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Key Points:

- Three spatially distinct groups of N₂-dominated, CO₂-dominated and H₂S-rich gases
- Significant geogenic CO₂ degassing of dominant crustal origin
- Up to 25% of mantle helium contribution

Supporting Information:

Supporting Information may be found in the online version of this article.

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Toward Solving the Mystery of Elevated Tectonic Degassing in South Eastern Europe: Insights From Gas Discharges Along the Vardar Suture (North Macedonia)

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Abstract Tectonic carbon degassing is an important contributor to the global carbon cycle. South Eastern Europe is an active extensional tectonic region. This is the result of intense geodynamic events related to the closure of the Tethys Ocean, whose remnants include an ophiolite orogenic belt and the Vardar megasuture. In North Macedonia, regional active fault systems, seismic activity, Cenozoic-Quaternary volcanism, large-scale degassing, and low-enthalpy geothermal resources are widespread. Nonetheless, a geochemical characterization of the gas manifestations is missing from the literature. Toward this contribution, we report the first characterization of chemical and isotopic compositions of fluids from the main geothermal and cold gas manifestations of North Macedonia, and we explore their origins, the processes controlling their chemistry, and their relationships with the regional geodynamic situation. Gas samples were collected along the whole country, and were analyzed for both their chemical (He, H₂, H₂S, O₂, N₂, CO₂, CH₄, Ar) and isotopic composition ($\delta^{13}\text{C}$ -CO₂, He, Ar). Based on their chemistry, samples can be subdivided into three groups: (a) N₂-dominated, (b) CO₂-dominated, and (c) H₂S-rich, which are geographically well separated, following regional distributions. The CO₂-dominated group is the most widespread, highlighting the importance of geogenic carbon degassing in the study area. Its origin is prevalently crustal ($\delta^{13}\text{C}$ -CO₂ = -4.6 – $+1.0$ ‰ vs. V-PDB; R/R_A = 0.1–1.8), but a significant, up to 25%, mantle contribution can be inferred from the He isotope composition.

Plain Language Summary The Earth emits a considerable quantity of deep gases, especially carbon dioxide, not only from the most well-known volcanic systems but also from structural systems, such as active fault systems that can generate earthquakes. The Balkan Peninsula is an area rich in degassing structural systems, which have not been as extensively studied as other areas. The objective of this study was to investigate the degassing manifestation in North Macedonia. This is the first study to examine the composition of the gases in order to ascertain their origin, the processes controlling their chemistry, and their relationship with the structural systems of the area. The samples can be classified into three groups based on the most abundant gas species: (a) N₂-dominated, (b) CO₂-dominated, and enrichments (c) H₂S-rich. These groups are geographically well separated and located in the eastern, central and western parts of the country, respectively. The CO₂-dominated group is the most widespread. This finding further highlights the importance of carbon degassing in the Balkan Peninsula. Carbon in the area predominantly derives from the crust, although evidence suggests a significant mantle contribution, as indicated by the helium isotope composition.

1. Introduction

During the last decades, scientific research concerning the estimation of endogenous carbon degassing into the atmosphere has sharply increased due to the major role of this element in controlling the Earth's climate over geological time (Foster et al., 2017). Among the greenhouse gases, carbon dioxide and methane are considered to be the most effective species in contributing to the changing of the global climate. The most recent observations from the NOAA Mauna Loa Observatory, updated to June 2024, report a mean abundance of CO₂ and CH₄ of

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426.9 ppm and 1,931 ppb, respectively, in the atmosphere (<https://gml.noaa.gov/ccgg/trends/>). In comparison, the global mean abundance in 2022 was estimated at 417.9 ± 0.2 ppm for CO₂ and at $1,923 \pm 2$ ppb for CH₄ (Nineteenth WMO Greenhouse Gas Bulletin, 2023), with an increment of about 3% with respect to the observations of 2018 reported in the Fifteenth WMO Greenhouse Gas Bulletin, 2019 (CO₂ = 407.8 ± 0.1 ppm; CH₄ $1,869 \pm 2$ ppb).

Despite a significant improvement in the worldwide data set, the global flux of CO₂ degassing from the Earth's interior is still the least well-quantified part of the global cycle (Berner & Lasaga, 1989). Many studies have been devoted to the quantification of the release of geogenic CO₂ to the atmosphere from different geological settings (e.g., Brune et al., 2017; Kerrick, 2001; Mörner & Etiope, 2002), and most of them have focused on the present-day CO₂ emission from volcanoes (Brantley & Koepnick, 1995; Burton et al., 2013; Werner et al., 2019). While the volcanic carbon budget is the most studied, its quantification is still far from being well defined. Fischer et al. (2019) estimated a global volcanic CO₂ flux budget of 51.3 ± 5.7 Tg a⁻¹ for weakly emitting volcanoes and 1.8 ± 0.9 Tg a⁻¹ for eruptive degassing during the 2005–2015 period.

Although the close relationship between tectonically active areas, fluid migration, and geogenic diffuse carbon emissions has long been evidenced (Barnes et al., 1978; Irwin & Barnes, 1980), only in the last decades has tectonic carbon degassing been emphasized as an important contribution to the global carbon cycle (e.g., Chiodini et al., 1999, 2000, 2011; D'Alessandro et al., 2020; Daskalopoulou et al., 2019; Frondini et al., 2019; Kerrick et al., 1995; Lewicki & Brantley, 2000; Li Vigni et al., 2022; Randazzo et al., 2021, 2022; Seward & Kerrick, 1996; Yuçe et al., 2017). At a global scale, the geographic distribution and the amount of deeply derived fluids are controlled by regional normal/transcurrent faulting (Tamburello et al., 2018) and continental rift lengths (Brune et al., 2017). Deep fault systems, due to their enhanced permeability and porosity, play an important role in the transfer of deeply derived volatiles (e.g., CO₂ and He). They create preferential pathways for advective gas-carrying fluids rising from the deep crust or the mantle to the Earth's surface (Caracausi & Sulli, 2019; Faulker et al., 2010; Hunt et al., 2017; Muirhead et al., 2016; Tamburello et al., 2018). The fluid flow, along regional fractures, has been observed to be rapid, with velocities ranging from 10⁻⁶ to 10⁻⁵ ms⁻¹, and relatively short-lived, with a duration in the order of a few hundreds of years (John et al., 2012; Kleine et al., 2016). Eventually, fluids and their corresponding volatiles escape through the soil into the atmosphere as a result of pressure decrease (King, 1986). Furthermore, these geogenic fluids play an active role in deep earthquake generation (Buttita et al., 2020; Caracausi et al., 2022; Chiodini et al., 2020; Du et al., 2006; Miller et al., 1999).

In South Eastern Europe (e.g., Balkan Peninsula), large-scale degassing of mantle-derived carbon, Cenozoic volcanism, seismic activity, and regional active fault systems are widespread (Burchfiel et al., 2008; Cvetkovic et al., 2016; Dumurdzanov et al., 2005; Jolivet & Brun, 2010). However, the estimation of endogenous CO₂ release from this area remains poorly quantified (D'Alessandro et al., 2020; Daskalopoulou et al., 2019; Lévy et al., 2023; Li Vigni et al., 2022; Kis et al., 2017, 2019; Minissale et al., 2023; Randazzo et al., 2021). North Macedonia belongs to the South Balkan extensional region (Dumurdzanov et al., 2005) and is considered one of the richest regions in low-temperature geothermal resources (Popovska-Vasilevska & Armenski, 2016). Indeed, the Macedonian region is characterized by positive geothermal anomalies (60–120 mW m⁻²; Gorgieva et al., 2000; Milivojevic, 1993), which together with crustal thinning favored the occurrence of 18 geothermal fields (Figure S1 in Supporting Information S1), whose surface expressions are more than 50 mineral and thermo-mineral springs (Gorgieva et al., 2000; Popovska-Vasilevska & Armenski, 2016).

Since ancient times, these geothermal systems have been used for balneology purposes as spas, with ruins of Roman and Turkish baths found near some of these thermal springs. Nowadays, the geothermal resources are also used for heating hotels and greenhouses, CO₂ extraction, or industrial utilization, whilst some discharges are without any use.

The geochemical characterization of these gas manifestations and the estimation of their outgassing rate have remained poorly studied and mainly focused on the Duvalo degassing system (Iloski et al., 1957; Li Vigni et al., 2022; Markoski et al., 2019; Trojanović, 1925). The present study reports, for the first time, the chemical and isotopic compositions of fluids (gases in both free and dissolved phase) released from the main geothermal and cold gas manifestations of North Macedonia. This research explores (a) the fluid sources, (b) the processes controlling the fluid chemistry, and (c) the relationships with the regional geodynamic situation of the area.

