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Looking for natural hydrogen in Albania and Kosova

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A regional geochemistry field study was conducted in Albania and Kosova to spot natural H_2 occurrences related to ophiolite massifs. A total of 21 sites, mainly consisting of natural springs, were studied, and nine were sampled for analyzing associated free gas and C and H isotopes of CH_4 and H_2 when possible. Four springs showed gas with H_2 occurrence, one particularly reaching 16% of H_2 in the north of Kosova in a location named Vuçe, which makes it the fifth gas seep most enriched in H_2 in the Dinarides, after H_2-rich gas seeps in Serbia and Bosnia and Herzegovina. This gas seep is associated with hyperalkaline water having a pH of about 10.7. This would favor the assumption that H_2 is derived from the serpentinization of peridotites, a process which is likely still ongoing. H_2 is associated mainly with N_2 and CH_4, like the other H_2-rich gas springs in the Dinarides. Based on C and H isotopes, CH_4 is abiotic or microbial. H isotopes suggest a formation of H_2 at about a 2-km depth. Another hyperalkaline spring was found in the south of Albania, at the border of the Korça Basin, with less than 200 ppm of H_2. No relation between H_2 and He was identified at the scale of Albania and Kosova, nor at the scale of the whole Dinarides. This work provides a completed map of the H_2 occurrences in the Dinarides and allows to highlight some hot spots for H_2 exploration, mainly located inside the ophiolite massifs like in other ophiolites (such as Oman, New Caledonia, and The Philippines), and not on major faults like in the Pyrenees.

KEYWORDS

H_2, Albania, Kosova, Dinarides, ophiolite, serpentinization

1 Introduction

Natural H_2, also known as white hydrogen in hydrogen's type classification, is a low impact and a potential low-cost energy (Moretti, 2019; Gaucher, 2020; Lapi et al., 2022) which could be present in large quantities in the subsurface (Zgonnik, 2020). From a couple of years, this resource is being increasingly studied in some countries such as Brazil (Prinzhofer et al., 2019) and Australia (Frery et al., 2021) and more recently in Europe, in Spain, and in France (Lefeuvre et al., 2022). Analogous with the oil and gas, natural hydrogen exploration can be approached through a "system" invoking source, migration, reservoir, trap, and seal to eventually lead to an accumulation in the subsurface. Hydrogen "source rock" is a rock able, by natural physicochemical processes, to generate hydrogen gas. Natural H_2 can be generated by different processes where the five major ones are 1) reduction of water *via* rock alteration, 2) radiolysis, 3) degassing of magmas, 4) *via* a reaction with surface radicals in fault environment (Zgonnik, 2020; Moretti et al., 2021), or 5) maturation of the organic matter (Horsfield et al., 2022; Mahlstedt et al., 2022). Serpentinization is the most well-known process in the literature, in particular the alteration of peridotites taking place on the mid-ocean ridge (MOR) (Charlou et al., 2002; Proskurowski et al., 2006; Andreani et al., 2014; Worman et al., 2020). However, apart from exceptions such as Iceland (Combaudon et al., 2022) or Ethiopia (Pasquet et al., 2022), MOR is particularly difficult to study and explore as it is located in deep water environment. On the contrary, the ophiolites, remains of an obducted oceanic lithosphere, are accessible targets. Their H_2 potential is, thus, far easier to apprehend.

Some ophiolites have been the subject of intense studies these last years, such as those in Oman and in New Caledonia, using direct and indirect techniques to constrain the H_2 origin (Neal and Stanger, 1983; Neal and Stanger, 1985; Deville and Prinzhofer, 2016; Vacquand et al., 2018). The indirect techniques consist in using proxy like the presence of hyperalkaline springs which is often related to the serpentinization:

$$\mathbf{Fe^{2+} + H_2O \rightarrow Fe^{3+} + 1/2\, H_2 + OH^-} \quad (1)$$

The closure of the Tethys Ocean leads to multiple ophiolite developments in Europe, especially in its southeastern part. We studied the Dinarides–Albanides which are a 1000-km long mountain range mainly made of ophiolites and covering Croatia, Bosnia and Herzegovina, Serbia, Kosova, Albania, and extending southward with Hellenides in Greece. In Serbia, a large amount of gas seeps or free gas bubbling in natural springs have been studied, and some sites contain up to 85% of H_2 (Randazzo et al., 2021). However, no systematic study has been performed so far to inventory and characterize such gases in Albania and Kosova in the frame of H_2 generation. The first step of the study consisted in listing and thoroughly locating all referenced gas occurrences at surface. Then, field acquisitions were realized (free gas, dissolved gas, and water sampling) to complete the existing dataset and provide a first overview of natural hydrogen potential associated with the Dinarides ophiolites.

2 Geological setting

The ophiolites from the Dinarides come from the suture of (i) one ocean or (ii) several ones, even if a consensus seems to appear in favor of the (i) model (Schmid et al., 2020). The ophiolitic oceanic crust and metamorphic soil were formed during the Middle Jurassic. This corresponds to the beginning of the closure of the Neo-Tethys Ocean initiated by the north east dipping subduction of the Adria plate under the Eurasian plate. Some rocks that are present in the ophiolite mélange trace the beginning of the obduction to the Late Jurassic. It lasted until the complete closure of the ocean forming the Sava Suture Zone which happened between the Late Cretaceous and Paleogene (Schmid et al., 2008; Maffione and van Hinsbergen, 2018; Schmid et al., 2020). During the shortening, the ophiolitic nappes have been thrusted onto about 200 km. The Tertiary slab roll back and possible break off resulted in Tertiary volcanism and intracontinental basins, mainly associated with normal faulting, filled with Miocene sediments (Schefer et al., 2011).

Studies conducted at surface in other areas suggest that hydrogen can be created by the interaction of water with mantle peridotites and migrate to the surface *via* major thrusts, like in the Pyrenees (Lefeuvre et al., 2022). Gas seeps or free gas bubbling in natural springs can also be found on the ophiolite massif itself, often associated with hyperalkaline waters (Vacquand et al., 2018). Some plutons can also act as a source of H_2 *via* their alteration of radiolysis (Truche et al., 2020). In the Dinarides, the major structure of interest is the ophiolite of the West Vardar where some H_2 has been measured in Bosnia and Herzegovina and Serbia with high content (Etiope et al., 2017; Randazzo et al., 2021) in free gas sampled in natural springs in ophiolite massifs. Therefore, the study will focus on the West Vardar zone in Albania and Kosova.

In Albania, the West Vardar ophiolite is represented by the Mirdita ophiolite, located in the Albanides mountain belt, a segment of the Dinarides–Albanides–Hellenides orogen (Figure 1). It is delimited on the east by the Pelagonian block and on the west by the Krasta, Cukali, and Kruja zone, considered as Adria-derived allochtons (Meshi et al., 2010; van Unen et al., 2019; Schmid et al., 2020). The Kruja zone is well-known for its geothermal potential because of deep thrust faults that allow hot fluids to reach the surface (Frasheri et al., 2009). The western massifs of the Mirdita ophiolite are mantle domes of a fossil oceanic core complex (OCC) (Nicolas et al., 2017) exhumed by a detachment rooted in the Moho transition zone under a slow-spreading MOR. The mantle is harzburgite, which is capped by mylonitic plagioclase-amphibole peridotite about 400 m thick. The eastern massifs of the Mirdita ophiolite are mainly harzburgite interpreted as derived from a supra-subduction zone [SSZ (Dilek et al., 2008)]. The thickness of the ophiolite can reach 14 km in its northeastern part, whereas on the west and southeast, it goes down to 2 km (Frasheri and Bushati, 2008). Some depressions in the ophiolite massifs have been filled with Tertiary deposits, leading to the formation of the basins of Korça and of Burrel. We can note that the ophiolite was little affected by alpine tectonics (Meshi et al., 2010).

