



GEOLOGY

A deep reservoir for hydrogen drives intense degassing in the Bulqizë ophiolite

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Deep crustal production of hydrogen (H_2) is a potential source of primary energy if recoverable accumulations in geological formations are sufficiently large. We report direct measurements of an elevated outgassing rate of 84% (by volume) of H_2 from the deep underground Bulqizë chromite mine in Albania. A minimum of 200 tons of H_2 is vented annually from the mine's galleries, making it one of the largest recorded H_2 flow rates to date. We cannot attribute the flux solely to the release of paleo-fluids trapped within the rocks or to present-day active and pervasive serpentinization of ultramafic rocks; rather, our results demonstrate the presence of a faulted reservoir deeply rooted in the Jurassic ophiolite massif. This discovery suggests that certain ophiolites may host economically useful accumulations of H_2 gas.

Hydrogen (H_2), like electricity, is a carbon-free energy carrier that plays an important role in modern industry and in the energy transition; however, most H_2 is manufactured using natural gas through a process that consumes energy and releases large amounts of carbon dioxide into the atmosphere. A previously overlooked geologic source of H_2 could contribute to diversifying our energy mix and reducing the carbon footprint of our economy.

Although geologic H_2 plays a central role in the abiotic synthesis of simple organic compounds in the Earth's crust and in supporting deep microbial communities (1–4), the high mobility of the molecule combined with its high reactivity were thought to prevent accumulation in the subsurface except in rare cases (5–8). This paradigm is called into question by recent findings of H_2 -rich fluids in surface seeps and underground mines or boreholes in specific geological settings, along with a reanalysis of historical drilling data (9–14). In particular, H_2 -rich fluids produced by subsurface reactions accompanying the serpentinization of ultramafic rocks such as peridotites are well-documented in uplifted orogenic and ophiolitic bodies (15–21). Despite these observations, our understanding of the processes and settings most conducive to the formation of substantial accumulations of H_2 are still evolving. Notwithstanding the possible importance of geologic H_2 as a clean fuel or as an energy source for life, the current knowledge of H_2 occurrences within the Earth's lithosphere is limited, with recoverable and economic resources of H_2 poorly quantified. The main reason for this lack of fundamental un-

derstanding of the H_2 system stems from the inherent challenges in sampling deep geological fluids and the lack of deep infrastructure targeting potentially fertile H_2 settings. This leads to the pivotal question of whether there is a H_2 geological system comparable to that of petroleum. Our study unveils a high emission rate of almost pure geologic H_2 , suggesting the potential for a new extractable primary energy source.

The Bulqizë mine: geological context and intense H_2 outgassing

We conducted an exploration campaign in the deep underground chromite mine of Bulqizë in Albania (Fig. 1), where the presence of flammable gas was first reported in 1992 at a depth of 620 m. After the discovery of the gas, major explosions occurred in 2011, 2017, and 2023. The Bulqizë chromite mine is one of the largest chromium extraction sites in the world, with total recovery of over 20 million tons of high-grade ore averaging 35 wt% Cr_2O_3 . The mine is situated within the Bulqizë Jurassic ultramafic massif (fig. S6), approximately 40 km northeast of Tirana. This massif is a component of the giant Eastern Mediterranean supra-subduction-zone ophiolite belt that extends from Turkey to Slovenia over more than 3000 km and represents one of the largest and most complete preserved segments of oceanic lithosphere on Earth (22–26). The massif spans an area of 370 km² to a depth of 6 km and hosts numerous folded and faulted concordant chromite ore bodies embedded in the mantle sequence (26–28).

