Abstract We report on the results of an extensive geochemical survey of fluids released in the Vardar zone (central-western Serbia), a mega-suture zone at the boundary between Eurasia and Africa plates. Thirty-one bubbling gas samples are investigated for their chemical and isotopic compositions (He, C, Ar) and cluster into three distinct groups (CO₂-dominated, N₂-dominated, and CH₄-dominated) based on the dominant gas species. The measured He isotope ratios range from 0.08 to 1.19 Ra (where Ra is the atmospheric ratio), and reveal for the first time the presence of a minor (<20%) but detectable regional mantle-derived component in Serbia. δ¹³C values range from −20.2‰ to −0.1‰ (versus PDB), with the more negative compositions observed in N₂-dominated samples. The carbon-helium relationship indicates that these negative δ¹³C compositions could be due to isotopic fractionation processes during CO₂ dissolution into groundwater. In contrast, CO₂-rich samples reflect mixing between crustal and mantle-derived CO₂. Our estimated mantle-derived He flux (9.0 × 10² atoms m⁻² s⁻¹) is up to 2 orders of magnitude higher than the typical fluxes in stable continental areas, suggesting a structural/tectonic setting favoring the migration of deep-mantle fluids through the crust.

1. Introduction

Recognizing and identifying the transfer of mantle-derived fluids (e.g., CO₂, N₂, noble gases) in continental regions is critical for investigating the processes that shape the deep and shallow Earth's evolution, such as subduction, volcanism, natural degassing, active tectonics, and earthquakes (e.g., Ballentine et al., 2001; Broadley et al., 2020; Caracausi & Sulli, 2019; Caracausi et al., 2013; Chiodini et al., 2020; Holland & Gilfillan, 2013; Kennedy & Van Soest, 2007; Labidi et al., 2020; Lowenstern et al., 2014; O'Nions & Oxburgh, 1988; Torgersen, 1993). During the last four decades, the migration and surface discharge of deep-mantle volatiles has been verified in many crustal segments, including western-central Europe (e.g., Brauer et al., 2013; Carreia et al., 2009; Mamyrin & Tolstikhin, 1984; Minissale, 2000). New efforts are currently undertaken to extend such studies in central-eastern Europe, in the attempt to (a) understand natural degassing in active tectonic regions (e.g., Etiöpe et al., 2003, 2004; Frunzeti, 2013; Ionescu et al., 2017; Italiano et al., 2017; Kis et al., 2017; Sarbu et al., 2018; Vaselli et al., 2002), (b) investigate the possible presence of magma at depth below “quiescent” volcanoes (e.g., Kis et al., 2019), and (c) assess the role of fluids in seismogenetic processes (e.g., Baciuc et al., 2007; Bräuer et al., 2004, 2005, 2008). Large-scale outgassing of mantle-derived fluids has been recognized in different European volcanic regions that last erupted thousands of years ago (e.g., Eger rift, Czech Republic; EIFEL, Germany; Carpathians, Romania; Pannonian basin; Aeschbach-Hertig et al., 1996; Ballentine et al., 1991; Bräuer et al., 2013, 2016; Kis et al., 2017, 2019; Palcsu et al., 2014; Sherwood Lollar et al., 1997; Szöcs et al., 2013). Further to the south, in Greece and Turkey, a link between fluid release (with mantle-derived components), tectonic setting, and seismicity has been demonstrated, in both volcanic and nonvolcanic areas (e.g., D’Alessandro et al., 2020; Daskalopoulou et al., 2019; De Leeuw et al., 2010; Dogan et al., 2009; Italiano et al., 2013; Mutlu et al., 2008; Rizzo et al., 2018; Shimizu et al., 2005).

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The Serbian segment of the seismically active central-western Balkan Peninsula (Marović et al., 2002) is sited at the suture zone between African (Adria) and European plate. The area is characterized by delamination and sinking of the Adria mantle lithosphere under the north-western and southern Dinarides, with hotter mantle materials filling the space left by the sinking slabs (e.g., Belinić et al., 2021). Serbia also exhibits high regional heat flow (up to 130 mW/m²) and geothermal energy potential (Doljak & Glavonjić, 2016; Horwarth et al., 2015). Previous work in the central-western Balkan Peninsula has found several natural gas manifestations and gas-rich thermal waters (e.g., Burić et al., 2016; Rosca et al., 2016; Todorović et al., 2016). However, the source of these gases, and the geological/tectonic controls on their migration through the crust, remain uncharacterized.