In Kosova, ophiolites outcrop on the eastern, center, southeastern, and northern part of the country, delimited by basin that can be filled by about 2 km of sediments. Apart from the southeastern ophiolite, the ophiolites are included in the West Vardar zone and are part of the Dinarides, in the continuity of Mirdita ophiolite. The central ophiolite of Kosova is represented by the massif of Golesh, bordered by Cenozoic basins (Elezaj, 2009), that suffered hydrothermal alteration (Ilich and Toshovich, 2005), leading to the precipitation of magnesite, currently exploited for their Mg content. The ophiolite in the north of Kosova is named Ibar. It was thrusted on the Jadar–Kopaonik block between Drina–Ivanjica and Serbo-Macedonian blocks (Toljić et al., 2019; Schmid et al., 2020; Spahic and Gaudenyi, 2020). It is mainly harzburgite and derived from an SSZ. Its thickness is not well constrained but based on some cross-sections, it can vary from several hundred (Miletić, 1995) of meters to ~2 km (Schmid et al., 2020) even if gravimetric data are lacking to give a precise value. Some basins are present on the ophiolite filled with Miocene sediments or Tertiary volcanic rocks associated with some plutons that were exhumed in the Kopaonik area. This exhumation is to be related to a high erosion rate that occurred during the Neogene (Schefer et al., 2011). Gas occurrences in natural springs or in boreholes have been reported on the published exhaustive map of thermal water made by Çitaku et al. (2006). However, gas compositional or isotopic analyses

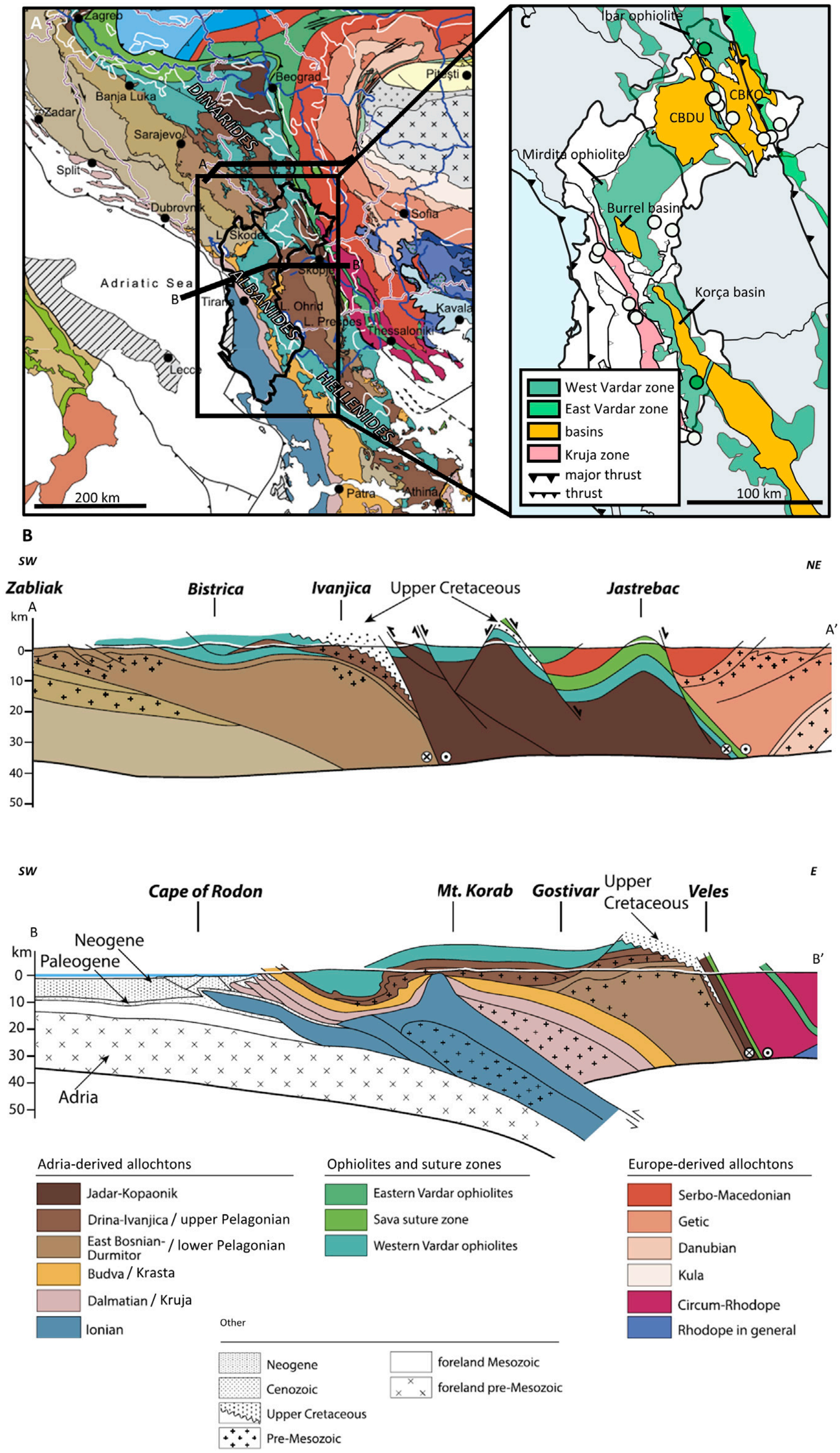

FIGURE 1
(A) Geological map of the Dinarides modified from Schmid et al. (2020) and **(B)** associated cross-sections A-A′ and B-B′ crosscutting West Vardar. **(C)** Simplified map of the zone of interest with the major structures related to the H_2 exploration: the ophiolites of West and East Vardar, the different basins, and the Kruja zone which is known as a geothermal area in Albania. The thrusts are also represented. CBDU, Cenozoic Basin of Dukagjin; CBDO, Cenozoic Basin of Kosova.

