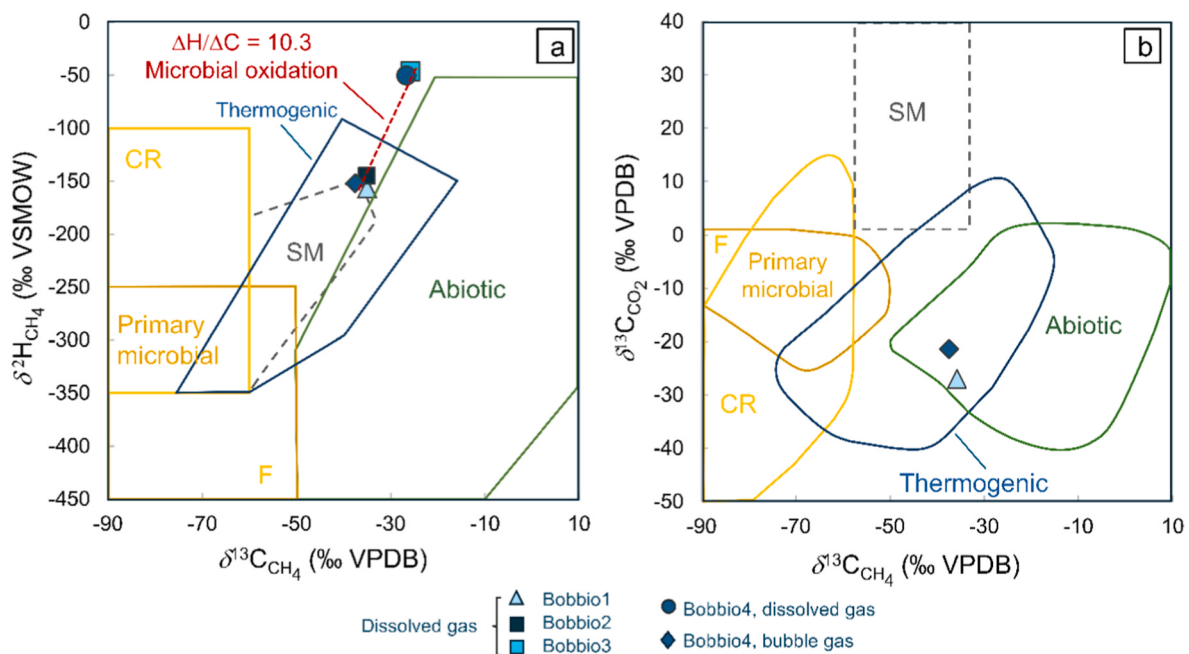


Fig. 6. Genetic diagrams of gas samples from the Bobbio zone. a) δ^2H vs. $\delta^{13}C$ diagram for methane. ΔH and ΔC represent the variations in $\delta^{13}C_{CH_4}$ and $\delta^2H_{CH_4}$ values during methane oxidation. The slope of the dashed red line (10.3) suggests that microbial oxidation could be active in the Bobbio3 and Bobbio4 springs. b) $\delta^{13}C_{CO_2}$ vs. $\delta^{13}C_{CH_4}$ diagram. Genetic fields were reported by Milkov and Etiope (2018). Notations: CR - CO₂ reduction, F - fermentation, and SM - secondary microbial. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

also be present, but our preliminary studies did not detect it. Additional dedicated studies are required to explore these hypotheses further.

Besides Fe-rich rocks as a source of H₂, active large fault zones may not only serve as pathways for H₂ migration from deep sources but could also drive H₂ generation processes via mechanoradical fracture-induced reduction of water (Zgonnik, 2020 and references therein). This H₂ generation mechanism has not been fully tested. In the Bobbio area, however, deep-seated faults may serve as pathways for H₂ migration from deep sources but are unlikely to generate H₂ through a mechanoradical process, as no active faults occur in the region (DISS Working Group, 2021). Additionally, a thermogenic origin of H₂ from overmature organic matter cannot be ruled out. The presence of nearby natural gas fields confirms that organic matter has reached thermal maturity, and further maturation beyond the gas window at higher temperatures could also lead to H₂ generation (Horsfield et al., 2022; Boreham et al., 2023).

The spring Bobbio2, although situated in the same area, has dissolved H₂ below the detection limit. The cause of this phenomenon remains unclear, but it may be attributed to either biotic or abiotic H₂ consumption or potentially inefficient migration pathways. The higher dissolved CH₄ concentration could suggest that H₂ has been consumed during CH₄ formation through Fischer-Tropsch type reactions. Nevertheless, the δ²H and δ¹³C isotopic values for methane do not support an abiotic source for methane.

5.3. Hypothesis for a natural H₂ system and its exploration

The results of this study suggest that a potentially natural H₂ system may exist in the External Ligurian ophiolites (Mt. Prinzerà and Groppo di Gorro) and in the Bobbio Tectonic Window. Table 5 summarizes elements of the potential natural H₂ systems in the Mt. Prinzerà and Bobbio areas.

In ophiolite-related areas, low concentrations of dissolved H₂ in water reduce the potential for direct H₂ exploitation. However, reservoir rocks are present in the Taro Valley region. Hydrocarbon reservoirs have been exploited since the early 20th century, including the now-inactive Vallezza oil field and currently active natural gas concessions of Fornovo di Taro and Monte Ardone, located approximately 5 km northeast of Mt. Prinzerà. The occurrence of porous rocks in the region suggests the potential presence of H₂-bearing reservoirs in the Mt. Prinzerà area, as illustrated in Fig. 5b.