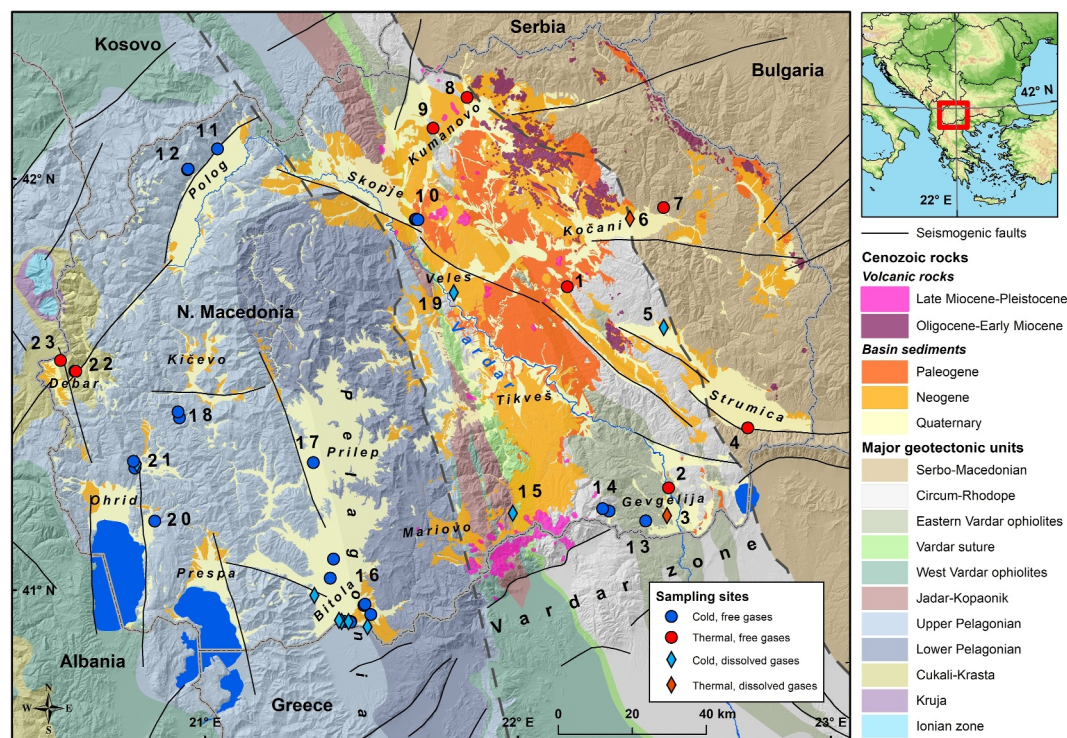


Figure 1. Location of the sampled sites: 1—Kežovica, 2—Smokvica, 3—Negorci, 4—Bansko, 5—Rakliš, 6—Dobra, 7—Istibanja, 8—Strnovac Banja, 9—Kumanovska Banja, 10—Katlanovo, 11—Lešok, 12—Banjiče, 13—Gorničet, 14—Smrdliva Voda and Makedonska Češma, 15—Topli Dol, 16—Bitola basin sites (Geogas, Logovardi, Kisela Voda, Medžitlija, Bitola, Bitola 2, Pelagonka, Pela Rosa, Germijan, Busemak, Gneotino 1, Gneotino 2), 17—Krušeani, 18—Svinjište and Kozica, 19—Sabotna Voda, 20—Duvalo (Kosel), 21—Botun, Petkoniva and Kiselo Klajnče, 22—Kosovrasti, 23—Banjište. Main geotectonic units from Schmid et al. (2020). Extension of Cenozoic sediments after Dumurdzanov et al. (2004, 2005) and volcanic rocks after Molnár et al. (2022). Seismogenic crustal faults from the European Database of Seismogenic Faults (EDSF; <https://edsf13.ingv.it/>). Dashed black lines approximate the extent of the Vardar zone. Extensional basins and geothermal fields mentioned in the text are also indicated.

2. Geological Settings

North Macedonia, in the central part of the Balkan Peninsula, is located at the junction of the Dinarides-Hellenides and Carpatho-Balkanides orogens, which were formed due to the convergence of the Adriatic microplate and the European plate (Figure 1). This led to the closure of the Neotethys in Late Cretaceous times, marked by the Vardar suture zone. Adria-derived units (e.g., Pelagonian massif, West-Macedonian zone) and obducted Western Vardar ophiolites are found west of the suture zone, while the area to the east is composed of Europe-derived units (e.g., Serbo-Macedonian massif, Circum-Rhodope), as well as Eastern Vardar ophiolites (Schmid et al., 2020). The wider area along the Vardar suture zone between the Dinarides-Hellenides and Carpatho-Balkanides orogens is known as the Vardar zone (Arsovski, 1997; Dumurdzanov et al., 2005; Kosmat, 1924).

These structures are overprinted by Cenozoic extension, as part of the South Balkan extensional regime, a northern segment of the Aegean extensional system (Burchfiel et al., 2008). Two periods of extension are identified, separated by a short period of compression. During the first extensional period, in the middle to late Eocene, extensional basins developed in relation to trench rollback along the northern Hellenic trench. This was followed by shortening in the late Oligocene to Early Miocene due to the arrival of the Kruja fragment on the Albanian subduction front. The second period of extension (middle Miocene to present) is related to the progressive rollback of the subducted slab at the northern Hellenic trench, resulting in the development of several types of basins (e.g., true grabens, tilted half-grabens and pull-apart basins along strike-slip faults; Dumurdzanov et al., 2004, 2005) dominated by NW-SE and E-W-trending faults. The latter are associated with the propagation of the North Anatolian fault in the Aegean Sea at ~6 Ma that partly decoupled the South Balkan extensional system in the north from the Aegean extensional system in the south (Burchfiel et al., 2008; Dumurdzanov

et al., 2005). The still active fault lines and zones are marked by scarps and offsets on Quaternary deposits in the basins, as well as by the locations of numerous earthquakes in recent times (Drogreška, 2018).

The Cenozoic evolution of North Macedonia was accompanied by extensive volcanism. The first period of volcanism took place in the eastern part mainly during the early Oligocene (Boev & Yanev, 2001) and was marked by the formation of large volcanic complexes with subduction-related geochemical characteristics. On the other hand, the second period occurred during Late Miocene—Pleistocene times (<10 Ma), when the volcanic activity within the region was focused in the Vardar zone and it is largely connected to the tectonic evolution of the South Balkan extensional system (Molnár et al., 2022; Yanev et al., 2008). During the latter phase, mainly small mafic volcanic centers with within-plate geochemical characteristics developed. Exception is the large Kožuf-Voras volcanic complex, located along the North Macedonia—Greece border, which has subduction-related characteristics (Kolios et al., 1980; Molnár et al., 2022; Yanev et al., 2008).

North Macedonia, especially in its central part, shows a relatively shallow depth of the Moho with values comprising between 32 and 35 km along the Vardar suture (Boykova, 1999; Grigoriadis et al., 2016) connecting two regional minima of about 30 km depth, one in the south (North Aegean Sea) and one in the north (along the Danube close to Belgrade). The depth of the Moho steeply increases in the eastern direction reaching 50 km behind the border of Bulgaria. A smoother increase is observed toward the west, reaching depths that exceed 40 km in Albania (Boykova, 1999).

3. Materials and Methods

During 2019–2022, 65 samples of free and dissolved gases were collected throughout North Macedonia. Among them, 45 were sampled from cold to lukewarm manifestations (<28°C) and 20 from thermal discharges (28°C to >74°C) (Figure 1; Supporting Information S1 and Supporting Information S2). The list of the sampling locations is reported in Supplementary Information (Figure S1 and Table S1 in Supporting Information S1). Analyses of chemical and isotopic composition of gas samples were carried out at the laboratories of Istituto Nazionale di Geofisica e Vulcanologia of Palermo (INGV-Pa).

The data set produced for this study is integrated with literature data of gas emissions from Greece, Serbia, Albania, Kosovo and Bulgaria for regional scale discussion (Daskalopoulou et al., 2019; Lévy et al., 2023; Minissale et al., 2023; Piperov et al., 1994; Randazzo et al., 2021).

3.1. Field Sampling and Chemical Analysis

Bubbling gases were sampled using an inverted funnel positioned above the emission point of the highest flux, whereas soil gases were collected by inserting a pipe in the soil at >50 cm depth and driving the gas by a syringe and a 3-way valve. Dry gases were collected in glass flasks equipped with two stopcocks (20–150 ml of volume) and/or in Exetainer® Labco vials (12 ml). Samples for dissolved gas analyses were collected in glass bottles (150 ml) sealed underwater by gastight rubber/teflon plugs.

Chemical composition (He, H₂, H₂S, O₂, N₂, CO₂, and CH₄) of dissolved and free gas samples were analyzed by an Agilent 7890B gas chromatograph combined with a Micro GC analyzer by Inficon. Concentrations of CO₂ and H₂S were determined by the Micro GC analyzer with He as carrier and equipped with a Poraplot-U column and TCD detector (detection limit about 100 and 10 μmol mol⁻¹, respectively). All the other gases were determined by the GC system with Ar as carrier and equipped with a 4-m Carbosieve S II column. A TCD detector was used to measure the concentrations of He, H₂, O₂, N₂ (detection limit about 3, 2, 50, and 100 μmol mol⁻¹, respectively) and an FID detector for CH₄ (detection limit about 1 μmol mol⁻¹). The analytical errors were less than 10% for He, H₂, and H₂S, and less than 5% for the remaining gases.