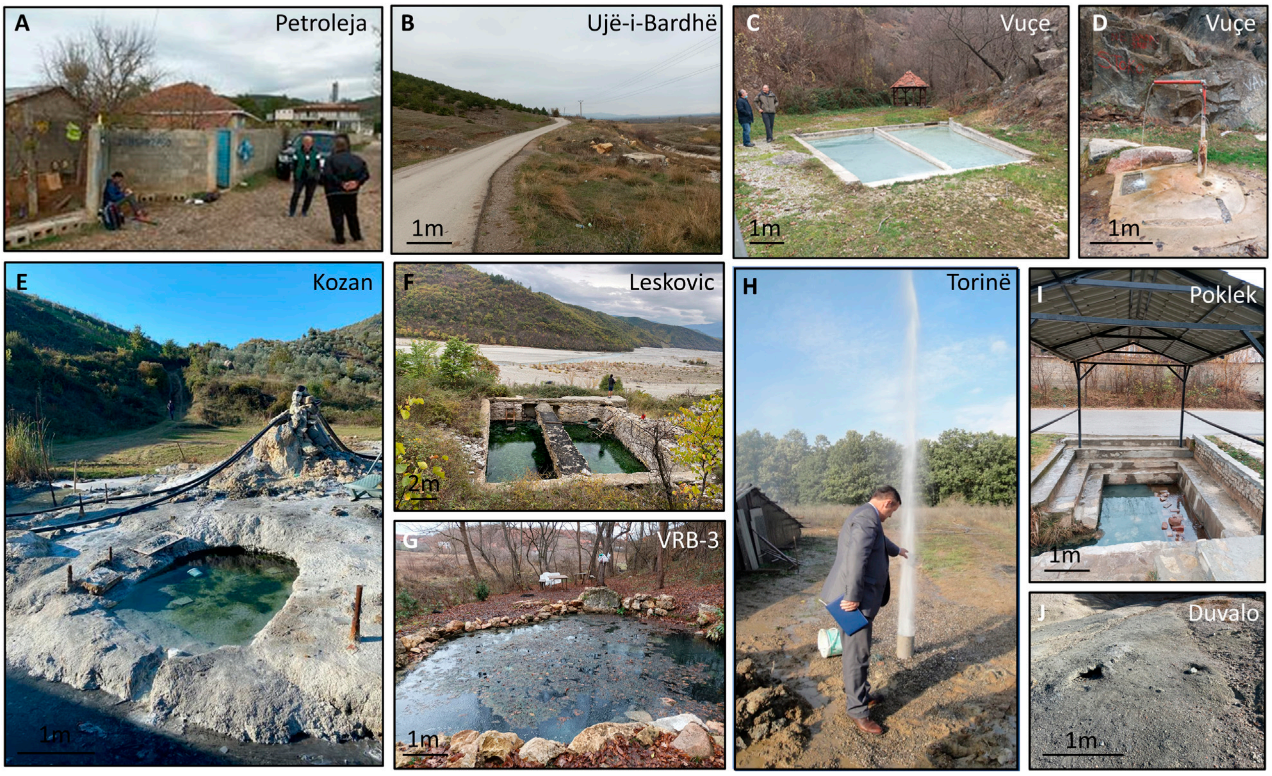

FIGURE 2
(A–J) Pictures taken in some sampled locations. Geographical coordinates in WGS84 datum are reported in Table 1.

were in general not performed. We can note the presence of one hyperalkaline spring in the north of Kosova (Çitaku et al., 2006).

In this part of the West Vardar zone, gas occurrences associated with natural springs are reported. However, only rare gas compositional analyses exist, and H_2 was never measured. Based on the high number of gas seeps in Albania and Kosova, we focused our effort on the regions of interest which are the Kruja zone, on the boundary between ophiolites and Cenozoic basins in Albania and Kosova, and on hyperalkaline springs. We can note that only the Duvalo, located in North Macedonia site, consisted in a "dry mofette" (i.e., crack or opening in a volcanic area emitting CO_2, water vapor, and other gases), with a low flow (Markoski et al., 2020). This site was analyzed because it was located near the zone of interest but without H_2 measurements.

3 Methods

3.1 Gas sampling

A total of 21 sites were analyzed, and different parameters such as temperature, pH, redox potential Eh, and weather conditions were systematically recorded. Free gas was collected from nine sites (Figure 2). For the other sites, the gas flow was too modest to collect a proper gas sample for laboratory analysis. The gas, bubbling into water at spring resurgence, was first collected in an open glass bottle reversed in water with progressive water flushed by gas. A funnel was also often used to collect bubbles faster. Once enough gas was collected, the bottle was closed with a septum cap in water. A volume of 15 ml of gas was then transferred with a syringe to a 10-ml glass tube. Three to five tubes were sampled in each site to enable major gas composition and isotopic analyses afterward at the lab.

The occurrence of H_2 in the gas was analyzed on the field using Geotech BIOGAS 5000 which measures *in situ* the gas composition of O_2, CO_2, CH_4, and H_2. Water vapor gas filters were always used during the measurements.

3.2 Molecular analyses

The composition of collected gas was obtained using gas chromatographic (GC) measurements carried out by 45-8 Energy (Metz, France) and ISOLAB (Neerijnen, Netherlands). H_2, O_2, N_2, CH_4, CO_2, and He were measured by 45-8 Energy, and H_2, O_2, N_2, CH_4, C2–C6+, CO_2, H_2S, and Ar were measured by ISOLAB. The gases were analyzed by 45-8 Energy on an Agilent 990 microGC. To measure He, H_2, Ne, O_2, and N_2, the microGC was equipped with a 20-m Molsieve column, a heated injection valve, a heated backflush valve, and a TCD detector with Ar as the carrier gas. To measure CO_2 and CH_4, it was equipped with a 10-m PoraPLOT-Q column for a heated injection valve, a heated backflush valve, and a TCD detector with He as the carrier gas.

TABLE 1 Location of the gas seeps with the coordinates in WGS84 datum, and parameters of the water and the weather conditions associated with sampling. The intensity of bubbling is qualitatively from low (+) to high (+++). T_{out} is for the temperature of the air during sampling. The hour was reported because some daily variations can sometimes appear (Prinzhofer et al., 2019; Cathles and Prinzhofer, 2020).

Name	Code	Country	Latitude	Longitude	Type	Depth m)	pH	T (°C)	Eh	Bubbling	Intensity	Date	Hour	T_{out} (°C)
Benjes	BEN	Albania	40.24423	20.4318	Spring		7.22	26	−158	No		11/17/2021	12:44 PM	16
Benjes	BEN	Albania	40.2447	20.43314	Spring		7.16	26	−205	No		11/17/2021	12:50 PM	16
Benjes pool	BEN	Albania	40.24395	20.43248	Spring		7.17	30	−121	Yes	+	11/17/2021	1:05 PM	16
Benjes river	BEN	Albania	40.24423	20.4318	Spring		7.52	23	6	No		11/17/2021	2:10 PM	16
Bilaj	BIL	Albania	41.48924	19.68239	Well	2420	6.16	55	−373	Yes	+++	11/14/2021		13
Cudhi #1	CUD	Albania	41.74650	20.27176	Spring		8.00	7	−30	No		11/21/2021	11:10 AM	14
Cudhi #2	CUD	Albania	41.74650	20.27176	Spring		7.69	9	−15	No		11/21/2021	11:16 AM	14
Doberçan	DOB	Kosova	42.47861	21.54129	Spring		6.44	24	123	No		11/22/2021		
Duvalo	DUV	Macedonia	41.16933	20.83725	Fumarole			7				11/20/2021	11:57 AM	15
Hydraj	HYD	Albania	41.02185	20.08782	Spring		6.27	36	−361	Yes	++	11/16/2021	1:00 PM	16
Hydraj	HYD	Albania	41.02260	20.08708	Spring		6.27	43	−361	Yes	++	11/16/2021	1:15 PM	16
Kilokot	KIL	Kosova	42.37076	21.37652	Spring		6.87	27	−33	No		11/22/2021	11:24 AM	11
Kozan	KOZ	Albania	41.12635	20.01663	Well	1837	6.04	65	−365	Yes	++	11/16/2021	9:41 AM	14
Kozan	KOZ	Albania	41.12635	20.01663	Well		5.82	60	−360	Yes	+++	11/16/2021	9:45 AM	14
Leskovik	LES	Albania	40.09686	20.67396	Spring		7.59	26	−138	No		11/18/2021	9:54 AM	9
Leskovik	LES	Albania	40.09686	20.67396	Spring		7.58	25	−96	No		11/18/2021	10:05 AM	9
Leskovik	LES	Albania	40.09694	20.67406	Spring		7.23	26	−270	Yes	++	11/18/2021	10:45 AM	12
Llixha	LLI	Albania	41.03259	20.0733	Spring		5.97	43	−359	Yes	+	11/16/2021	11:30 AM	15
Llixha	LLI	Albania	41.03271	20.07291	Spring		6.31	53	−361	Yes	+	11/16/2021	11:15 AM	15
Lushtë	LUS	Kosova	42.84803	20.81136	Spring		6.42	12	10	No		11/25/2021		
Nosale #1	NOS	Kosova	42.38724	21.44985	Spring		6.66	6	0	Yes	+	11/22/2021		
Nosale #2	NOS	Kosova	42.37076	21.37652	Spring		6.29	12	−90	No		11/22/2021		
Nosale well	NOS	Kosova	42.38348	21.44662	Well	115				Yes	+++	11/24/2021	12:33 PM	12
Peshkopi #1	PES	Albania	41.68551	20.45439	Spring		6.93	9	−120	No		11/21/2021	9:08 AM	7
Peshkopi #2	PES	Albania	41.68548	20.45045	Spring		6.56	43	−270	No		11/21/2021	9:17 AM	7
Petroleja	PET	Albania	41.53926	19.70976	Well		8.45	18	−130	Yes	++	11/15/2021	12:16 PM	14