Here, we report on the results of a geochemical survey (carried out in autumn 2019) aimed at investigating the origin (e.g., atmospheric versus crustal versus mantle-sourced) of the volatiles outgassed in Serbia. We also attempt at a better characterization of the processes that control the chemistry of the fluids during their storage in, and transit through, the crust. Our study contributes to filling a knowledge gap on the nature of fluids circulating in this sector of Europe, and helps better reconstructing the complex geodynamic of the area.

2. Geological Setting

The sector of the Vardar zone in Serbia (south eastern Europe, SEE) is part of the mega-suture stretching along the entire Balkan Peninsula (e.g., Cvetković et al., 2016). Its present-day geological setting is the result of a complex geodynamic and tectonic evolution over the last ~200 Ma (from the middle Mesozoic to the present) that progressively involved subduction, continental collision, and finally lithospheric extension (e.g., Belinić et al., 2021; Cvetković et al., 2004). The engine of the regional geodynamic evolution is the interaction between Eurasian (Europe) and Gondwana (Africa) continental plates (Cvetković et al., 2016).

More in detail, Serbia is part of the orogenic system composed by the Alpine, Carpathian, and Dinaride belts (e.g., Marović et al., 2007; Schmidt et al., 2008, 2019) and its territory can be divided into distinct tectonic units: (a) the Pannonian basin (northern part), (b) the Dinaric Alps (central-western part), (c) the Vardar zone, divided in East and West zones (the study area, Figure 1), (d) the Serbian-Macedonian Massif, a belt stretching in north-south direction into north-western Macedonia and northern Greece, (e) the Carpatho-Balkan Region (eastern part), and (f) the Dacia basin (Bazylev et al., 2009; Cvetković et al., 2004; Jelenković et al., 2008; Moores & Fairbridge, 1997).

In the study area, volcanism has recurrently insisted over the last ~200 Ma (e.g., Cvetković et al., 2016; Zelić et al., 2010), and includes alkaline magmatism during the middle to late Triassic rifting stage (Bortolotti et al., 2008), intrusive magmatic activity with calc-alkaline granitoids in the Late Jurassic-Miocene, and granitoid products in the early Eocene-late Oligocene (Pamić et al., 2002; Saric et al., 2009). Since the Oligocene, widespread volcanism occurred throughout SEE, associated to the formation of a variety of volcanic landforms. Volcanism in Serbia concentrated along an NW-SE-trending belt (Cvetković et al., 2016), with the youngest volcanic activity pulse dating 16.8-8.6 Ma (Zelić et al., 2010, and reference therein). Currently, in the region, there are widespread outcrops of volcanic rocks, ranging in composition from andesites to basanites (upper Cretaceous-middle Paleogene), shoshonites and high-K calc-alkaline series with occurrence of lamproites (Cvetković et al., 2000; Djordjević, 2005; Pamić, 1997; Prelević et al., 2005; Zelić et al., 2010).

The final stage of the regional geodynamic evolution involved an extensional phase of lithospheric thinning (Cvetković et al., 2016) that culminates in the Pannonian Basin and the Serbian-Macedonian Massif (40–50 km of lithospheric crust) and is associated to an asthenosphere up-rise (Cvetković et al., 2016; Milivojević, 1993). The heat flow distribution in the Pannonian basin is consequently high (from 50 to 130 mW/m²), and the highest values are observed in the Great Hungarian Plain, the Pannonian part of Serbia (Vojvodina) including its continuation into the Vardar zone (Horvath et al., 2015; Lenkey et al., 2002).