Gases in the dissolved phase were analyzed following the “headspace technique” (Capasso & Inguaggiato, 1998) and were extracted after equilibrium was reached at a constant temperature with a host-gas (high-purity Ar) being injected in the sample bottle. The chemical composition of the dissolved gas phase was obtained from the gas-chromatographic analyses considering the solubility coefficients (Bunsen coefficient “β,” $c_{\text{gas}} L_{\text{water}}^{-1}$ STP) of each gas species, the volume of gas extracted and the volume of the water sample (Capasso & Inguaggiato, 1998; Liotta & Martelli, 2012). Starting from the total amount of dissolved gases (ccSTP L⁻¹), the relative abundances of each gas species in equilibrium with the dissolved gas phase were recalculated and the analytical

results were expressed in $\mu\text{mol mol}^{-1}$ of gas at atmospheric pressure, allowing the comparison of gases found in dissolved and free phases.

3.2. Isotopic Analysis of C, He, and Ar

The $^{13}\text{C}/^{12}\text{C}$ ratios of CO_2 (expressed as $\delta^{13}\text{C}\text{-CO}_2$ ‰ vs. V-PDB) were measured with a Finnigan Delta S mass spectrometer after purification of the gas mixture by standard procedures using cryogenic traps (precision $\pm 1\sigma = 0.1$ ‰).

Helium isotope composition was analyzed directly from the sample bottles after purification in the high-vacuum inlet line of the mass spectrometer. The isotope composition of dissolved He was analyzed by headspace equilibration (Inguaggiato & Rizzo, 2004; Italiano et al., 2014). The $^3\text{He}/^4\text{He}$ and $^4\text{He}/^{20}\text{Ne}$ ratios were determined after cryogenic separation by a GVI Helix SFT mass spectrometer. The analytical errors were, generally, $<1\%$. Helium isotope composition is expressed as R/R_A , namely $^3\text{He}/^4\text{He}$ of the sample versus the atmospheric $^3\text{He}/^4\text{He}$ ($R_A = 1.386 \times 10^{-6}$; Ozima & Podosek, 2002).

Argon concentration and its isotope composition (^{40}Ar , ^{38}Ar and ^{36}Ar) were analyzed by mass spectrometry, using a multi-collector Helix MC-GVI, with analytical uncertainty (1σ) for single $^{40}\text{Ar}/^{36}\text{Ar}$ measurements of $<0.05\%$.

4. Results

4.1. Chemical Composition of the Gases

The chemical composition (He, H_2 , H_2S , O_2 , N_2 , CO_2 , CH_4 , and Ar) of the collected samples, together with the isotopic composition of C in CO_2 , He and Ar, as well as their coordinates and the physico-chemical parameters of related waters are included in an open-access data set (Li Vigni et al., 2025).

Nitrogen and CO_2 are the most abundant gas components with concentrations that range from 1,300 to 989,200 $\mu\text{mol mol}^{-1}$ and from 112 to 999,000 $\mu\text{mol mol}^{-1}$, respectively. Ar and O_2 show concentrations up to 11,100 $\mu\text{mol mol}^{-1}$ and 205,700 $\mu\text{mol mol}^{-1}$, respectively. Methane concentration varies from 2 to 7,100 $\mu\text{mol mol}^{-1}$. Only the samples collected at Smokvica (Figure S1 and Table S1 in Supporting Information S1) present a slight enrichment in CH_4 with values up to 22,500 $\mu\text{mol mol}^{-1}$. Hydrogen sulfide varies from <10 to 12,800 $\mu\text{mol mol}^{-1}$. Helium values are up to 3,600 $\mu\text{mol mol}^{-1}$.

Based on the measured gas composition, the data set has been divided into three groups: (a) N_2 -dominated (N_2 from 822,800 to 989,200 $\mu\text{mol mol}^{-1}$), (b) CO_2 -dominated (CO_2 from 474,200 to 999,000 $\mu\text{mol mol}^{-1}$), and (c) H_2S -rich (H_2S from 11 to 12,800 $\mu\text{mol mol}^{-1}$) (Figure 2). The 3rd group consisted of N_2 - and CO_2 -dominated gases that presented H_2S enrichments up to 1%. From this group, the N_2 -dominated gases correspond to gas that are found in the dissolved gas phase, whilst the CO_2 -dominated gases include only free gas samples. It is worth noting that even though the dissolved gas samples of Botun 1 and Kiselo Klajnc̃e do not have H_2S in their gas composition, they are also included in this group. These samples are located in the vicinity of Botun and Petkoniva (Figure S1 and Table S1 in Supporting Information S1) that show enhanced H_2S contents but, as will be discussed in Section 5.3, their inclusion was not based only on geographical criteria.

4.2. Isotopic Composition of the Gases

The $\delta^{13}\text{C}\text{-CO}_2$ values vary between -15.7 and $+1.0$ ‰. The N_2 -dominated gases show the most negative $\delta^{13}\text{C}\text{-CO}_2$ values (from -15.7 to -3.2 ‰). Most CO_2 -dominated and H_2S -rich gases show $\delta^{13}\text{C}\text{-CO}_2$ values from -4.6 to $+1.0$ ‰ and from -1.7 to $+0.70$ ‰, respectively. Few samples belonging to the CO_2 -dominated group (Geogas, Kozica 1 and Krušani. Figure S1 and Table S1 in Supporting Information S1) show $\delta^{13}\text{C}\text{-CO}_2$ values from -7.7 to -6.5 ‰.

The isotopic composition of He varies from 0.1 to 1.8 R_A with $^4\text{He}/^{20}\text{Ne}$ ratios ranging between 0.5 and 2066. Samples of the N_2 -dominated group have R/R_A and $^4\text{He}/^{20}\text{Ne}$ ranging from 0.15 to 1.09 and from 1.25 to 203, respectively. Gases of the CO_2 -dominated group show R/R_A values between 0.1 and 1.8, with corresponding $^4\text{He}/^{20}\text{Ne}$ ratios from 0.5 to 473. The H_2S -rich group shows R/R_A between 0.08 and 0.36, whereas $^4\text{He}/^{20}\text{Ne}$ ratios range between 11.2 and 2066.

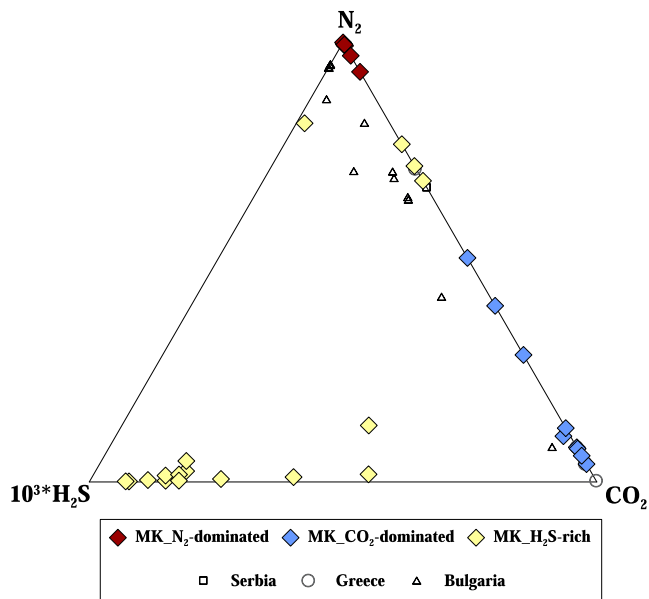


Figure 2. Chemical composition of the sampled gases. H₂S-CO₂-N₂ ternary diagram. Data from the neighboring countries are included: Bulgaria (Minissale et al., 2023; Piperov et al., 1994), Greece (Daskalopoulou et al., 2019), and Serbia (Randazzo et al., 2021).

The N₂-dominated group shows isotopic compositions of argon comprising between 294 and 302 for ⁴⁰Ar/³⁶Ar and between 0.187 and 0.191 for ³⁸Ar/³⁶Ar. The ⁴⁰Ar/³⁶Ar of CO₂-dominated samples ranges between 285 and 307, with corresponding ³⁸Ar/³⁶Ar in the range of 0.182–0.198, while the gases of H₂S-rich group show ⁴⁰Ar/³⁶Ar values that vary from 295 to 372 and ³⁸Ar/³⁶Ar ratios that range between 0.186 and 0.191 (Figure S2 in Supporting Information S1).