(Continued on following page)

TABLE 1 (*Continued*) Location of the gas seeps with the coordinates in WGS84 datum, and parameters of the water and the weather conditions associated with sampling. The intensity of bubbling is qualitatively from low (+) to high (+++). T_{out} is for the temperature of the air during sampling. The hour was reported because some daily variations can sometimes appear (Prinzhofer et al., 2019; Cathles and Prinzhofer, 2020).

Name	Code	Country	Latitude	Longitude	Type	Depth m)	pH	T (°C)	Eh	Bubbling	Intensity	Date	Hour	T_{out} (°C)
Poklek	POK	Kosova	42.62215	20.91534	Spring		6.24	12	20	Yes	++	11/23/2021	9:53 AM	6
Torinë	TOR	Kosova	42.52725	21.06325	Well	15	7.68	12	−122	Yes	+++	11/26/2021	9:29 AM	6
Ujë-i-Bardhë	UJE	Albania	40.52639	20.69821	Spring		10.73	12	−144	Yes	++	11/18/2021	2:00 PM	13
Ujë-i-Bardhë	UJE	Albania	40.52639	20.69821	Spring		7.79	8	0	No		11/18/2021	2:20 PM	13
Ujë-i-Bardhë	UJE	Albania	40.52639	20.69821	Spring		10.79	12	−144	Yes	++	11/19/2021	2:28 PM	12
VRB-3	VRB	Kosova	42.67599	20.87454	Spring		6.42	15	39	Yes	++	11/23/2021	12:17 PM	12
VRB-4	VRB	Kosova	42.66766	20.85320	Spring		6.49	13	106	Yes	+	11/23/2021	11:14 AM	11
Vuce	VUC	Kosova	43.03894	20.77756	Spring		10.75	21	−125	Yes	++	11/25/2021	10:38 AM	10
Vuce	VUC	Kosova	43.03894	20.77756	Well	60	10.66	32	−153	Yes	++	11/25/2021	11:15 AM	10

In ISOLAB, H_2, O_2+Ar, N_2, and CH_4 were analyzed on an Agilent 7890A GC (Agilent Technologies, Santa Clara, US) equipped with a 12-m, 0.32-mm Molsieve column, a heated injection valve, and a TCD detector. Hydrocarbons and CO_2 were analyzed on an Agilent 7890B GC equipped with a 50-m, 0.32-mm Porabond-Q column, a heated injection valve, a heated backflush valve (for C6+), a TCD detector (for CO_2), and a FID detector (for hydrocarbons). From the results of all three detectors, one complete composition was calculated. Detector responses were calibrated several times a day using various reference standards.

3.3 Isotopic analyses

Carbon and hydrogen isotopic signatures of CH_4 and hydrogen isotopic analyses of H_2 were undertaken using ISOLAB (Neerijnen, Netherlands). Carbon isotopes of CH_4 were analyzed with an Agilent 6890N GC (Agilent Technologies, Santa Clara, US) interfaced to a Finnigan Delta SIRMS (Finnigan is now part of Thermo Scientific, Bremen, Germany) using a Finnigan GC-C II interface. The GC was equipped with a 12-m, 0.32-mm Molsieve column (Agilent) and an injection valve. Hydrogen isotopes of CH_4 and H_2 were analyzed on an Agilent 7890A GC (Agilent Technologies, Santa Clara, US) interfaced to a MAT 253 IRMS (Thermo Scientific, Bremen, Germany) using a GC-Isolink interface from Thermo. The GC was equipped with a 25-m, 0.32-mm Molsieve column (Agilent) and an injection valve. The samples were calibrated regularly against a calibration standard. The results are reported with the $\delta^{13}C$ and δD notations, using vPDB and vSMOW standards.

4 Results

4.1 Geochemical analyses

4.1.1 Chemistry of waters

The different parameters such as temperature, redox potential (Eh), and pH were systematically measured at every location where gas was bubbling in water (Table 1; Figure 3). The hottest spring exhibited between 55 °C and 65 °C and was observed near and in the Kruja Zone where some deep drilling reach about 2 km (Table 1), like Bilaj and Kozan wells. Llixha and Hydraj are located next to thermal stations that use the hot water of the well of Kozan. Therefore, these two springs are connected to the Kozan well and have similar chemical parameters. Only one spring was at high temperature up to 43 °C in Peshkopi in the northeastern part of Albania. Lower temperature springs with recorded temperature between 20 °C and 35 °C were analyzed in the south of Albania (Benjes and Leskovik) and in the east of Kosova (Doberçan). The Vuçe well with a depth of 60 m also showed moderate temperature of 32 °C, whereas the Vuçe spring is at 21 °C. The remaining springs showed cold waters below 20 °C.