We observed very intense outgassing in the deeper levels of the mine, specifically at depths ranging from 500 to 1000 m below the surface (Fig. 1 and Table 1). The most intense gas discharge in the mine galleries is located in a tectonic zone, i.e., a highly faulted domain, where focused and intense bubbling is visible in drainage pools and runoff streams located at level L19 (fig. S1 and movie S1). The water in

the mine has an origin distinct from the gas. The water percolates from the upper levels of the mine, mainly draining through the shafts, whereas the lower levels of the mine are apparently dry as miners reported no evidence of water inflow during the excavation of the deepest galleries (28). However, this does not rule out the involvement of meteoric distal water or water from other origins in serpentinization elsewhere in the geological formation or below. We measured a gas flow rate of 5 ± 1 L/s (at 25°C and 1.031×10^5 Pa) from several vigorous bubbling zones located in a small 30 m² pool (28). This gas is composed of H_2 (84.0 vol%) and CH_4 (13.2 vol%) with minor concentrations of N_2 (2.7 vol%). Therefore, the amount of H_2 discharged in the gallery from this single pool is 11 t/yr (~30 kg/day) to the minimum, as we did not account for the many minor bubbling points.

Since 2017, advancements in monitoring technology have enabled precise measurements of the H_2 flow rate throughout the mine (28). This has been made possible by the installation of H_2 sensors and flow meters on both the ventilation circuit of inner shaft N9 (at L19) and a dense network of 38 boreholes, extending from L17 to L21 (170 m deep) through the fault zone (figs. S2 and S3). The stale air from L19 to L21, containing 0.40 vol% H_2 , is discharged through shaft N9 at a flow rate of 840 Nm³/min (29). This leads to a H_2 flow rate of 3.4 Nm³/min or 158 t/yr. Notably, the small 30 m² pool emits by itself 7% of the H_2 flow vented through shaft N9, demonstrating the importance of the fault zone as a major drain or reservoir for H_2 (28). The 38 interconnected boreholes were drilled to manage the discharge of H_2 from the tectonic zone intersecting the mine galleries and the ore body. The boreholes are constantly flushed by 4530 Nm³/hr of air. The exhaust gases, containing 1.20 vol% H_2 , are channeled outside the mine through a dedicated pipe, thus providing an additional H_2 flow rate of 54 Nm³/hr (42 t/yr). This flow rate has remained constant over a six-year observation period. Only a fraction of the total amount of air vented from the mine is monitored for H_2 . Indeed, 100 Nm³/sec of air is circulated through the mine by the main ventilation system. Thus, a minimum of 200 tons of H_2 are released from the mine every year (1.0×10^8 mol/yr). Such a relatively large flow of H_2 greatly exceeds the few outgassing rates previously reported from dry seeps and hyperalkaline springs hosted in ophiolites (Table 1). The H_2 outgassing rates we report are minimum values that have been accurately measured and are not extrapolated from single point surface measurements and diffusive flux models.

Revealing the presence of a deep reservoir

The elevated H_2 output raises the question of whether the outgassing results from active