5. Discussion

The three identified groups of gases (N₂-dominated, CO₂-dominated and H₂S-rich gases) are geographically moderately well separated (Figure 3). The manifestations characterized by N₂-dominated gases are located in the easternmost part of the country and comprise the geothermal fields of Kežovica, Gevgelija, and Strumica, as well as the Dobra borehole of the Kočani geothermal field, and the cold gas manifestation of Rakliš. The CO₂-dominated group is mostly located in the central part of the country and includes gas samples from the thermal springs of Kumanovo and Katlanovo, from the geothermal fields of Kumanovo and Skopje, the Istibanja borehole in the Kočani geothermal field, and almost all of the cold gas manifestations: (a) Smrdliva Voda, Gorničet, Makedonka Češma, and Topli Dol in the mountainous border of Kožuf Mts. west of the Gevgelija basin; (b) Lešok and Banjiče, near the Polog basin; (c) Pelagonia basin, in south-west of the country. Lastly, all the gas samples of the H₂S-rich group are located in a narrow area within the Debar geothermal field, Botun and Kosel, in the

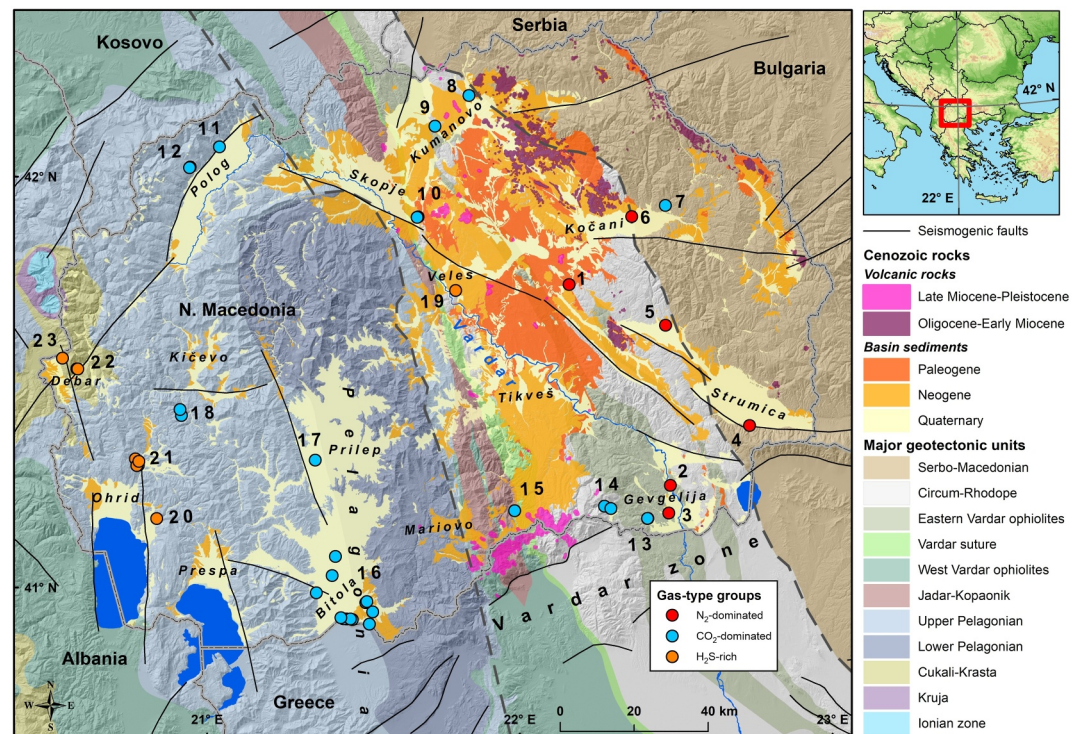


Figure 3. Spatial distribution of the three identified gas-type groups. Sampling sites as in Figure 1. Main geotectonic units from Schmid et al. (2020). Extension of Cenozoic sediments after Dumurdzanov et al. (2004, 2005) and volcanic rocks after Molnár et al. (2022). Seismogenic crustal faults from the European Database of Seismogenic Faults (EDSF; <https://edsf13.ingv.it/>). Dashed black lines approximate the extent of the Vardar zone. Extensional basins and geothermal fields mentioned in the text are also indicated.

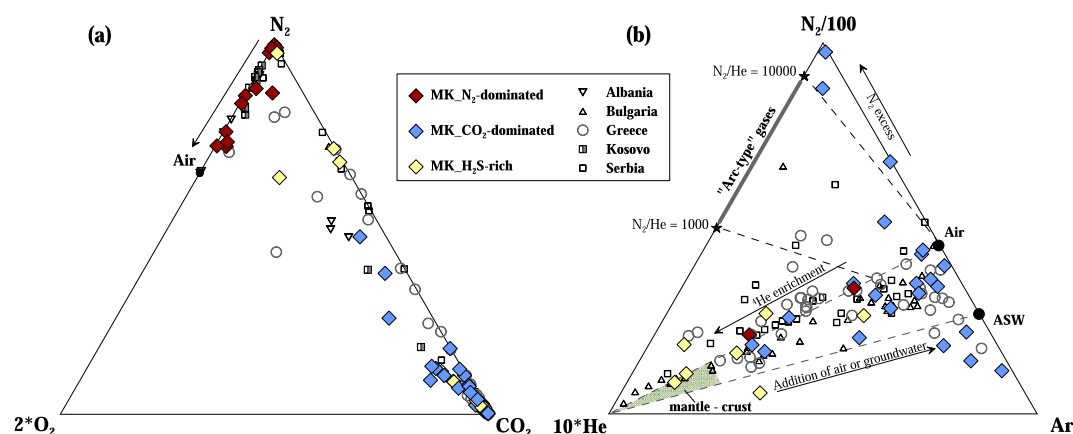


Figure 4. (a) O_2 - CO_2 - N_2 and (b) He-Ar- N_2 ternary diagrams. The atmospheric air ($N_2/Ar = 83$ —Giggenbach et al., 1983), Air Saturated Water (ASW; $N_2/Ar = 38$ —Fischer et al., 1998), arc-type, mantle and crustal gases (Giggenbach, 1996) compositions are also plotted. Data from the neighboring countries are included: Albania (Lévy et al., 2023), Bulgaria (Minissale et al., 2023; Piperov et al., 1994), Greece (Daskalopoulou et al., 2019), Kosovo (Lévy et al., 2023), and Serbia (Randazzo et al., 2021).

westernmost part of the country, with the only exception being the Sabotna Voda that is close to Veles town (Figure 3).

5.1. Origin(s) of N_2 and Ar

Samples collected from North Macedonia present N_2/O_2 ratios mostly higher than air (Figure 4a). This is indicative of inorganic or/and organic redox reactions that take place in the subsol or in the aquifer consuming O_2 , virtually enriching N_2 in the samples that present concentrations up to $989,200 \mu\text{mol mol}^{-1}$. These processes mostly affect dissolved gas samples. If no additional gases mix in while the water circulates through the aquifer, the dissolved gases that are already depleted in O_2 will not generate enough pressure to form a separate free gas phase. Therefore, the atmospheric component will remain dissolved until the water reaches the spring outlet. As a result, N_2 -dominant gases are most commonly found in dissolved gas samples. Notable exceptions are the gases from the thermal springs of Negorci, Smokvica, and Bansko (Figures 1 and 3), where the N_2 solubility is lowered by the high temperatures (45 – 74°C) of the waters, leading to the separation of a N_2 -rich free gas phase. Addition of non-atmospheric N_2 may also be a possibility. However, in the absence of N_2 isotopic data, this hypothesis cannot be confirmed.

Samples from Bansko, Dobra, Kežovica, and Rakliš deviate from the N_2 - CO_2 alignment toward the compositional point of atmospheric air (Figure 4a). The presence of abundant O_2 (up to $157,800 \mu\text{mol mol}^{-1}$) together with the N_2/O_2 ratios show values close to the atmospheric one, thereby suggesting a possible shallow atmospheric input. In the case of soil gases, such components may mostly derive from atmospheric air diffusion within the soil. In the case of bubbling gases, the mixing with a shallow aquifer in equilibrium with the atmosphere should be considered as well. In both cases, some contamination during sampling cannot be ruled out.

The He-Ar- N_2 ternary diagram (Figure 4b) is a helpful tool to discriminate mixing processes between crustal, mantle, and atmospheric components (Giggenbach et al., 1983). The majority of the samples are found inside the triangle delimited by the He apex and N_2/Ar of air saturated waters (ASW) and air ($N_2/Ar = 83.6$ and 36.9 at 20°C , respectively, Kipfer et al., 2002). This distribution suggests a two-component mixing relationship between geogenic (crustal or magmatic) and atmospheric sources. The deep component is more evident in the H_2S -rich category, likely due to a long residence time in the crust (Mazor, 1991). Most of the CO_2 -dominated samples show N_2/Ar ratio values close to either atmospheric or air-saturated water points. This suggests that N_2 and Ar of prevailing atmospheric origin are added to the uprising gases by the meteoric recharge of the hydrologic circuit that is feeding the sampled manifestations. Nevertheless, the atmospheric origin is supported by the isotopic composition of Ar (^{36}Ar , ^{38}Ar , and ^{40}Ar). The atmospheric mixture is composed mainly of ^{40}Ar , but the ^{36}Ar is considered exclusively of atmospheric origin, whilst the ^{40}Ar budget derives from the radiogenic decay of ^{40}K in the crust (Holland & Gilfillan, 2013). The gas samples have a small range of Ar isotopic values, mostly close to