The Eh of the spring waters shows very low values down to −365 mV in locations where high temperatures were measured (Figures 3A, B, 4A). For spring waters with a temperature lower than 35 °C, this relation is less clear where the Eh values were mainly

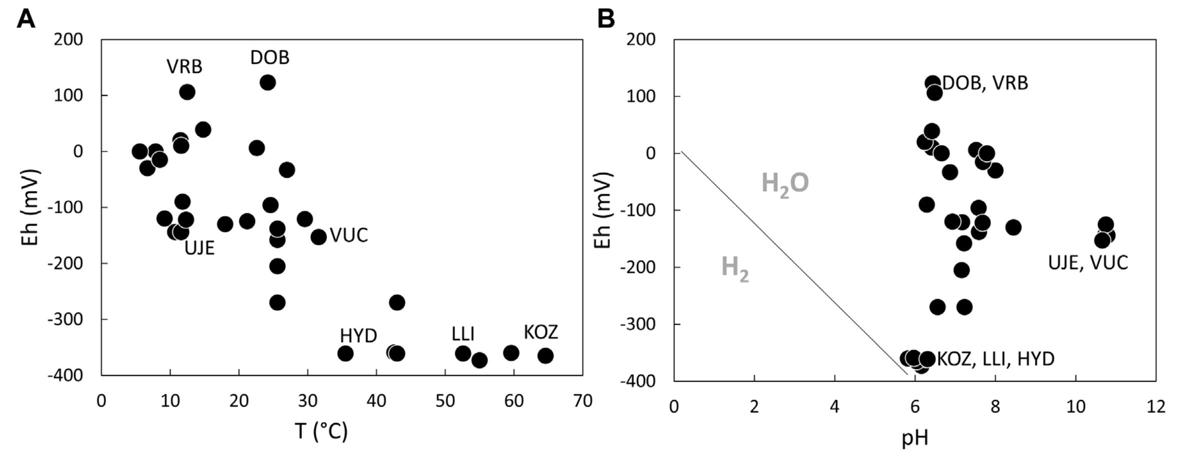

FIGURE 3
(A) Redox potential Eh against the temperature. We observe that for temperatures above 35 °C, the Eh is below −300 mV. **(B)** Redox potential Eh against pH. This highlights the presence of hyperalkaline springs in Vuçe and Ujë-i-Bardhë.

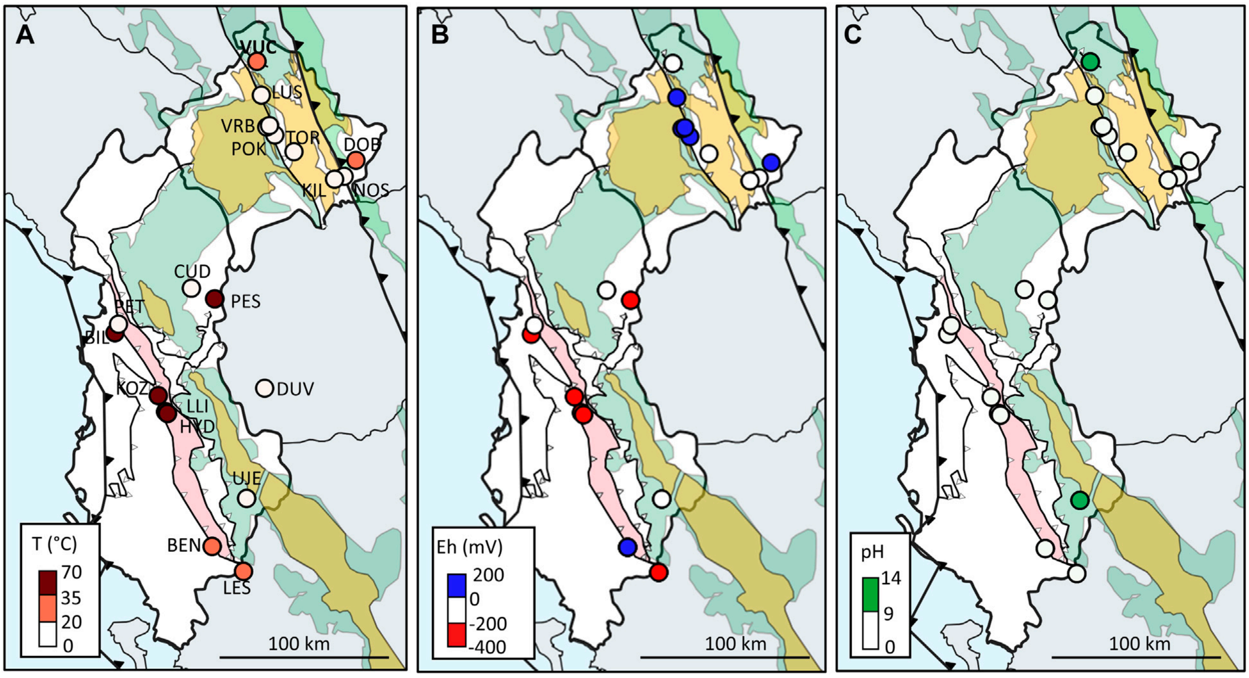

FIGURE 4
(A) Temperature, **(B)** redox potential Eh, and **(C)** pH are represented on the map shown in Figure 1C.

between −200 and 100 mV. Some high Eh values were recorded in Doberçan (123 mV) and VRB-3 (106 mV) locations.

The pH levels of bubbling waters were mainly between 6 and 8, whereas the springs from Ujë-i-Bardhë, located at the border of the Korça Basin and the ophiolite massif of Voskopoja in the south of Albania, and in Vuçe (spring and well), in the north of Kosova, have a pH at about ~10.7. This does not seem related to temperature nor Eh (Figure 4).

4.1.2 Gas composition

The composition of major elements of the sampled gases are represented in Figures 5, 6 (Table 2), corrected from air contamination. The raw gas compositions of the gases are reported in Supplementary Table S1. We note that for the Kozan sample, H_2S peak detected by 45-8 Energy's GC could not be quantified (not calibrated for it). Therefore, for this sample, only data from ISOLAB are reported, without H_2 and He quantification.

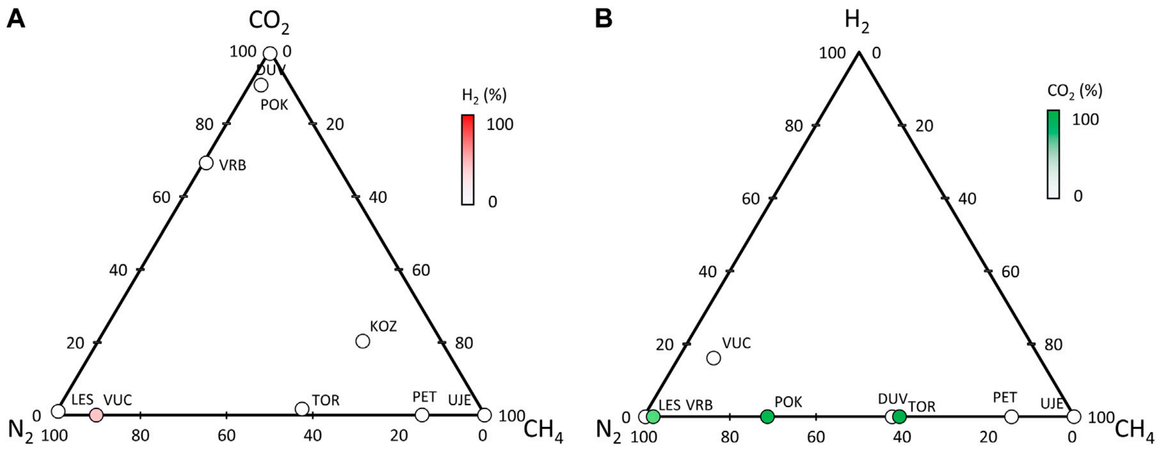

FIGURE 5
Gas compositions represented in ternary diagrams of **(A)** $CO_2-N_2-CH_4$ and **(B)** $H_2-N_2-CH_4$. For each diagram, the contents in H_2 and CO_2 are represented in red and green colors, respectively. See locations in Table 1.