The region is characterized by active seismicity with earthquake magnitudes up to 6.5 and hypocenters down to 20–30-km depth (http://www.seismo.gov.rs/Seizmicnost/Katalog-zemljotresa.pdf) and this depth coincides with the regional crust-mantle boundary (Marović et al., 2007; Metois et al., 2015).
Figure 1. (a) Simplified geological sketch map of south eastern Europe with the main tectonic units (for detailed information see Cvetkovic et al. [2016]). The studied area is highlighted by the dashed ellipse on the map. Small inset at the bottom left indicates the European areas in which geochemical studies on natural degassing have been conducted (shaded yellow area); (b) geological map of Serbia with sample locations, main regional faults (red), and neotectonic faults (black). The small inset is a zoom on the area in which a sample with lowest R/Ra has been collected in correspondence to a granitoid intrusion.
3. Materials and Methods

Thirty-one bubbling gas samples were collected from north to south in the central and western sectors of Serbia (Figure 1b). The bubbling gases were sampled by using an inverted funnel that was positioned above the bubbles, so the gases flowed through a two valves glass or steel bottle to avoid air contamination. Once the bottles had been flushed with an amount of gas at least tens of times the volume of the bottles (20–30 cc) the valves were closed to trap the gases into the bottles. All chemical and isotopic analyses were carried out at the laboratories of the INGV-Palermo within 1 month from the sampling in order to prevent isotopic fractionation due to storage of gases. Water temperature and pH were measured in the field by using a portable multiparameter instrument (WTW Multi 350i), which was previously calibrated using standard solutions (Table 1). The chemical composition of the gases was analyzed by an Agilent 7890B gas chromatograph using Ar as carrier gas, and equipped with 4-m Carbosieve S II and PoraPlot-U columns. A thermal conductivity detector (TCD) was used to measure the concentrations of O\textsubscript{2} N\textsubscript{2}, and CO\textsubscript{2}, while a flame ionization detector (FID) was used for CH\textsubscript{4}. Analytical errors of the measured concentrations are always within 5%.

The $^{13}$C/$^{12}$C ratios of CO\textsubscript{2} (expressed as $^{53}$C-CO\textsubscript{2} in ‰ versus the V-PDB standard) were measured with a Finnigan Delta S mass spectrometer after purification of the gas mixture by standard procedures using cryogenic traps with precision of ±0.1‰. He isotopes were analyzed using a static vacuum mass spectrometer (GVI Helix SFT), using a double collector in order to detect $^4$He and $^4$He ion beams simultaneously (precision for isotopic ratio within ±0.5‰). The $^4$He/$^3$He ratio was determined by measuring $^3$He in an electron multiplier detector and $^4$He in an axial Faraday detector. $^3$Ne was measured with a multicolonlector Thermo-Helix MC Plus mass spectrometer. Helium isotope compositions are expressed as R/Ra, normalizing the $^4$He/$^3$He ratio of the sample against the atmospheric $^3$He/$^4$He ratio ($Ra = 1.386 \times 10^{-6}$; Ozima & Podosek, 2002). The Ar concentrations and its isotope compositions ($^{40}$Ar, $^{38}$Ar, and $^{36}$Ar) were analyzed by multicolonlector Helix MC-GVI mass spectrometer with analytical uncertainty (1σ) for single $^{40}$Ar/$^{36}$Ar measurements of <0.1‰.

4. Results

The chemical composition of the sampled gases, together with the isotopic composition of He, Ar, and C (CO\textsubscript{2}), are presented in Table 1.

On the base of their chemical compositions, the studied gases are subdivided into three different groups: CO\textsubscript{2}-dominated (CO\textsubscript{2} > 50%), N\textsubscript{2}-dominated (N\textsubscript{2} > 50%), and CH\textsubscript{4}-dominated (this includes only sample SRB31, being methane-rich: 87%) (Table 1). CO\textsubscript{2}-dominated and N\textsubscript{2}-dominated samples have CH\textsubscript{4} concentrations ranging from 0.02% to 19. Ar and O\textsubscript{2} concentrations are typically ≤1% (Table 1), and He and Ne are present in trace amounts (ppmv). The CH\textsubscript{4}-dominated sample has a CO\textsubscript{2} concentration of 0.51% and N\textsubscript{2} of 11%. Also, for this sample, the CH\textsubscript{4} and Ar concentration are very low (<1%) with He and Ne present in trace (37.3 and 0.24 ppmv). CO\textsubscript{2} and N\textsubscript{2} exhibit a negative correlation, as implied by their being the two dominant gas species (Figure 2). Only the CH\textsubscript{4}-rich sample, and two other N\textsubscript{2}-dominated samples (10.1–51.6% of N\textsubscript{2}) that are bubbling gases from hyperalkaline waters (pH from 11.6 to 12.2) depart from a pure CO\textsubscript{2}-pure N\textsubscript{2} mixing line. Gases in hyperalkaline waters have high amount of H\textsubscript{2} (85% and 34%) and very low CO\textsubscript{2} amounts (<0.15%).