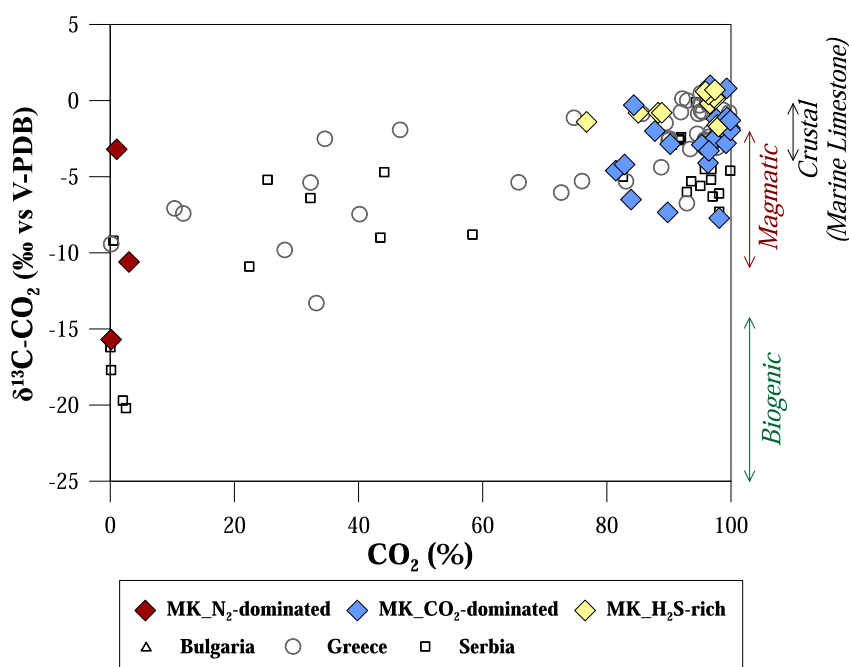


Figure 5. Binary plot of CO_2 concentrations (%) versus $\delta^{13}\text{C}\text{-CO}_2$ (‰ vs. V-PDB) values. The three, colored arrows represent the $\delta^{13}\text{C}\text{-CO}_2$ ranges of the three different sources (from Jenden et al., 1993): biogenic (green), magmatic (red), and crustal (black). Data from the neighboring countries are included: Bulgaria (Minissale et al., 2023; Piperov et al., 1994), Greece (Daskalopoulou et al., 2019) and Serbia (Randazzo et al., 2021).

the typical atmospheric signature ($^{40}\text{Ar}/^{36}\text{Ar} = 298.56$ and $^{38}\text{Ar}/^{36}\text{Ar} = 0.188$; Lee et al., 2006; Ozima & Podosek, 2002). Exceptions are the samples from Busemak, Geogas, Pela Rosa and Kozica 1, all in the Bitola basin, that present a high N_2/Ar ratio (from 134 to 5,383; Figure 4b), pointing toward a possible addition of non-atmospheric N_2 (metamorphic and/or from decay of organic matter; Haendel et al., 1986; Javoy et al., 1984; Jenden et al., 1988).

5.2. Source(s) of CO_2 and He

Carbon dioxide is one of the major deep gases and represents the main carrier of mantle-derived fluids. The $\delta^{13}\text{C}\text{-CO}_2$ versus CO_2 diagram (Figure 5) allows discrimination between the diverse possible carbon sources: biogenic, magmatic, and crustal. The results show that the gas samples fall mostly within the typical range for crustal and magmatic carbon (Figure 5). Exception is the Smokvica sample that presents the lowest isotopic carbon value (-15.7‰), because of isotopic fractionation, likely, due to a strong CO_2 loss (Figure S4 in Supporting Information S1).

Considering a mixing model between magmatic carbon and crustal, both reduced and oxidized, carbon (Figure S3 in Supporting Information S1), a possible crustal contribution may be derived from decarbonation processes within carbonate rocks by means of a heat source (e.g., intrusion of a magmatic body into the crust), which forms metamorphic CO_2 with a mean value of $\delta^{13}\text{C}$ of about 0.3‰ (Clark & Fritz, 1997; Hunt, 1996). Any contributions from organic sediments to fluids deriving from a descending slab are limited. Nonetheless, the isotopic signature of metamorphic CO_2 is a topic of ongoing debate; some authors have reported ^{13}C values of the CO_2 similar to those of source rocks (e.g., Sharp et al., 2003), whilst others have observed that metamorphic decarbonation processes produce CO_2 fluids enriched in ^{13}C up to $+3.8\text{‰}$ compared to the carbon of the protoliths (e.g., Evans et al., 2008; Marini & Chiodini, 1994).

Metamorphic decarbonation reactions occur commonly during regional metamorphic processes and involve carbonate-bearing metasediments. These reactions are triggered by increasing temperature and pressure, resulting in the reaction of carbonate minerals with silicate minerals that results in the formation of Ca-silicate minerals and the release of CO_2 (Stewart et al., 2019). This applies to the thermal samples from Istibanja, Katlanovo and

Kumanovo hydro-systems, whose reservoirs are hosted in carbonate-rich aquifers (Precambrian gneiss and Paleozoic carbonate schist, Precambrian and Paleozoic marbles, and Paleozoic marbles, respectively; Popovska-Vasilevska & Armenski, 2016). In these samples, decarbonation reactions are favored by high temperatures (Gorgieva, 1989). Another possibility is that metamorphic decarbonation reactions occur in fault core zones (Kleine et al., 2014), where CO₂-bearing fluids and rocks are in disequilibrium. The flow of fluids within the rocks surrounding the fault structure remains slow in comparison to the decarbonation reaction rate, thereby buffering the fraction of CO₂ contained within this fluid. Conversely, fluid channeled along the fault core zone shows higher flux compared to the surrounding rocks, inhibiting the progress of decarbonation reactions (Kleine et al., 2014).

Because of the multiple carbon sources (e.g., hydrocarbon oxidation, organic matter decay, respiration, decarbonation of marine carbonates and degassing of magmatic bodies) and the numerous secondary, deep or shallow processes (e.g., fluid-rock interactions, dissolution, mixing, redox reactions) that may isotopically fractionate CO₂ (Jenden et al., 1993; Wycherley et al., 1999), the interpretation of $\delta^{13}\text{C-CO}_2$ values alone does not provide direct evidence to the origin of the fluids (note the overlapping magmatic and crustal fields around -4% in Figure 5). The isotope composition of noble gases (He, Ne, and Ar) and the comparison with the carbon isotope composition are more effective to distinguish the fluid origin and quantify possible mixing between the different sources; inert noble gases have a more distinct isotopic signature in terrestrial reservoirs (atmosphere, mantle, and crust; Holland & Gilfillan, 2013).

The coupled R/R_A and $^4\text{He}/^{20}\text{Ne}$ ratios (Figure 6a) can be used to identify and quantify the possible sources of He. Gas samples belonging to the CO₂- and N₂-dominated groups show a prevailing crustal source of He (continental crust $0.01\text{--}0.02\text{R}_A$; Ballentine & Burnard, 2002), with a mantle contribution between 1% and 20%, considering a Mid Ocean Ridge (MOR) end-member ($\text{R/R}_A \approx 8 \pm 1$; Ozima & Podosek, 2002). As North Macedonia is located in a continental setting subjected to an extensional tectonic regime, the European Subcontinental Lithospheric Mantle (ESCLM, with R/R_A value of 6.32 ± 0.39 ; Gautheron et al., 2005) could be considered as an alternative mantle end-member to MOR (Figure 6a). For instance, assuming the ESCLM, mantle contribution arrives at 25% for the samples with the highest R/R_A ratios (Figure S4 in Supporting Information S1). Li Vigni et al. (2022) and Molnár et al. (2021) suggested that the mantle source beneath the study area could be characterized by an even more radiogenic value for He, as geochemical characteristics of the youngest volcanic rocks suggest the occurrence of a metasomatized lithospheric mantle in the area (Molnár et al., 2022; Yanev et al., 2008). This is also supported by the lower R/R_A values than the ESCLM (between 3.1 and 4.5) that were obtained from fluid inclusions in olivine phenocrysts hosted in the Pleistocene (1.8 ± 0.1 Ma) lavas of Mlado Nagoričane volcanic center in Kumanovo basin (Molnár et al., 2021). If the mantle beneath North Macedonia is indeed contaminated by subduction-related U-Th-rich crustal material, then the mantle contribution will potentially exceed 25%.

The highest mantle input in the studied samples was found in two areas. The first is recognized in the southern part of the country, along the Nidže-Kožuf mountains, between Mariovo and Gevgelija grabens. This may be related to the activity of the Neogene-Quaternary Kožuf-Voras volcanic system (Kolios et al., 1980; Molnár et al., 2022, 2023). Studies on hypogene karst systems of this area indicate fluid circulation along deep fault systems causing groundwater interaction with the rocks of the Kožuf-Voras volcanic system and consequently the addition of metamorphic CO₂ and up to 10% mantle He to the water (Temovski et al., 2021, 2022). The second area with high mantle input for He is found in the northern part of the country, on the western side of the Polog graben close to Tetovo. Here, enhanced $^3\text{He}/^4\text{He}$ ratios may be associated with an active regional fault system and/or with the seismically active secondary normal faults found in the border of the basin (Dumurdzanov et al., 2005). Such faults may act as preferential escape pathways for mantle fluids.