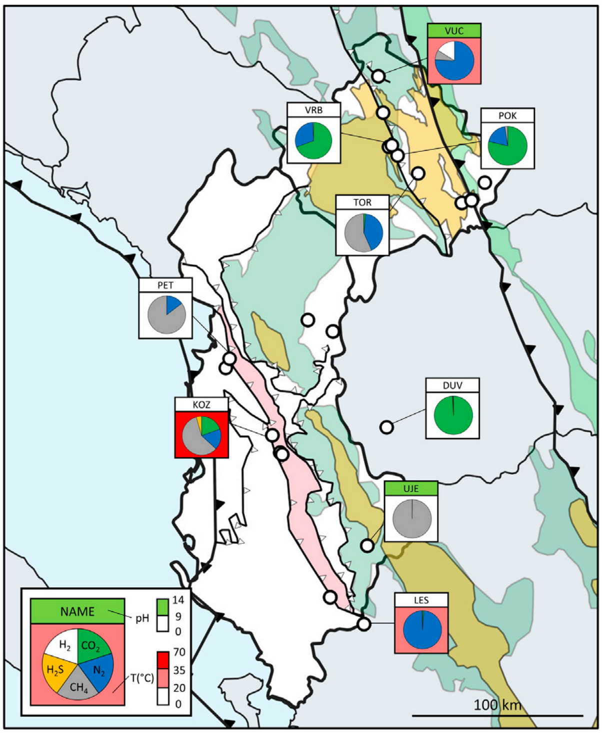

FIGURE 6
Gas composition of the different gas seeps with the temperature and pH of the associated water represented on the map shown in Figure 1C. The white points represent the studied gas seeps.

We can distinguish three types of gas: CH_4-rich, CO_2-rich, and N_2-rich gas. It can be noted that Kozan and Vuçe also contain as a major gas 4.31% ± 0.01% of H_2S and 16.13% ± 0.04% of H_2, respectively.

H_2 was also detected in the other gases with content down to several ppm except in Petroleja and Ujë-i-Bardhë that contain 195 ± 0.3 ppm and 369 ± 33.8 ppm, respectively. Kozan also contains several hundreds of ppm of H_2 but as discussed in the methods, reported concentration is rather qualitative than quantitative. He was also detected as a minor gas. Its content is below 200 ppm for most of the gases, except from Torinë and Leskovik which have a He content of 1078 ± 8.3 ppm and 1676 ± 9.4 ppm. No relation is observed between H_2 and He which seem to be de-correlated (Figure 7).

4.2 Isotopic analyses

To constrain the biotic or abiotic origin of CH_4, its C and H isotopic signatures have been measured (Table 3; Figure 8) when the gas contained enough CH_4. We observe that Torinë and Petroleja contain microbial CH_4, whereas CH_4 from Kozan and Ujë-i-Bardhë seems thermogenic. The analyses related to Vuçe spring and Vuçe show close isotopic signatures of CH_4 with δD values of −338 ± 2 and −336 ± 2 and $\delta^{13}C$ values of −31.6 ± 0.2 and −30.6 ± 0.2, respectively. These isotopic values can be associated with abiotic CH_4 related to serpentinization (Etiope, 2017) or to microbial CH_4 (Xia and Gao, 2021; Xia and Gao, 2022). Finally, the measurement made in Leskovik gas shows an isotopic signature of CH_4 that is out of the classical signatures reported in the literature. This would need more analyses to be confirmed.

The H isotopic signature of H_2 was also measured in the gas of Vuçe spring and Vuçe well, in which H_2 is abundant. The measurements revealed a δD of −728‰ ± 2‰ and −731‰ ± 2‰, respectively. Based on the equations of Horibe and Craig (1995), a temperature of about −70 °C can be estimated using the CH_4–H_2 couple and about −45 °C for the H_2–H_2O couple. The meaning of these temperatures will be explored in the discussion.

TABLE 2 Gas compositions of N_2, CH_4, CO_2, H_2S, H_2, and He with the associated air content used for air correction. The O_2 content is not represented being at 0%. The symbol * is used on the sample ID when the analysis is an average between analyses from the GC of 45-8 Energy and ISOLAB, the symbol ** when the analysis only comes from ISOLAB and when it is only from 45-8 Energy there is not any symbol.

Sample ID	N_2 (%)	CH_4 (%)	CO_2 (%)	H_2S (%)	H_2 (ppm)	He (ppm)	Air correction (%)
KOZ**	16.78 ± 0.41	56.63 ± 0.89	18.72 ± 0.29	4.31 ± 0.07	n.m.	n.m.	12
PET*	14.57 ± 0.76	85.15 ± 0.81	0.07 ± 0.02	n.d	195 ± 0.3	74 ± 4.1	17
POK	6.75 ± 0.01	2.72 ± 0.01	90.52 ± 0.03	n.m.	3 ± 0.2	48 ± 0.5	16
TOR*	41.56 ± 1.71	56.59 ± 2.04	1.71 ± 0.55	n.d	26 ± 23.5	1 078 ± 8.3	22
VUC*	75.67 ± 0.06	8.18 ± 0.02	0.03 ± 0.01	n.d.	161 281 ± 387.4	10 ± 0.6	16
UJE*	0.11 ± 0.08	99.79 ± 0.52	0.03 ± 0.00	n.d	369 ± 33.8	18 ± 8.4	16
DUV	0.34 ± 0.24	0.49 ± 0.17	99.17 ± 0.45	n.m.	2 ± 0.2	67 ± 0.8	18
LES*	98.06 ± 0.66	0.39 ± 0.14	1.05 ± 0.03	n.d	17 ± 0.5	1 676 ± 9.4	21
VRB	30.09 ± 0.07	0.68 ± 0.00	69.21 ± 0.07	n.m.	2 ± 0.1	186 ± 0.4	21

TABLE 3 Isotopic data of CH_4 and H_2 and the estimated temperature of equilibration based on the equation of Horibe and Craig (1995).

Sample ID	Code	$\delta^{13}C_{CH4}$ (‰)	δD_{CH4} (‰)	δD_{H2} (‰)	$T_{CH4\text{-}H2}$ (°C)	$T_{H2O\text{-}H2}$ (°C)
VUC-106/107	VUC	−31.6 ± 0.2	−338 ± 2	−728 ± 2	72.9 ± 2.0	45.9 +1.3/−1.5
W-VUC-300 M2	VUC	−30.6 ± 0.2	−336 ± 2	−731 ± 2	69.0 ± 2.0	43.8 +1.3/−1.4
BEL-102	UJE	−29.7 ± 0.2	−157 ± 2			
KOZ-102	KOZ	−35.4 ± 0.2	−133 ± 2			
TOR-102	TOR	−72.9 ± 0.2	−248 ± 2			
LES-102	LES	−10.0 ± 0.2	66 ± 2			
PET-103	PET	−68.2 ± 0.2	−227 ± 2			

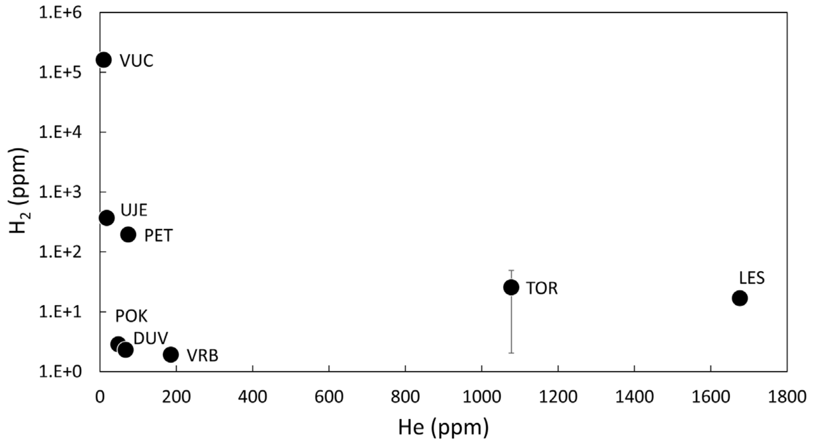

FIGURE 7
H_2 content against the He content. No correlation between H_2 and He is observed.