The $^{13}$C/CO\textsubscript{2} values vary from −20.2‰ to −0.1‰ (Table 1). The N\textsubscript{2}-dominated gases exhibit the lowest $^{13}$C/CO\textsubscript{2} values, especially those with CO\textsubscript{2} <3% that plot in the field of biogenic CO\textsubscript{2} (Figure 3). The CO\textsubscript{2}-C isotopic compositions of bubbling gases in hyperalkaline waters also plot in the same biogenic field (Figure 3).

The He isotopic ratios, expressed as R/Ra, vary from 0.08 to 1.2 Ra, and the N\textsubscript{2}-dominated gases have the lowest He isotopic ratios (Figure 4). The $^4$He/$^3$Ne ratios mostly range from 13 to 1,300, and are much higher than the atmospheric ratio (0.318; Ozima & Podosek, 2002), indicating a low air He contribution to the sampled gases. On the contrary, the two hyperalkaline samples have $^4$He/$^3$Ne values of 0.53 and 0.59 indicating a dominant atmospheric component.
| Name          | Code | Date     | Temperature (°C) | Water O2 (%) | CO (%) | CO2 (%) | Ar/He | Ar/Ne | V-PDB δ34S (ppm) | V-PDB δ13C (ppm) | V-PDB δ18O (‰) | V-PDB δ17O (‰) | V-PDB δD (‰) | V-PDB δ37Ar (‰) | V-PDB δ38Ar (‰) |
|---------------|------|----------|------------------|--------------|--------|---------|-------|-------|------------------|-----------------|----------------|----------------|-------------|----------------|----------------|
| Vrnjačka Banja | SRB1 | 06/11/2019 | 17.4              | 3.2           | 0.4    | 0.0     | 1.0   | 0.0   | 97.6             | 98.4            | -7            | -2.6           | 4.8           | 6.5           | 15.7           |
| Vranješica     | SRB2 | 07/11/2019 | 17.3              | 3.0           | 0.3    | 0.0     | 1.0   | 0.0   | 97.1             | 97.9            | -7            | -2.6           | 4.8           | 6.5           | 15.7           |
| Vranjačka Banja | SRB3 | 08/11/2019 | 17.2              | 2.9           | 0.2    | 0.0     | 1.0   | 0.0   | 97.0             | 97.8            | -7            | -2.6           | 4.8           | 6.5           | 15.7           |
| Vranjačka Banja | SRB4 | 09/11/2019 | 17.1              | 2.8           | 0.2    | 0.0     | 1.0   | 0.0   | 96.9             | 97.7            | -7            | -2.6           | 4.8           | 6.5           | 15.7           |
| Vranjačka Banja | SRB5 | 10/11/2019 | 17.0              | 2.7           | 0.2    | 0.0     | 1.0   | 0.0   | 96.8             | 97.6            | -7            | -2.6           | 4.8           | 6.5           | 15.7           |
| Vranjačka Banja | SRB6 | 11/11/2019 | 16.9              | 2.6           | 0.2    | 0.0     | 1.0   | 0.0   | 96.7             | 97.5            | -7            | -2.6           | 4.8           | 6.5           | 15.7           |
| Vranjačka Banja | SRB7 | 12/11/2019 | 16.8              | 2.5           | 0.2    | 0.0     | 1.0   | 0.0   | 96.6             | 97.4            | -7            | -2.6           | 4.8           | 6.5           | 15.7           |

**Note:** Major elements in %, H2 in ‰ versus V-PDB. Percentage of atmosphere (Atm) and mantle calculated following Sano et al. (1985).
Figure 2. A scatter plot of $N_2$ versus $CO_2$ concentrations (in ppm) in Serbian gases. See legend for symbols of three groups of fluids in the studied area. Purple open circles that along the y axis are two samples of bubbling gases in hyperalkaline water. The light blue diamonds and the dark blue crosses depict data from some central and eastern Europe areas (Eger rift; Weinlich et al., 1999) and from the Austria/Slovenia border, Pannonian basin (Bräuer et al., 2016).