With regard to the crustal source of He, one potential origin is attributable to the radiogenic decay of U and Th from granitic intrusions and metamorphic rocks within the crust, which increase the ^4He concentration in the circulating fluids. This process may occur in geothermal fields located in the eastern part of the country, within the Serbo-Macedonian Zone, where Precambrian crystalline basement and granitic intrusions are present. As previously mentioned, gas samples collected from these geothermal systems are N₂-dominated, have low R/R_A ratios (<1.1), and show a high He content (up to $3,600 \mu\text{mol mol}^{-1}$). Interestingly, the reservoirs of these systems are hosted in Paleozoic granite and/or Paleozoic metamorphic formations (Gorgieva et al., 2000; Micevski et al., 2007; Naunov, 2003; Spasovski, 2012), where radiogenic decay can produce significant amounts of ^4He .

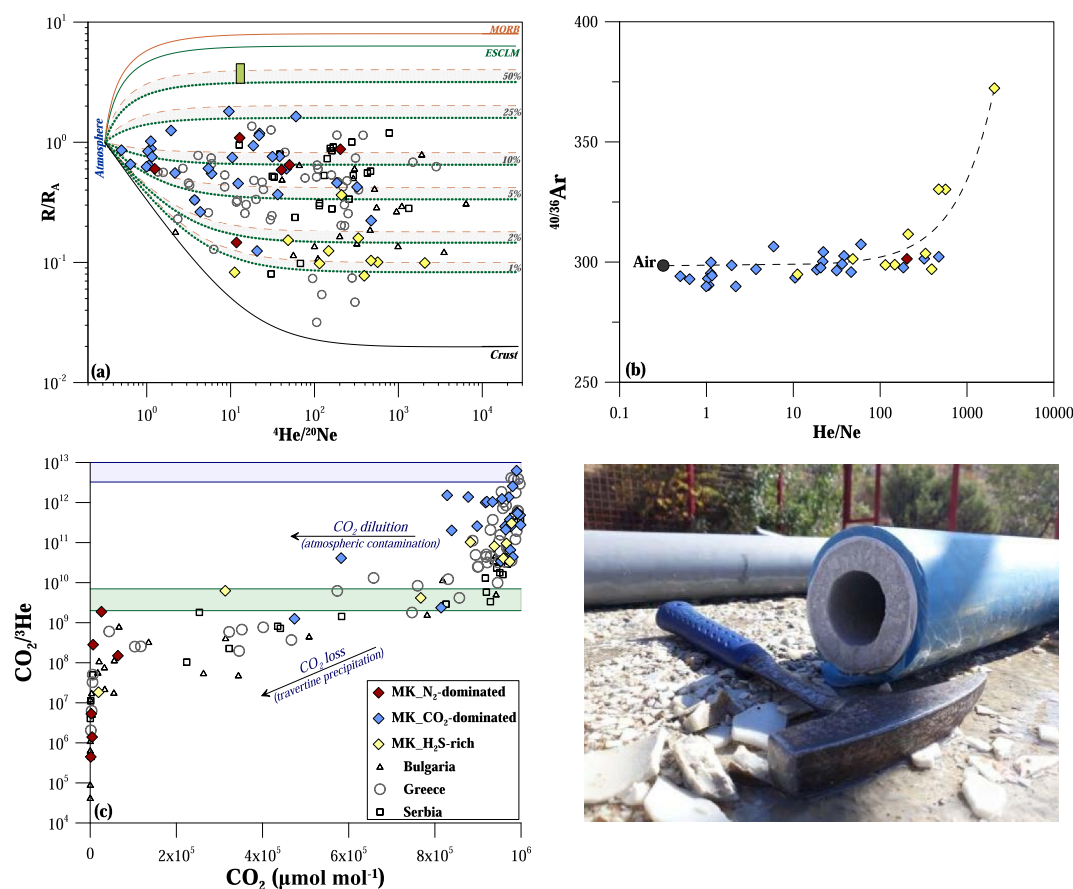


Figure 6. (a) Binary plot of R/R_A ratio versus $^4\text{He}/^{20}\text{Ne}$ ratio. The dashed lines represent the mixing between atmosphere ($1R_A$, Ozima & Podosek, 2002; $^4\text{He}/^{20}\text{Ne} = 0.318$, Sano & Wakita, 1985), crust ($0.01\text{--}0.02R_A$, Ballentine & Burnard, 2002; $^4\text{He}/^{20}\text{Ne} > 1,000$, Sano & Wakita, 1985), MORB-type ($8 \pm 1 R_A$, Ozima & Podosek, 2002; $^4\text{He}/^{20}\text{Ne} > 1,000$, Sano & Wakita, 1985) and ESCLM-type ($6.32 \pm 0.39 R_A$, Gautheron et al., 2005; $^4\text{He}/^{20}\text{Ne} > 1,000$, Sano & Wakita, 1985) mantle at different percentages. The green area represents the R/R_A and $^4\text{He}/^{20}\text{Ne}$ data from fluid inclusions hosted in olivine phenocrysts from the Mlado Nagoricane volcanic center (North Macedonia) (Molnar et al., 2021). (b) Binary plot of $^{40}\text{Ar}/^{36}\text{Ar}$ ratio versus $^4\text{He}/^{20}\text{Ne}$ ratio. The dashed lines represent the mixing between the atmosphere ($^{40}\text{Ar}/^{36}\text{Ar} = 298.56$; Lee et al., 2006; $^4\text{He}/^{20}\text{Ne} = 0.318$, Sano & Wakita, 1985) and the Macedonian sample with the highest argon ratio. (c) Binary plot of CO_2 concentration ($\mu\text{mol mol}^{-1}$) versus CO_2/He ratio. The shaded regions highlighted the CO_2/He values of ESCLM (CO_2/He from 2 to 7×10^9 ; Brauer et al., 2016; Marty et al., 2020) in green, and the crust in blue. (d) Picture of calcite deposition in a pipe at the Katlanovo sampling site.

Some samples, mostly from the CO_2 -dominated group, are characterized by $^4\text{He}/^{20}\text{Ne}$ ratios that are close to the atmospheric end-member (0.318, Sano & Wakita, 1985). This indicates a strong atmospheric input likely related to the composition of the gas dissolved in the waters through which they bubble or due to mixing between the deep-circulating fluids and shallower air-saturated waters. On the contrary, the atmospheric contribution is negligible for the gas samples of the H_2S -rich ($^4\text{He}/^{20}\text{Ne}$ ratios > 11). These samples present low R/R_A values (all except one from 0.08 to 0.16), indicating a nearly pure crustal origin for He ($R/R_A < 0.16 R/R_A$ correspond to $< 2\%$ of mantle contribution—Figure 6a). A negligible non-atmospheric contribution to these gases can also be highlighted by the isotope composition of Ar (Figure 6b). Gas samples from Botun, and Kosel seem to have experienced minor ingrowths of ^{40}Ar (up to $^{40}\text{Ar}/^{36}\text{Ar} = 372$; Figure 6b). Considering the positive correlation of the $^{40}\text{Ar}/^{36}\text{Ar}$ ratios with the $^4\text{He}/^{20}\text{Ne}$ ratios and the corresponding crustal-derived $^3\text{He}/^4\text{He}$ ratios of the former, an additional crustal input from radioactive decay of ^{40}K cannot be excluded.

The sample of Sabotna Voda, which is the only H_2S -rich sample located outside the westernmost area, displays a mantle contribution of nearly 5% (R/R_A 0.36). This contribution is much higher with respect to the remaining samples of this group. The ultrapotassic mafic volcanic center of Kišino, the youngest volcanic site in Macedonia

(1.5 Ma—Yanev et al., 2008) that is found nearby, east of Sabotna Voda, possibly justifies the small mantle He contribution in this spring.

The combination of CO₂ and ³He, expressed as CO₂/³He ratio, is used to evaluate any depletion or enrichment relative to the mantle signature of the fluid. Figure 6c compares the CO₂/³He ratio with the CO₂ concentration of the collected gases. The CO₂/³He values of the studied gas samples varied between 4.5×10^5 and 6.2×10^{12} , showing a wide range spanning over seven orders of magnitude. The collected gas samples of the CO₂-dominated and H₂S-rich groups mostly have higher CO₂/³He ratios (1.2×10^9 – 6.2×10^{12} and 1.8×10^7 – 3.1×10^{11} , respectively) and are distributed in the area found between the crust and ESCLM ranges. Samples that plot above the ESCLM range demonstrate very low ³He concentrations, indicating a prevailing crustal source of CO₂ due to geogenic (i.e., metamorphic decarbonation reactions; Figure 5) or biogenic processes (Sano & Marty, 1995). Conversely, samples that plot within or close to the ESCLM range have a significant amount of ³He. This suggests either a prevailing mantle contribution or a loss of CO₂ during gas-water-rock interactions. Gases of the N₂-dominated group and Sabotna Voda (H₂S-rich group) present low CO₂/³He ratios. Considering their chemical and isotopic compositions, the occurrence of secondary processes that changed the pristine composition of the gases is possible. One explanation for the CO₂ loss is the deposition of thermogenic travertine (mineral trapping), a common secondary process occurring within geothermal systems (Barry et al., 2020; Gilfillan et al., 2009; Ray et al., 2009; Stefánsson et al., 2017). The solubility of CO₂ in water depends on the temperature and pressure conditions of the water; high temperature results in a decreased CO₂ solubility. The dissolution of large quantities of CO₂ may result in chemical disequilibria within the aquifer, potentially leading to reactions that involve the dissolution and precipitation of minerals (Baines & Worden, 2004). On dissolution in circumneutral to alkaline groundwater, CO₂ reacts with H₂O and forms H₂CO₃. The latter rapidly dissociates into HCO₃[−] and CO₃^{2−} ions and reacts with Ca²⁺ and Mg²⁺ ions. Extensive CO₂ dissolution in the hydrothermal environment may result in the oversaturation of calcite and/or aragonite, leading to the precipitation of these mineral phases (Stefánsson et al., 2016, 2017). This causes a strong decrease of CO₂ content, with a consequent virtually increase of N₂ concentration, and a fractionation of δ¹³C values, thus increasing the lighter component in the residual gases. The pH range, which spans from 6.9 to 8.8, the high temperature (up to 70°C), and the extensive travertine deposition located in these geothermal systems supports this hypothesis (Figure 6d). Randazzo et al. (2021), following the model proposed by Gilfillan et al. (2009), interpret the presence of N₂-dominated manifestation in Serbia as the result of varying degrees of CO₂ loss by dissolution processes occurring at pH values between 5.6 and 7. This leads to an enrichment of the fluids in N₂. No travertine deposits are found near Sabotna Voda, where the CO₂ loss is likely due to a differential dissolution caused by the interaction with shallow aquifers during its migration toward the surface (Ray et al., 2009). In this case, the higher solubility of CO₂ (solubility trapping) with respect to N₂ and noble gases in aquatic systems results in the enrichment of the latter gas species (Ozima & Podosek, 2002; Figure 6c).