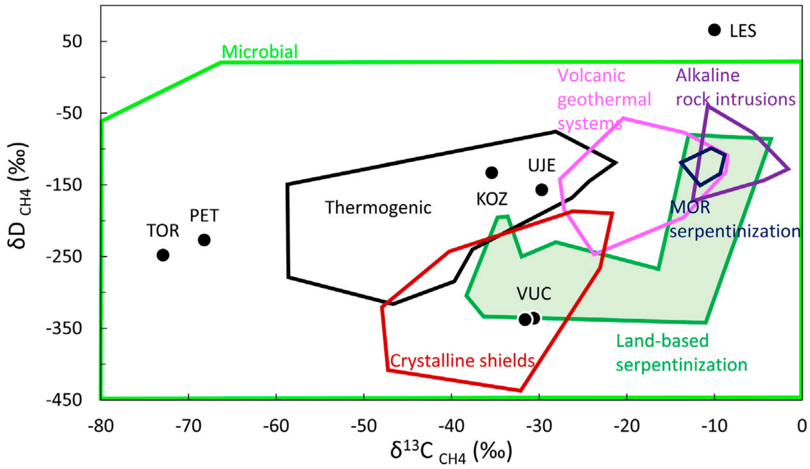

FIGURE 8
δD of CH_4 against $\delta^{13}C$ of CH_4. The different zones on the diagram are from Etiope (2017) apart from the range defining microbial isotopic signatures that was extended based on the study by Xia and Gao (2022).

5 Discussion

The obtained surface gas seeps dataset showed that, as anticipated, some locations exhibit a fraction of H_2. We will first discuss which locations are promising for H_2 exploration. The process at the origin of H_2 will be then discussed, before concluding about the important locations for H_2 exploration in the Dinarides.

5.1 Zones of interest for H_2 exploration

Four locations showed the presence of H_2 in the gas blend with more than 100 ppm in the area of interest: Kozan (−170 ppm before air correction), Petroleja (195 ± 0.3 ppm), Ujë-i-Bardhë (369 ± 33.8 ppm), and Vuçe (16.13% ± 0.04%). Associated with that, we can add that the gas flow is very important in Kozan, moderate in Vuçe and Ujë-i-Bardhë, and weak in Petroleja.

All these gases are associated with a variable fraction of CH_4, the highest one being Petroleja and Ujë-i-Bardhë with more than 85% of CH_4. Assessing the origin of CH_4 is key to highlighting possible reactions between H_2 and CO_2 that would, therefore, suggest that more H_2 has been/is being generated in the system but has been transformed into abiotic CH_4. This could be the case in Vuçe where CH_4 shows a potential abiotic signature and is likely to have formed *via* the Sabatier reaction:

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \qquad (2)$$

However, the isotopic signature of CH_4 in Vuçe can also be related to microbial origin (Xia and Gao, 2021; 2022). For Kozan and Petroleja, the C and H isotopic signatures of CH_4 reveal a clear microbial origin, whereas for Ujë-i-Bardhë, it is thermogenic. The gas composition of Kozan in C_1–C_6+ (Supplementary Table S2) shows the presence of C_2–C_4 molecules which is consistent with the thermogenic origin. For Petroleja and Ujë-i-Bardhë, it cannot be ruled out that CH_4 is the result of the mixing of CH_4 of at least two different origins. The presence of C_2 in both gases could be related to a thermogenic origin like in Kozan. Petroleja could thus be a mix between microbial and thermogenic CH_4. Moreover, Ujë-i-Bardhë is a hyperalkaline spring, like Vuçe, with a pH of about 10.7. This high pH suggests that the process of serpentinization is likely to be currently ongoing (Barnes et al., 1967; Neal and Stanger, 1983; Abrajano et al., 1988; Deville and Prinzhofer, 2016), leading to the presence of OH^- based on reaction [1]. Then, CH_4 in Ujë-i-Bardhë could be a mix between CH_4 coming from thermogenic and serpentinization processes.

The area where serpentinization seems to occur is in the West Vardar zone which is consistent with the presence of ophiolites. However, no potential abiotic CH_4 was recorded in the Kruja zone which is a tectonic zone where thrusts go down to the ophiolites. The serpentinization seems, therefore, ongoing on the massif at rather low depth (<2 km), but more data are needed to know if it is also ongoing at great depth.

5.2 Origin of H_2

For the gas seeping out of the ophiolite massif in Vuçe and Ujë-i-Bardhë, where the water is hyperalkaline with a pH at about 10.7, we can infer that H_2 is likely to come from serpentinization. However, Vuçe and Ujë-i-Bardhë have to be discussed separately to better constrain how the serpentinization process might proceed.

Ujë-i-Bardhë is located at the southeastern boundary of the Korça Basin with the outcropping ophiolite, known as the massif of Voskopoja. The ophiolite is rich in lherzolite and known as intensively altered in this zone (Hoeck et al., 2014). The associated CH_4 is mainly thermogenic even if it can be partially abiotic. The fluid at the origin of the alteration could be recent

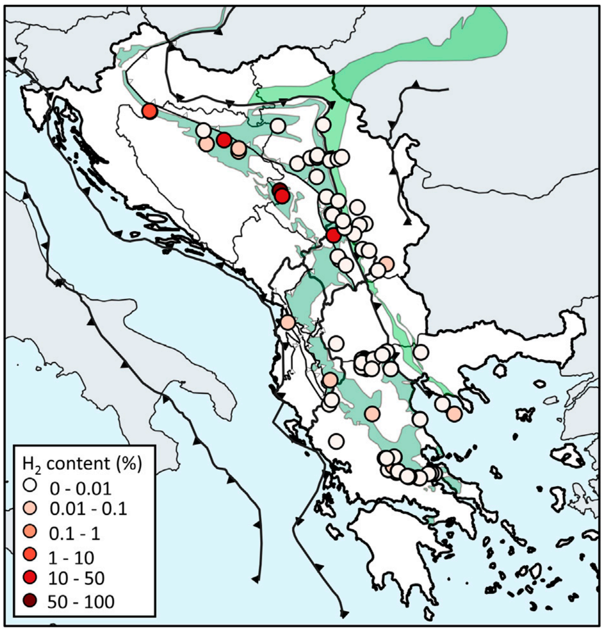

FIGURE 9
Compilation of the H_2 content in gas seeps in the Dinarides from this study and others in the literature (Minissale et al., 1989; Daskalopoulou, 2017; Etiope et al., 2017; Randazzo et al., 2021).

meteoric water or an old aquifer. The gas is a blend with thermogenic CH_4 that could have been formed in the Korça Basin itself and could then have migrated *via* the boundary of the Korça Basin with the ophiolite. The low content of H_2 in the gas below 400 ppm could be related to a limited temperature slowing down the kinetics, or the fact that the peridotites are already highly serpentinized, limiting the process of serpentinization. A part of H_2 could also have been combined with CO_2 to form CH_4 by an abiotic or biotic process, but as the isotopic signature of CH_4 is mainly thermogenic, these processes seem limited.