Figure 3. A scatter plot of $CO_2$ concentrations versus $CO_2$ carbon isotopic composition ($\delta^{13}C$). $N_2$-dominated gases (especially those with $CO_2 < 3\%$) exhibit the lowest $\delta^{13}C_{CO_2}$ values, falling in the field of the biogenic $CO_2$ (green bar). Gases from hyperalkaline waters also plot in the same field of biogenic $CO_2$. $CO_2$-rich samples have more positive carbon isotopic compositions, falling within the magmatic (orange) and metamorphic (blue) fields. The three colored boxes indicate the typical $\delta^{13}C$ ranges for the three different sources: green = biogenic, orange = magmatic, blue = metamorphic. Note the overlap between the two field (magmatic-metamorphic) at $\sim 4\%$ (from Holland and Gilfillan [2013]).
reflecting an atmospheric derivation. SRB12 show higher mantle He contribution like CO
(5a–5c) with mantle He contributions up to 5%. For these samples only Figure 4.
Samples from the hyperalkaline waters have the lowest 
-7-dominated samples (red squares) exhibit the 4He/20Ne ratios (expressed as R/Ra) versus Geochemistry, Geophysics, Geosystems
The European Subcontinental Lithospheric Mantle, ESCLM (Gautheron & Moreira, 2002); (b) 0.01–0.02 Ra, for pure crustal fluids dominated by radiogenic 4He produced by U and Th decay (Ballentine & Burnard, 2002); (c) 1 Ra, for air (Ozima & Podosek, 2002). 4He/20Ne ratios are >1,000 for crust and mantle and 0.318 for air respectively (Sano et al., 1985). Because of these different end-member compositions, He isotopes in natural fluids, coupled with their 4He/20Ne ratios, can be used to resolve the relative He contributions from the three sources (e.g., Caracausi & Sulli, 2019; Sano & Waki- ita, 1985; Sano et al., 1997, and references therein). Using the approach proposed in Sano et al. (1997), and assuming that all 20Ne is atmospheric, we estimate low atmospheric contributions (<3%, Table 1) for all samples, except those collected from the hyperalkaline waters, and mantle helium fractions of 1% to ~20%, with the highest fractions calculated for the CO2-dominated samples (Figure 4).

It is interesting to note that the two N2-rich samples (SRB10 and SRB11) with the lowest He isotopic signatures (R/Ra < 0.1; mantle component ~1%) have been collected nearby two large granite intrusions (see inset in Figure 1) that are characterized by high U and Th concentrations (of, respectively, 563 and 270 ppm) (Schefer et al., 2011). Hence, it is reasonable that these low He isotopic ratios reflect the high radiogenic 4He production in the U-Th-rich lithologies.

5. Discussion

He in natural fluids from tectonically active regions is typically interpreted as originating from three distinct sources: the mantle, the crust, and air (e.g., Burnard et al., 2013; O’Nions & Oxburgh, 1988; Sano et al., 1997). These three sources are characterized by distinct He isotopic signatures: (a) 6.1 ± 0.9 Ra, for the European Subcontinental Lithospheric Mantle, ESCLM (Gautheron & Moreira, 2002); (b) 0.01–0.02 Ra, for pure crustal fluids dominated by radiogenic 4He produced by U and Th decay (Ballentine & Burnard, 2002); (c) 1 Ra, for air (Ozima & Podosek, 2002). 4He/20Ne ratios are >1,000 for crust and mantle and 0.318 for air respectively (Sano et al., 1985). Because of these different end-member compositions, He isotopes in natural fluids, coupled with their 4He/20Ne ratios, can be used to resolve the relative He contributions from the three sources (e.g., Caracausi & Sulli, 2019; Sano & Wak- ita, 1985; Sano et al., 1997, and references therein). Using the approach proposed in Sano et al. (1997), and assuming that all 20Ne is atmospheric, we estimate low atmospheric contributions (<3%, Table 1) for all samples, except those collected from the hyperalkaline waters, and mantle helium fractions of 1% to ~20%, with the highest fractions calculated for the CO2-dominated samples (Figure 4).