An emerging technique known as geological hydrogen stimulation could also enable future H₂ exploitation at ultramafic bodies. This technique focuses on hydraulic and chemical stimulation of iron-rich rocks to increase the rate of H₂ generation while also controlling the temperature, biological activity, and fluids production (Osselin et al., 2022). Ongoing studies are assessing the feasibility of this method, with notable projects in Oman (Templeton et al., 2024) and the United States. If validated, these engineered water/rock reactions could provide an application in ultramafic massifs like those in the Northern Apennines. However, the potential success of these methods also depends on factors such as the size of each ultramafic body and the proportion of fresh peridotite, which would determine whether there is sufficient rock

volume to support significant H₂ production.

The potential of geological H₂ generation within the Bobbio Tectonic Window represents an interesting case study from a scientific perspective since it is not associated with active serpentinization of outcropping ultramafic bodies. From an economic perspective, the H₂ occurrences identified in this study do not indicate a significant surface H₂ flux, particularly in terms of free gas. However, the area holds the potential to contain key elements of a natural hydrogen system, such as generation rocks, reservoirs, seals, and traps.

The region of Bobbio may host reservoirs in several geological units, such as Miocene turbiditic foredeep deposits and Triassic dolomites, which were previously targeted by the oil and gas industry in nearby areas (Coparex International, 1989; Agip, 1990; Eni, 2003). Furthermore, an active oil and gas production field named Pigazzano is located 15 km northeast. Although these reservoirs have not been previously tested for H₂, they could potentially host this gas, particularly considering H₂ generation at greater depths in the Bobbio Tectonic Window.

Finally, it is important to highlight that natural hydrogen exploration is currently unregulated in Italy. Discussions on establishing a dedicated regulatory framework, similar to initiatives underway in other countries, are essential to foster this potentially emerging sector in Italy.

6. Conclusions

This study demonstrates the presence of dissolved H₂ of likely geological origin at two sites in the Northern Apennines: hyperalkaline spring regions associated with the External Ligurian ophiolites (Mt. Prinzerà and Groppo di Gorro) and the Bobbio Tectonic Window, respectively at the foothills and hinterland of the Northern Apennines orogenic wedge. Conversely, no H₂ was detected in the Internal Ligurian ophiolites (Castagnola area) or neutral pH springs linked to ultramafic rocks of External Ligurian (Mt. Sant’Agostino, Mt. Zirone, and Rocca Galgana). An exception is the neutral pH spring Prin3 at Mt. Prinzerà, located relatively close to the hyperalkaline spring, where H₂ has also been detected. No appreciable H₂ seepage in the soil was detected in the surroundings of the investigated springs.

In the ophiolitic massifs of Mt. Prinzerà and Groppo di Gorro, the interaction of groundwater with ultramafic rocks is likely responsible for the observed dissolved H₂. Petrographic studies reveal peridotites with varying degrees of serpentinization (45 %–100 %), with original olivine and ortho-/clinopyroxenes replaced by serpentine, which also occurs in veins with magnetite. However, the estimated limited thickness of the Mt. Prinzerà (~250 m) appears insufficient to produce hyperalkaline water and provides the optimal conditions for H₂ generation via serpentinization. This thickness limitation suggests that the hyperalkaline water and H₂ origin may instead be linked to deeper-seated peridotite bodies undergoing serpentinization. Notably, while H₂ concentrations at Mt. Prinzerà were relatively low compared to other hyperalkaline waters associated with ultramafic units, they have remained constant over the years.

Although the Bobbio Tectonic Window lacks exposed ophiolitic outcrops, it still shows low to intermediate concentrations of dissolved

Table 5
Presence of key elements of the natural H₂ system for the initial stage of hydrogen exploration at Mt. Prinzerà and the Bobbio Tectonic Window, where the studies are primarily focused.

Site	H ₂ indicators	Generation Rocks/Process	Migration Pathways and traps	Accumulation in subsurface
Mt. Prinzerà	Yes	Yes	Possible	Possible
	Low concentrations of dissolved (likely) geological H ₂	H ₂ generation probably via serpentinization. Peridotite and serpentinite outcrops.	Apenninic thrusts and locally normal faults	Porous rocks confirmed in nearby areas (presence of oil and gas accumulations)
Bobbio Tectonic Window	Yes	Yes	Possible	Possible
	Low to intermediate levels of dissolved geological H ₂ .	H ₂ generation origin still uncertain. Probably serpentinization of hidden ultramafic rocks.	Apenninic thrusts and locally normal faults	Porous rocks confirmed in nearby areas (presence of gas accumulations)

H₂, likely of geological origin. A plausible explanation is the potential presence of hidden ultramafic bodies of the Ligurian units hosted within the sedimentary rocks of the Tuscan units.

Further studies may involve the interpretation of available geophysical surveys (e.g., seismic reflection, gravimetric and magnetic surveys) to investigate potential accumulation targets and generation rocks at depth, as well as additional petrographic and geochemical analyses of rocks and minerals to assess the H₂ generation potential of the outcropping ultramafic rocks.

CRediT authorship contribution statement

Vivian Azor de Freitas: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Alessandra Montanini:** Writing – review & editing, Investigation, Funding acquisition. **Isabelle Moretti:** Writing – review & editing, Resources, Conceptualization. **Andrea Artoni:** Writing – review & editing. **Stefano Segadelli:** Writing – review & editing, Investigation. **Jean de la Paix Izerumugaba:** Writing – review & editing, Investigation. **Anne Battani:** Writing – review & editing, Resources, Investigation. **Giuseppe Etiope:** Writing – review & editing, Validation, Resources, Methodology, Investigation, Funding acquisition, Formal analysis.

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Declaration of competing interest

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.

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Data availability

Data will be made available on request.

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