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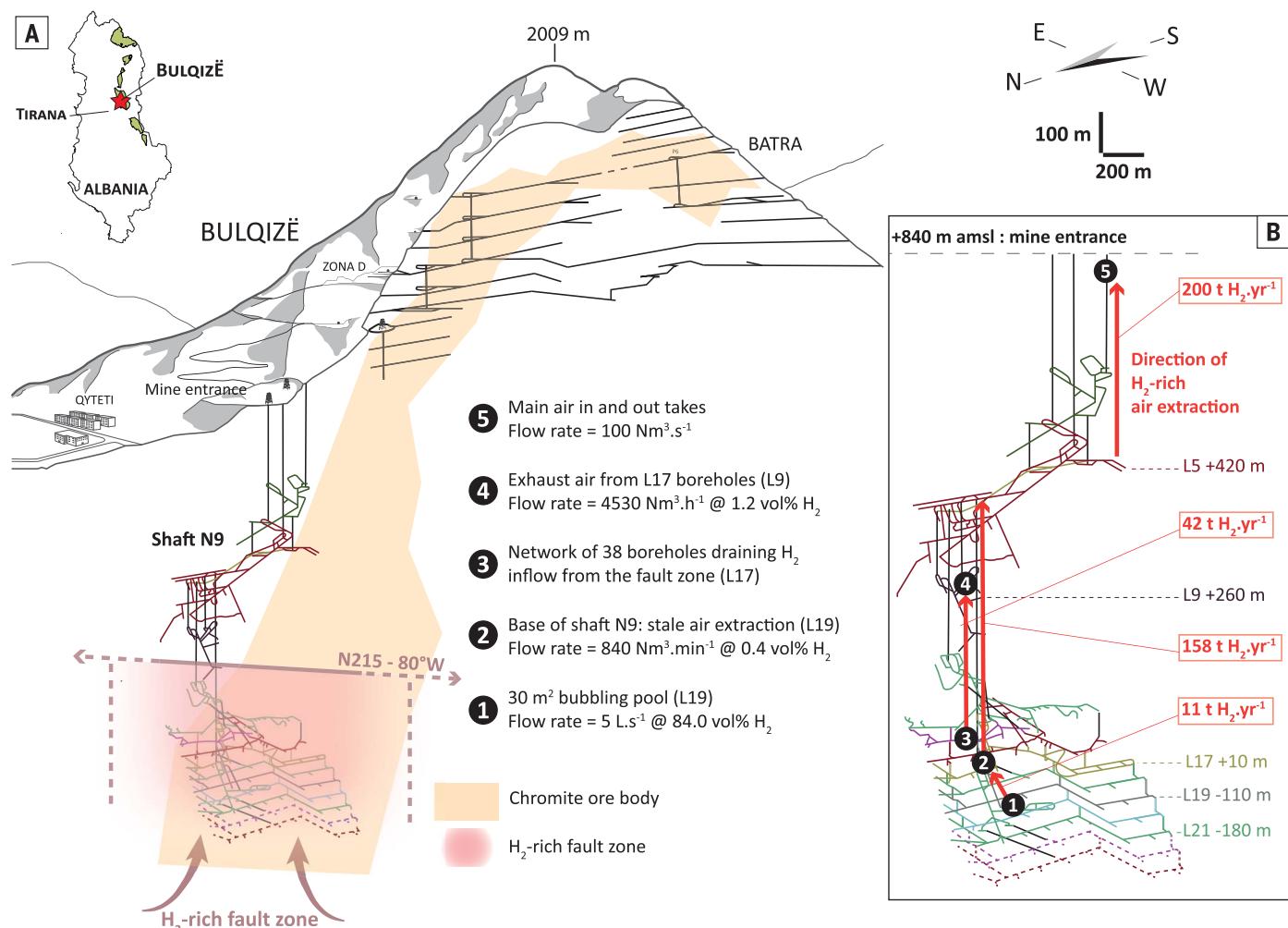


Fig. 1. Schematic 3D view of the Bulqizë underground chromite mine. (A) Map of the deeper levels with location of the H_2 -bearing fault zone indicated. **(B)** Locations where H_2 outgassing rates have been measured. The entrance of the mine is at an altitude of 840 m above mean sea level (amsl).

Table 1. Outgassing rates of H_2 from different sites. Concentrations of H_2 and CH_4 in the free gas phase from the Bulqizë mine (N_2 and O_2 concentrations are given in table S1) and other ophiolite-hosted seeps and bubbling pools.

H_2 outgassing site	Ref.	Area (m ²)	H_2 flow (t/yr)	H_2 (vol%)	CH_4 (vol%)	H_2/CH_4 (vol/vol)
Oman, Haylany pool (bubbles + diffuse)	20	~200	0.158	86.4	6.7	12.9
Oman, Misfah pool (bubbles + diffuse)	20	~1000	0.056	66.9	7.2	9.3
Turkey, Chimaera (diffuse dry seeps)	21	2000	3.5	9.9	87.0	0.11
Albania, Bulqizë mine, L19 pool (focused bubbling)	This study	30	11	84.0	13.2	6.4
Albania, Bulqizë mine, L17 tectonic zone (boreholes)	This study	400	42	1.20	0.15	8.0
Albania, Bulqizë mine, level L19 (shaft N9)	This study	~20,000*	158	0.40	0.05	8.0