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5.1. Insights From CO2/3He Ratios

Additional insights into volatile sources and sinks, and into the processes occurring during (a) the migration of fluids through the crust and (b) their storage in shallow crustal layers can be derived from a joint analysis and interpretation of He and carbon isotopic signatures (e.g., Barry et al., 2020; Holland & Gilfillan, 2013). Our study highlights that natural gases in the Vardar zone of Serbia are dominated by either CO2 or N2 (Figure 2) and are characterized by a significant spread of δ13C compositions (Figure 3) and R/Ra ratios (Figure 4) that could reflect a multiplicity of gas sources involved. 3He in natural fluids is mainly primordial and sourced from the mantle. Thus, combining CO2 and 3He (into the CO2/3He ratio) allows evaluating enrichments or depletions relative to a mantle-like signature (Figure 5).

However, in continental environments, the lithospheric mantle often brings record of heterogeneities caused by metasomatizing events (Rizzo et al., 2018) that can lead to C enrichment (CO2/3He ratio of 7 × 105) with respect to the MORB (1.5–2 × 106; Marty et al., 2020). The European Subcontinental Lithospheric Mantle (ESCLM) is thought to be also isotopically heavier than the MORB (δ13C of MORB from −8‰ to −4‰; Bräuer et al., 2016; Rizzo et al., 2018, and references therein), so that we assume here a CO2/3He ratio of 2–7 × 109 and δ13C of −3.5‰ (Bräuer et al., 2016) for the local mantle source.

Our CO2-rich and N2-rich fluids are characterized by distinct CO2/3He ratios that are, respectively, higher (up to 5.25 × 1011) and lower (as low as 5.89 × 109) than the above defined mantle range (Figure 5). In tane- dem with gas samples from nearby regions (Eger rift, Weinlich et al., 1999; Austria/Slovenia border region, Pannonian basin; Bräuer et al., 2016), our samples identify a continuous trend from (a) a CO2-rich, high CO2/3He ratio end-member, and (b) a 4He/20Ne-rich, low CO2/3He ratio end-member (Figures 5a–5c). The high CO2/3He ratios (1012–1014) of most CO2-rich crustal continental gases are commonly interpreted (Sano & Marty, 1995; Sherwood Lollar et al., 1997) to result from decarbonation reaction and biological processes in the crust that produce a CO2-rich, 3He-free gas. We thus propose that the CO2-dominated gases are mix-
areas follow the same trend (dark blue crosses, Bräuer et al., Figure 5. CO₂/³He concentrations. The panel shows a trend from CO₂-rich, high CO₂/³He (low in He and Ne) samples to He-Ne-rich, low CO₂/³He ratio samples. The SCLM range is given by the shaded area (CO₂/³He = 2–7 × 10⁻⁹; Bräuer et al., 2016; Marty et al., 2020). Data for other central and eastern Europe areas follow the same trend (dark blue crosses, Bräuer et al., 2016; light blue diamonds, Weinlich et al., 1999).

The SCLM range is given by the shaded area (CO₂/³He = 2–7 × 10⁻⁹; Marty et al., 2016; Rizzo et al., 2018), limestone (CO₂/³He = 10⁻¹³, δ¹³C = 0‰), and sediment (CO₂/³He = 10⁻¹⁰, δ¹³C = −30‰) after Sano and Marty (1995). Interpreting the N₂-dominated samples is less straightforward. However, except for sample SRB12, He in all the investigated N₂-dominated gases is minimally contributed by the mantle (<5%; Figure 4) and by atmosphere (Figure 5). Furthermore, these samples exhibit the highest ⁴He and ²⁰Ne contents (Figures 5b and 5c), and the lowest CO₂/³He ratios and He isotopic signatures (Figure 6). Although there is no a priori reason to expect a correlation between ⁴He and ²⁰Ne with the CO₂/³He ratio, such a correlation has been found regionally in natural gases (Ballentine et al., 2002; Gilfillan et al., 2009). ⁴He is constantly produced in the subsurface by the radiogenic decay of U, Th, while ²⁰Ne enters subsurface groundwater systems as a component of air-saturated meteoric water (Ballentine & Sherwood Lollar, 2002). This atmospheric component can then be transferred to natural fluids in crustal layers, interacting with the groundwater that are able to trap the air component together with large amount of radiogenic volatiles (e.g., ⁴He) produced over time into the crust and degassing through it (e.g., Ballentine et al., 2002). Previous studies indicated that such correlations are the result of ⁴He accumulating in the groundwater which also contains atmospheric-derived ²⁰Ne, and subsequent quantitative partitioning of both ⁴He and ²⁰Ne into the gas phase due to fractionation events, probably in the groundwater (e.g., Gilfillan et al., 2008). It is worth noting that gases from gas-fields from central and eastern Europe (e.g., Eger rift, Austria/Slovenia border region, Pannonian basin) fit with similar CO₂:N₂-He concentration arrays (e.g., Bräuer et al., 2016; Weinlich et al., 1999), supporting the recurrence of solubility-dependent volatile fractionation.