The gas associated with Vuçe springs is located next to a thrust delimiting the ophiolite outcrop described as rich in harzburgite and Paleozoic gneiss belonging to the Jadar–Kopaonic block which constitutes the basement of the ophiolite (Supplementary Figure S1). H_2 is abundant in the gas with about −16% of H_2. By the presence of CH_4, whatever its origin, we can assume that more H_2 has been or is currently present in depth before the recombination of H_2 with CO_2. Based on the hydrogen isotopes of CH_4 and H_2, equilibrium temperatures of CH_4–H_2 and H_2–H_2O have been estimated to be about 70 °C and 45 °C, respectively. This means that the system CH_4–H_2–H_2O is in disequilibrium. This is typical of low-temperature serpentinization (Pester et al., 2018), where CH_4 and H_2 isotopic exchange is slower than that between H_2O and H_2. Hence, the H_2O–H_2 geothermometer represents a temperature of re-equilibration (Pester et al., 2018) which is lower than the CH_4–H_2 geothermometer. This latter geothermometer represents a temperature of equilibration between H_2 and CH_4 which can be associated with the alteration of H_2 into CH_4. This means that at 70 °C, H_2 was already formed. This temperature corresponds to a minimal temperature of serpentinization. Using a mean geothermal gradient of 30 °C/km, we can estimate that H_2 could have already been formed at about 2.3 km. The high pH suggests that this process is still ongoing. The thrust between the ophiolite and the gneiss is a favored path for gas.

The origin of H_2 in Kozan can be related to the thermogenic process where H_2 can be formed at high temperatures (Li et al., 2015; Horsfield et al., 2022). It is possible that a part of H_2 led to the formation of H_2S. Finally, we can propose that the H_2 in Petroleja could have been formed by thermogenics and/or bacteria. More work would be necessary to better constrain the origin of H_2 for

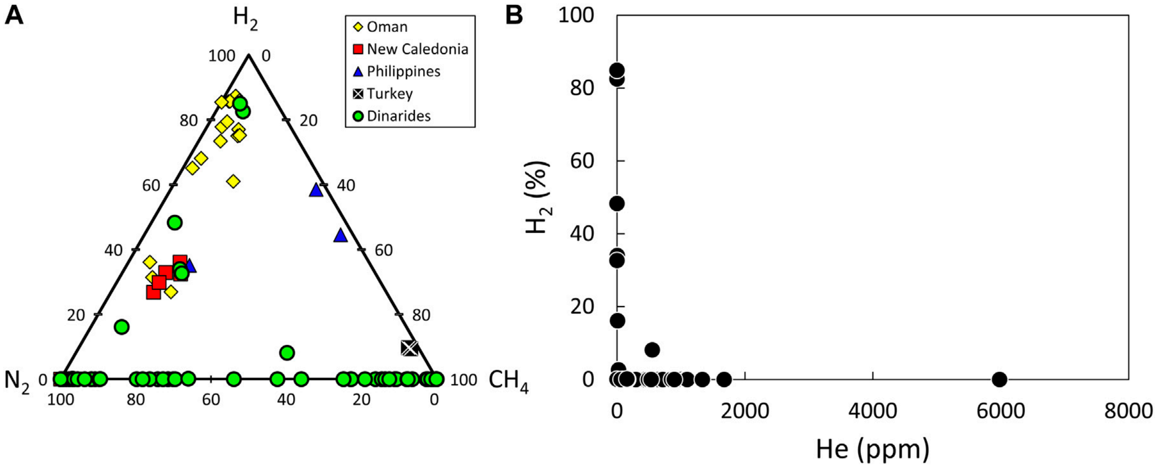

FIGURE 10
Compilation of gas compositions in the Dinarides represented in **(A)** ternary diagram of H_2–N_2–CH_4 in addition to gas compositions in Oman, New Caledonia, The Philippines, and Turkey (Vacquand et al., 2018) and plotted in **(B)** graph of H_2 content against He content.

Kozan and Petroleja. The origin of other sources with a low content of H_2 will not be discussed.

5.3 H_2 in the Dinarides

Based on this study and several other gas geochemistry studies conducted in the Dinarides area (Minissale et al., 1989; Daskalopoulou, 2017; Etiope et al., 2017; Randazzo et al., 2021), we now are able to fill in the map of H_2 occurrences in this region (Figure 9). To compare the data, we have corrected all the data in the literature from the air contamination. We observe that some hot spots for natural hydrogen appear in Bosnia and Herzegovina (8%–48% H_2), southeast Serbia (32%–85% H_2), and in the north of Kosova in Vuçe (16% H_2). H_2 is mainly associated with N_2 with several percent of CH_4 (Figure 10A). Regardless of the gas flow rate in the analyzed springs (which is in general modest and therefore could not be precisely measured), these locations are great to be considered in an H_2 exploration. Most of these H_2-rich springs are hyperalkaline and embedded in an ophiolite, therefore, inferring that H_2 is likely to be derived from serpentinization. Based on equilibrium temperatures of CH_4–H_2 and H_2–H_2O (Etiope et al., 2017) and despite re-equilibration, the serpentinization seems to occur at low temperatures (<100 °C).

It can be noted that the H_2-rich gases sampled in the Dinarides have comparable chemical compositions with the gases studied in other ophiolites such as those in Oman, New Caledonia, or The Philippines [Figure 10 (Vacquand et al., 2018)]. We can add that at the scale of the Dinarides, like for Albania and Kosova, H_2 does not seem related to He (Figure 10B). Therefore, they are de-correlated and have different sources, H_2 coming from serpentinization and He from crustal and/or mantle sources (Randazzo et al., 2021).

6 Conclusion

New gas measurements associated with natural springs in Albania and Kosova were made including H_2 data. Different types of springs were measured: CO_2-rich, N_2-rich, and CH_4-rich. Four springs with H_2 occurrence were analyzed. Three of them contained several hundred ppm of H_2, and one, 16% of H_2. This latter spring was sampled in the north of Kosova in a location named Vuçe. The main process at the origin of H_2 is likely to be serpentinization, occurring at about a 2-km depth based on H isotopic signatures and assuming normal geothermal gradient. No relation was found with He. With this new discovery, five seeps with more than 10% of H_2 are now referenced in Bosnia and Herzegovina, Serbia, and Kosova.

This study completes data at the scale of the Dinarides and shows that H_2 gas seeps are mainly located inside ophiolite massifs and not on major faults in the Kruja zone where the gas could have migrated like it is suggested in the Pyrenees (Lefeuvre et al., 2022). More work is now needed to better understand how the H_2-rich gas migrates to the surface and locate the potential gas traps in order to look for a reservoir of natural H_2.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding author.

Author contributions

DL wrote the paper with the contribution of all co-authors. The fieldtrip was made by DL and MB-M who acquired field data, guided by AM in Albania and by IF in Kosova. The analyses on the GC from 45-8 Energy were conducted by MB-M and TG. BH and NP led the direction of the project.

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Conflict of interest

MB-M, TG, BH, and NP were employed by the company 45-8 Energy.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/feart.2023.1167634/full#supplementary-material

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