*The area of level L19 (~20,000 m²) corresponds to the horizontal projection of the mining works' footprint, and not to the H_2 outgassing area, which is unknown but mostly concerns the fault zone. These estimates provide an indication of the scale of the sites, even if the areas of surface and underground outgassing sites are not directly comparable.

serpentization or from the liberation of fossil H_2 entrapped within the rock. Evaluating the volume of rock involved in this H_2 gas generation and outgassing is therefore crucial. We explored three scenarios that could account for the observed H_2 flow rate of 1.0×10^8 mol/yr, emphasizing the respective roles of the fault zone, the mine's drainage volume, and the

entire Bulqizë massif. Our aim is to differentiate between active (present-day) flows and stocks (i.e., accumulations), with the latter arising from a combination of ancient (possibly fossil) and ongoing H_2 generation processes. Although multiple sources of geologic H_2 in the subsurface are recognized (6, 8), our analysis concentrates on three scenarios that are

particularly relevant to the ophiolitic context (5, 8, 17–21, 28, 30).

Our first scenario considers both the decrepitation of fluid inclusions and the release of H_2 occluded in microporous minerals and microfractures. In this case, H_2 is considered a paleo byproduct of the early stages of a serpentization process that started 165 to 160 Myr ago (26).

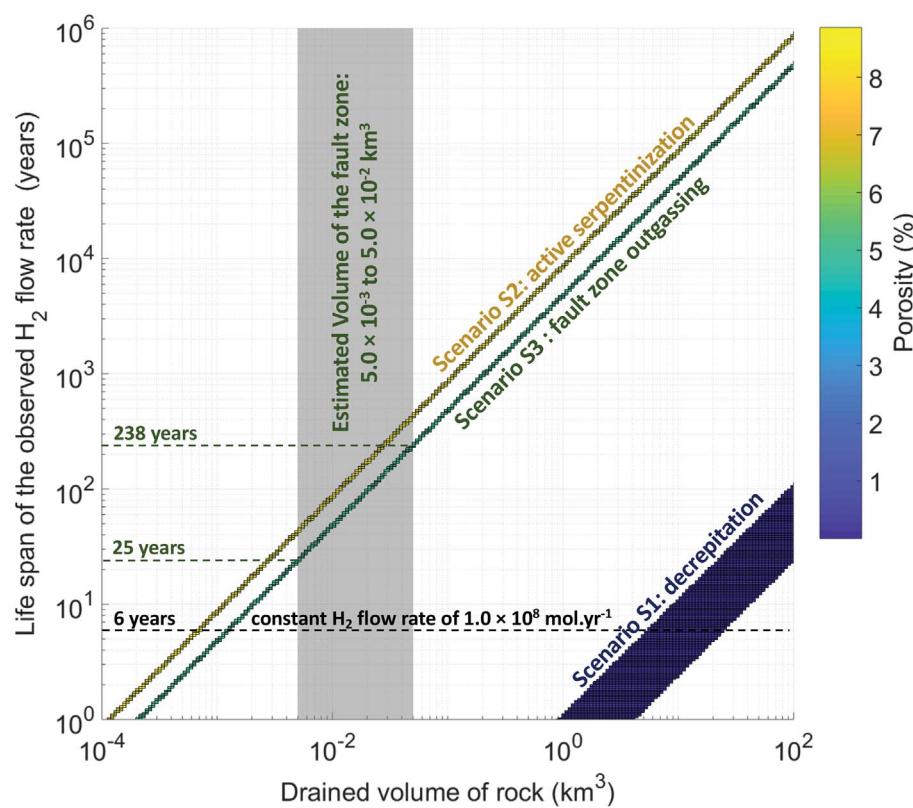


Fig. 2. Three different scenarios for H₂ production. Life span of a constant H₂ flow rate of 1.0×10^8 mol/yr as function of the drained volume of rock and porosity, according to three different scenarios. Scenario 1: decrepitation of paleo H₂ occluded in the rock (dark blue); Scenario 2: active serpentinization at low temperature (yellow); Scenario 3: release of H₂ trapped inside the fault zone which acts as a reservoir (green). The gray area represents the estimated volume range of the fault zone acting as a reservoir.