5.3. Origin of H₂S

Hydrogen sulfide in natural gases can be found in three main geogenic environments: magmatic (e.g., Allard et al., 1991; Giggenbach, 1987), hydrothermal (Giggenbach, 1997; Ohmoto & Lasaga, 1982), and sedimentary systems. Among the latter, the main H₂S generating processes are the alteration of sulfide minerals (e.g., Giggenbach, 1980), the reactions of sulfate reduction (e.g., Machel, 2001), and the emission from shallow sediments rich in organic matter and anoxic waters (Thode, 1991).

The presence of H₂S in the fluid can be related to the evaporitic sulfate minerals that are found in the stratigraphic sequences of the area. Evaporite outcrops of supposedly Upper Cretaceous age (gypsum, anhydrides, salts, multicolored clays and breccias with interbedded dolomite and thin organic-rich shales) are present in the western part, on Dešat and Stogovo mountains near Debar (Frashëri et al., 1996; Jančev et al., 1999), whilst Triassic evaporite (Ionian unit; Schmid et al., 2020) is only hypothesized at depth in Duvalo Kosel, Botun and Petkoniva areas (Li Vigni et al., 2022).

Hydrogen sulfide might be produced during either thermochemically (TSR) or microbially (MSR) driven sulfate reduction processes (Machel, 2001) that occur in these evaporite deposits. TSR processes take place in deep burial settings in a temperature range between 100°C and 140°C (Machel, 2001), such as in gas provinces of western Canada (Manzano et al., 1997), the United States (Heydari, 1997) and Abu Dhabi (Worden et al., 1996). On the other hand, MSR is widespread in shallow burial environments in a temperature range of 0–80°C (Machel, 2001).

The latter process was observed in the Frasassi cave system (northeastern Apennines, Italy), where several H₂S-rich springs are present. In this case, the H₂S is produced through bacterial sulfate reduction in black shale within deep-seated Triassic evaporites (D'Angeli et al., 2019; Peterson et al., 2013).

At the Duvalo site, the most extended H₂S-rich gas manifestation of the area, the gas derives from thermochemical sulfate reduction (Li Vigni et al., 2022). According to the authors, this hypothesis is further supported by the isotopic composition of methane, which suggests a thermogenic origin, and the tectonic contact between sulfate-bearing strata and organic-rich shales of metamorphic basement, which favor sulfate reduction reactions. However, for the other sites, the contribution of microbially mediated sulfate reduction cannot be excluded. Data on the isotopic composition of sulfur are currently not available.

Gas samples of Botun and Kiselo Klajnce were included in the group of H₂S-rich gases. Even though H₂S is below the detection limit in these gases, they are included in group iii due to their geographical position. Specifically, they are found in the area of Botun, close to Duvalo. There, free gas samples showed a CO₂-dominated composition while the dissolved ones were N₂-dominated. The endogenous gases on their transit toward the soil surface interact with a series of shallow cold aquifers or with stagnant meteoric water accumulations at the surface. Consequently, H₂S can dissolve in water due to its higher solubility with respect to other main gases. The high solubility may also justify the lower CO₂ content compared to the nearby free gas samples. As the solubility increases according to N₂ < CO₂ < H₂S, the generation of a gas with H₂S below the detection limit and with N₂ as the prevailing gas species is plausible. Furthermore, the disappearance of H₂S can be attributed to biologically and/or inorganically driven oxidation processes within the soil (Wróblewski et al., 2024). Oxidation reaction produces great quantities of H⁺ ions, which increases the ionic power and acidifies the water. This explains the low pH values (4.5–5.5) of the water measured at the sampling points, which cannot be justified only by the amount of dissolved CO₂.

For Sabotna Voda, collected in the central part of the Vardar zone, although Triassic rocks are present nearby, no evaporite formations have been identified in the sequence (Arsovski, 1997). Thus, the presence of H₂S might derive from reduction processes of sulfate coming from either Triassic limestone-bound sulfate or may be related to S-rich coal beds within the Veles basin (Dumurdzanov et al., 2004).

6. Tectonic Implications

Data from the gas manifestations of North Macedonia are compared with those from the neighbor countries of Greece (Daskalopoulou et al., 2019), Serbia (Randazzo et al., 2021), Albania, Kosovo (Lévy et al., 2023), and Bulgaria (Minissale et al., 2023; Piperov et al., 1994). The gas manifestations of the South Balkan Peninsula are mainly related to the extensional tectonic structures of the area, with the impact of the latter being reflected in their spatial distribution (Figure 7). Such structures are associated with boundaries between the major geotectonic units, that is, the Vardar suture. The spatial distribution of the dominant gas follows a general trend from west to east (Figure 7a), with CH₄-dominated manifestations observed in Albania (west), CO₂-dominated ones in North Macedonia, and N₂-dominated ones in Bulgaria (east).

Albania is recognized as an oil and gas province, where several reservoirs are exploited (Nieuwland et al., 2001; Velaj, 2015). Several oil seeps and some reservoirs are also found in western Greece (Etiopé et al., 2013; Zeligidis et al., 2015). The hydrocarbon fields are linked to the sedimentary regime, in which organic matter is abundant, favoring the occurrence of hydrocarbon deposits (Daskalopoulou et al., 2018). They belong to carbonate reservoirs of the Ionian fold-and-thrust belt and are related to the presence of Triassic evaporitic rocks, which provided an efficient seal for the oil and gas migration (Bega & Soto, 2017 and reference therein). Moreover, some CH₄-rich manifestations are associated to ophiolite complexes, such as the Mirdita ophiolite complex in Albania and Kosovo (Lévy et al., 2023; Truche et al., 2024), or the Pindos, Othrys, and Argolis ophiolite massifs in Greece, where abiotic CH₄ formation has been attributed to ongoing serpentinization processes (D'Alessandro et al., 2018; Etiopé et al., 2013; Li Vigni et al., 2021).

Moving eastwards, CO₂-dominated gas manifestations became widespread in the region (Figures 7a and 7b). Two possible geogenic carbon sources are hypothesized for two different parts of the country. In the case of some geothermal fields, such as Istibanja, Katlanovo and Kumanovo hydro-systems in the eastern part of North Macedonia, CO₂ is associated with metamorphic decarbonation reactions within their reservoirs as they are hosted in carbonate rocks (Popovska-Vasilevska & Armenski, 2016). On the other hand, in the western part of