The low CO₂ concentrations and low CO₂/³He ratios in the N₂-dominated gases (Figures 4–6), combined with their more negative δ¹³C-compositions (Figure 7), imply some mechanism of CO₂ removal during gas-water-rock interactions. During their migration through the crust, volatiles can interact with groundwater and, due to its high solubility, CO₂ dissolves preferentially in water relative to He (in the range of temperature up to 90 °C: CO₂ solubility > He solubility; Ballentine et al., 2002; Clever et al., 1979; Gilfillan et al., 2009; Scharlin et al., 1996). Furthermore, groundwater can also precipitate carbonate minerals, additionally modifying the dissolved carbonate equilibria (Barry et al., 2020; Gilfillan et al., 2009). In both cases, CO₂ is retained either in form of carbonate minerals (mineral trapping) or dissolved in solution (solubility trapping) (e.g., Baines et al., 2004; Bradshaw et al., 2005) leading to decreased CO₂/³He ratios and more negative δ¹³C in the residual gases.
In order to interpret the variability of $\text{CO}_2^{13}\text{He}$ ratios coupled to that of $\delta^{13}\text{C}$ that we recognized in the Vardar zone samples, we investigate the processes of $\text{CO}_2$ partial dissolution in water, and calcite precipitation, by modeling (see Gillfillan et al., 2009) their potential control on $\text{CO}_2^{13}\text{He}$ ratios and $\text{CO}_2$ carbon isotopic compositions ($\delta^{13}\text{C}$) (Figure 7). According to Gillfillan et al. (2009), the process can be modeled as (a) an open-system degassing (Rayleigh type) at isotopic equilibrium (between phases) and (b) calcite precipitation (Figure 7). We model the progressive variation of the $\text{CO}_2^{13}\text{He}$ ratio in the residual gas assuming that the $\text{CO}_2^{13}\text{He}$ ratio and the $\delta^{13}\text{C}_{\text{CO}_2}$ of the pristine gas are of mantle-type ($\text{CO}_2^{13}\text{He}$ range = $2–7 \times 10^{-4}$; $\delta^{13}\text{C} = −3.5\%$; Bräuer et al., 2016; Marty et al., 2020; Rizzo et al., 2018). We stress that here we consider the case of a pristine gas as the mantle end-member, but the choice of a different end-member, resulting from the mixing between crustal (limestone + organic-biogenic) and mantle-derived fluids, would lead to similar (but shifted) model curves.

Our model curves, obtained over a range of pH values for increasing extents of gas dissolution, are plotted in Figure 7. Overall, we find the model $\text{CO}_2$ dissolution lines at pH between 5.6 and 7 fit the data set nicely. This comparison demonstrates the $N_c$-dominated samples can be interpreted as due to different degrees of $\text{CO}_2$ loss by dissolution, from about 50% (for samples SRB 14, SRB 25, SRB 26) to about 99% for more fractionated samples. These gas/water fractionations ultimately result in $^{13}\text{C}$-depleted compositions and $\text{CO}_2^{13}\text{He}$ spanning over 3 orders of magnitude.