In our second scenario, we assume that the observed H₂ flow within the mine results from present-day low-temperature serpentinization. In our third scenario, we assume that the release of H₂ occurs when a previously sealed fault zone is opened during mining operations. In this latter case, H₂ is stored within the fractures and connected porosity of the fault zone at a filling flow rate substantially lower than the outgassing rate measured today within the mine. For all three scenarios, we calculated the life span of the measured current H₂ flow rate in the mine as a function of the drained volume of rock (Fig. 2). We assume a rock density of 3000 kg/m³ and consider an average temperature and hydrostatic pressure of 100°C and 30 MPa at 3 km depth, respectively. We also use these parameters to estimate an equivalent porosity containing gaseous H₂ (28, 31). We also consider a 3-km average depth for the ophiolite layer due to its bowl-shaped geometry, with a maximum depth of 6 km (26).

In scenario 1, which involves the release of paleofluids occluded in the rocks (20, 28, 30, 32, 33), we measured a range of H₂ content from 7.5×10^{-6} to 39.0×10^{-6} mol/kg_{rock} (average = 15.4×10^{-6} mol/kg_{rock}; $n = 9$ samples)

in the bulk harzburgite, dunite, and chromitite rock samples collected in the deepest levels of the mine (table S2 and fig. S4). Given that the H₂ flow rate in the mine has remained constant during the last 6 years, this requires a drained rock volume of 5 to 27 km³. If we assume that the mine is the sole outlet for H₂, this implies that the total volume of ophiolite constituting the entire Bulqizé massif (i.e., $370 \text{ km}^2 \times 3 \text{ km}$) would be depleted in 250 to 1300 years. Thus, this scenario seems unlikely, as all H₂ within the massif would have vanished instantaneously on a geological timescale.

In scenario 2, which involves the direct consequences of an active serpentinization process at depth in the presence of water, a volume of 1.2×10^{-4} km³ must be altered every year to account for the observed H₂ flow rate of 1.0×10^8 mol/yr, assuming that 0.3 mol of H₂ are produced per kg of serpentinized peridotite at temperatures below 100°C (20). If we consider a peridotite area of 1 km², this would result in a serpentinization front advancing by 0.15 m per year. Notably, this rate is 250 times faster than the regional uplift rate of 0.6 mm/yr for the Bulqizé ophiolite (34). Thus, if the uplift is negligible and the velocity of the serpentinization

front remained constant over time, the reaction front would have advanced beyond the maximum thickness of the ophiolite (6 km) in 40,000 years, implying that the H₂ production potential should be exhausted by now. A similar conclusion can be reached by considering a maximum mine drainage volume of 135 km³, corresponding to the effective rainwater catchment area of the mine of 45 km² (fig. S7) and a rock thickness of 3 km. In this case, the whole drainage volume should have been fully serpentinized in only 13.5 Ma whereas final exhumation of the massif is dated at 15 to 45 Ma (24). Another independent line of evidence to rule out present-day active serpentinization as the source of H₂ monitored in the mine comes from the comparison of the observed H₂ flow rate with the global estimates of H₂ production rate from both the oceanic lithosphere and the Precambrian continental crust. The latter ranges from 1.0×10^{10} to 1.2×10^{12} mol/yr (35–37), meaning that the contribution from the Bulqizé mine alone would be 0.01 to 1% of this global flux. This amount is an unrealistic contribution, considering the small size of the Bulqizé ultramafic massif compared with both the 80,000-km-long oceanic ridge system and the 1.06×10^8 km² Precambrian shield surface area. Therefore, H₂ produced by serpentinization or any other processes must have accumulated over a long period of time in a reservoir rock, the most realistic one being the fault zone as indicated by its intense degassing. This conclusion does not mean that decrepitation (scenario 1) or serpentinization (scenario 2) do not happen, but they alone cannot explain the actual resulting flow rate.