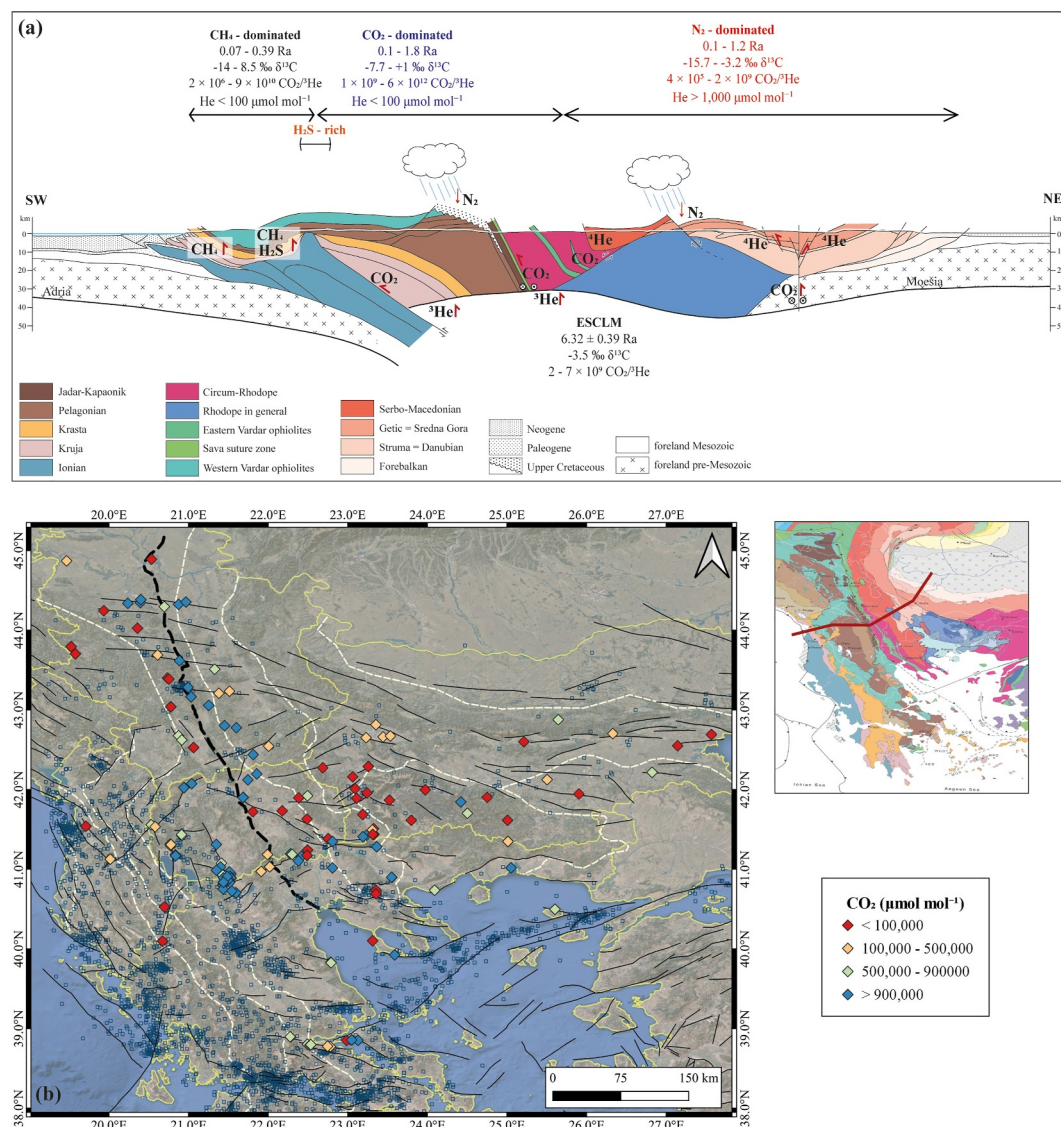


Figure 7. (a) Geological section from Schmid et al. (2020). Location of geological section is also added. Red arrows represent the potential fluid pathways. (b) Geographical distribution of CO₂ concentrations (μmol mol⁻¹) of the Southern Balkan Peninsula from the European Database of Seismogenic Faults (EDSF) compiled in the framework of the Project SHARE by INGV (<https://edsf13.ingv.it>). Earthquakes (blue squares) with a magnitude of ≥M4 and median depth value of 13 km, since 1960, from the USGS Earthquakes Hazard Program (<https://earthquake.usgs.gov/earthquakes/search/>). The black dashed line represents the Vardar suture, whilst the white dashed line represents the border of the geotectonic units. Data from this study: Daskalopoulou et al. (2019); Lévy et al. (2023); Minissale et al. (2023); Piperov et al. (1994); Randazzo et al. (2021).

North Macedonia, CO₂ of the cold CO₂-rich manifestations is linked to the active deep fault structures bordering Cenozoic horst-graben systems, where seismic activity is concentrated (Figure 7b; Burchfiel et al., 2008; Cvetkovic et al., 2016; Dumurdzanov et al., 2005) and favored also by the relatively shallow Moho in this area (Boykova, 1999). This points to a deeper origin of CO₂ (mantle or descending slab) in this area with respect to the eastern part. Historically, the western part of the Southern Balkan extensional regime has been affected by several moderate to strong earthquakes, and sometimes with destructive character, such as the M 6.1 in 1963 at Skopje (North Macedonia) or the M 6.4 in 2019 at Durrës (Albania). Seismicity is widely distributed in the area (Figure 7b). However, it has been noticed that seismic events are more frequent in the western part (Albania, western Greece, and western part of North Macedonia) and less frequent in the eastern part (Burchfiel et al., 2006). This observation is consistent with the distribution of active neotectonic faulting, which occurs as

new ruptures are created along old structures. This type of seismicity may be related to highly pressurized CO₂ that is accumulated in crustal reservoirs, and favors mechanisms of fault weakening (Miller et al., 2004). As hypothesized for the Apennine chain in Italy (Chiodini et al., 2020), that has a similar geodynamic regime, CO₂ in the western part of the South Balkan Peninsula may be continuously released from carbonates in the slab to the mantle wedge and to the lower crust (Frezzotti et al., 2009). CO₂ ascends from depth and the increasing pressure within the deep reservoirs may drive the migration toward the uppermost crustal layers (Chiodini et al., 2013). Gas exsolution from deep CO₂ reservoirs during seismic events results in an increased gas release to the atmosphere (Chiodini et al., 2020).

An example of extensive degassing through widespread cold CO₂-rich manifestations is the Pelagonian basin (Prilep-Bitola-Florina basin). This is an NNW-SSE oriented intra-montane graben (Arsovski, 1997) sited in the southern part of the country, which extends for more than 100 km from Prilep in North Macedonia to Kozani in Greece. Here, several CO₂-rich mineral springs and wells are found, resulting from the migration of CO₂ from depth to the surface along faults and fracture zones (Koukouzas et al., 2015). Although great amounts of CO₂ are extracted from companies in both countries, the presence of extensive natural CO₂ accumulations is well documented only on the Greek side (D'Alessandro et al., 2011; Gemeni et al., 2015; Karakatsanis et al., 2007; Pearce et al., 2004; Ziogou et al., 2013). No data have been published for North Macedonia. Thus, the gas manifestations collected in the Bitola basin during this work represent the first geochemical evidence of CO₂ degassing for this area (Figure S1b in Supporting Information S1).

The dominant gas species at the Vardar suture undergo a notable shift toward the east, transitioning to a predominantly N₂ composition (Figure 7a; Figure S5 in Supporting Information S1) and are characterized by higher He content (Figure S6 in Supporting Information S1). These features can be ascribable both (a) to the lithology of their reservoirs, whose basement is characterized by Precambrian and Cambrian metamorphic rocks, which were strongly deformed during the formation of Variscan orogenic belt, and by several intrusions of granitic rocks (Arsovski, 1997; Schmid et al., 2020; Wang et al., 2024), and (b) to CO₂ loss through secondary processes within the reservoir and/or during gas ascent (Daskalopoulou et al., 2019; Minissale et al., 2023; Randazzo et al., 2021). The N₂-dominant composition of the thermal gas manifestations is likely caused by CO₂ removal, for example, precipitation of carbonate minerals, preferential dissolution of CO₂ in water compared to other less soluble volatiles. The high He content, together with its low isotopic ratio, indicates a long residence time of the circulating waters within the crust, where granitic intrusive and metamorphic formations, being enriched in U and Th, produce abundant He by radiogenic decay, increasing the ⁴He content in the parent fluids. A similar situation is present in the Himalayan belt, where the sutures divide the purely crustal He of the Himalayan orogen from the mantle helium of the Tibet plateau (Hao et al., 2023; Klemperer et al., 2022; Li et al., 2024). Gas manifestations on the Tibet plateau are related to an extensional regime, where volatiles derived from enriched mantle wedge (CO₂ and ³He), subducted Indian slab-carbonate (CO₂), metamorphic decarbonation reactions (CO₂) and radiogenic decay (⁴He) within the crust (Hao et al., 2023).

Additionally, the geographical distribution of the geothermal fields has to be taken into account. The Vardar and the Serbo-Macedonian zones are characterized by a positive geothermal anomaly (Gorgieva et al., 2000), which is likely associated with Cenozoic volcanic activity that occurred throughout the Balkan Peninsula, following a NW-SE trending belt (Boev & Yanev, 2001; Cvetkovic et al., 2016; Molnár et al., 2022; Yanev et al., 2008). During the Late Miocene—Pliocene period, volcanism in Macedonia occurred within the Vardar zone. This resulted in the development of small-volume centers along main fault lines and/or boundaries of geotectonic units (Molnár et al., 2022). These contribute to the increased heat flow, together with radiogenic decay in the local granitoid intrusions. Exception is the Debar geothermal field, located at the border region between Albania and North Macedonia, where several hot water springs are located along an active fault on the east side of the Debar half graben (Dumurdzanov et al., 2005). Unlike the other geothermal fields, the Debar geothermal system is linked to the Peshkopia geotectonic zone (Frashëri et al., 2004). This is likely associated with deep faults at the periphery of a Triassic gypsum diapir, which represents a high thermal conductivity body (Kodhelaj, 2018).

Summing up, North Macedonia has a complex geological history and presents some of the most important structures of the Alpine-Himalayan orogenic activity. Consequently, it can be considered as one of the most active tectonic-related geogenic carbon degassing hot-spots of the Balkan peninsula.

Data Availability Statement

The data used in this study are available at EarthChem Library via Li Vigni et al. (2025).

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