In scenario 3, we consider that the flow measured in the mine results from the degassing of H₂ gas trapped in the fault zone only after being produced. The mine perforated the top of the fault zone at several points when it reached a depth ranging from 0.5 to 1 km, releasing the gas stored in this sealed volume, which acts as a porous reservoir. Based on in situ observations (28), the fault zone is ~10 m wide, with a length varying from 100 m to 1 km, and a maximum height of 5 km (with the sealed top being around 500 m deep in the mine). These dimensions yield volumes of rock ranging from 5.0×10^{-3} to 5.0×10^{-2} km³ (represented by the gray area in Fig. 2). The total pore space volume generated by the overall amount of fractures present in this highly damaged zone is unknown, so we assume that the equivalent porosity has an average value of 5% at depth as measured in fault zones in Oman ophiolites (38). Thus, a fault volume of 1.3×10^{-3} km³ with a porosity of 5% would be sufficient to sustain the observed H₂ flow rate for 6 years. Considering the estimated range of fault volume and the same porosity, the measured flow rate could be sustained for 25 to 238 years. In other words, the total amount of H₂ stored in the fault zone would range from

5000 to ~50,000 tons. The temperature ranging from 40° to 160°C (28), along with the dry conditions in the deep horizons of the ophiolite may have hampered consumption of H₂ by both microbial activity (too hot) and abiotic redox (too cold) reactions, at least in the deepest part of the reservoir. Hydrogen-rich fluids isolated in the crust for billions of years have already been reported in deep fracture networks from underground mines and boreholes in Precambrian shields demonstrating that H₂ can accumulate over geological timescales (9, 39).

Implications for geologic H₂ exploration

What sets our discovery apart is the large flux of almost pure H₂ gas we have observed. In the context of energy transition, our findings could substantially affect the ongoing search for new energy resources. We reveal that ophiolites, which are mantle rocks from the oceanic crust obducted onto continents, not only constitute effective source rocks, but also have the potential to host high-quality, H₂-rich gas reservoirs. These geological formations, prevalent across all the continents, extend beyond being mere geological anomalies. In fact, many ophiolites worldwide have been found to contain springs or seeps that release H₂ gas. Within this geological context, H₂ exhibits potential for commercial extraction as it can be focused into fracture zones and trapped.

In the past, the oil and gas industry has largely ignored ophiolites, considering them unsuitable for hydrocarbon resource exploitation. However, these onshore formations might offer potential for large-scale H₂ accumulations and therefore constitute a promising target for H₂ exploration. A key point is the presence of drainage systems such as faults and tectonic zones in these geological settings. As a result, a holistic understanding of the tectonic and petrophysical factors influencing the migration pathways and accumulation of H₂ is needed to guide exploration. The configuration and properties of the seal remain uncertain, but the ore body and the necking of the faults may play crucial roles. Chromitite, commonly found

in ophiolites, is noteworthy as several known H₂-rich seeps are situated near chromite mines (32, 40, 41). The possible connection between chromitite and H₂ emissions, though not yet confirmed, must be ascertained. Finally, in the emerging quest for geologic H₂, it is crucial to consider both the nature of these H₂ resources—whether they are ancient (fossil) or recent—and the potential impact on deep-seated microbial ecosystems that thrive on H₂ (42, 43). A comprehensive understanding of these factors is essential to mitigate risks and ensure a sustainable development of H₂ resources.

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SUPPLEMENTARY MATERIALS

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Materials and Methods

Supplementary Text

Figs. S1 to S10

Tables S1 to S3

References (44–50)

Movie S1

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