We caution that, for a thick crustal sector with a potentially high number of stratified aquifer such as in Serbia, a simple open-system degassing (Rayleigh type) model approach is evidently a simplified approach. In fact, it is possible that more complex gas-aquifer interactions, such as complete gas dissolution in deep aquifer, followed by multistep degassing upon groundwater upward migration (Chiodini et al., 2011), could have taken place instead. Also, we cannot exclude the lowest $\delta^{13}\text{C}_{\text{CO}_2}$ values are not at least partially reflecting a biogenic origin, and carbonate precipitation (together with $\text{CO}_2$ dissolution at a lower pH than 5.6–7; Gillfillan et al., 2009) has not taken a role. This notwithstanding, although simplified, our model clearly highlights the role played by gas-water interaction in determining the composition of Serbian gas manifestations.

### 5.2. Mantle Helium Source and Tectonic Implications

The chemistry of both $\text{CO}_2$-dominated and $N_c$-dominated gas samples unravels the active outgassing of mantle-derived volatiles (He and, to a lesser extent, $\text{CO}_2$) in Serbia. In continental areas far from any evidence of active volcanism, the possible main sources of mantle-derived volatiles are (a) reservoirs of fossil mantle-derived volatiles (e.g., Ballentine et al., 2001), (b) the presence of magmatic intrusions into the crust, and (c) the transfer of mantle He through lithospheric faults (e.g., Burnard et al., 2013; Caracausi & Sulli, 2019; Kennedy et al., 2007; Lee et al., 2019). A reservoir of fossil mantle-derived volatiles as a source of the mantle He should not be associated to a heat-excess, as presently observed at regional scale in Serbia (up to 130 mW/m²). Magmatic intrusions in the crust could in principle supply both mantle-derived heat and fluids toward the surface. However, at a regional scale, a magmatic intrusion can be considered as a localized source of both volatiles and heat. In spite of some possible long-range transport through groundwaters, the He isotopic ratio and heat flux anomaly should thus decrease upon increasing distance from the position of the source at depth. In the study area, in contrast, we recognize a fairly homogeneous and generalized outgassing of mantle-derived He (Figure 1) and high regional heat flow. Therefore, it is unlikely that isolated magmatic intrusions in the crust are involved.
Volatiles (i.e., CO$_2$, He) can reach the surface directly from the mantle through lithospheric faults (e.g., Burnard et al., 2012; Caracausi & Sulli, 2019; Lee et al., 2019), acting as a network of pathways of high permeability enhancing the transfer of deep fluids and heat through the crust. The study area is strongly affected by active tectonics as indicated by seismicity (http://www.seismo.gov.rs/Seizmicnost/Katalog-zemljotresa.pdf). All the investigated emissions are located along tectonic discontinuities, even if all of them are not in correspondence of the main regional faults (Figure 1). Hence, a system of well-connected faults with roots down to the mantle, through which the fluids and heat from the mantle can cross the crust and reach the surface, seems the most plausible mechanism to explain the combined high heat flux and regional-scale outgassing of mantle He in the study area.

In Serbia, crustal thickness progressively increases in ~260 km, from about 25 km in the north up to 35 km in the south (Horváth et al., 2015; Marovic et al., 2007). The greater thickness in the south of Serbia could lead to a higher production of He by the U and Th decay if we assume a homogeneous and constant distribution of U and Th concentrations in the crust below the study area. However, we find no geographical control on He isotopic signature, and a large He isotope variability occurs sometimes over short distances (e.g., 1 order of magnitude change in only 27 km) (see Figure S1 in Supporting Information S1). Therefore, the variability of the He isotopic signature does not appear to correlate with crustal thickness. Moreover, we highlight that the lowest He isotopic signatures (SRB10 site, 0.08 Ra; SRB11 site, 0.10 Ra) have been measured in fluids that circulate in U-rich and Th-rich granitic rocks. Thus, it is reasonable that the lowest He isotopic signatures could be due to local high production of He (Figure S1 in Supporting Information S1; Section b) from granitoid lithologies.

A quantitative He flux estimate can provide insights into the transfer of volatiles through the crust. Estimates of the He flux in continental regions are mainly based on calculations of in-situ production and steady-state degassing through the continental crust, and these calculations yield a crustal 4He degassing flux of ~3.3 ± 0.5 × 10$^{20}$ atoms m$^{-2}$ s$^{-1}$ (Buttitta et al., 2020, and references therein). However, experimental work highlights that the release of volatiles from rock increases in an active stress field, which implies that He degassing through the crust can be episodic in active tectonic areas (e.g., Bräuer et al., 2016; Honda et al., 1982; Torgersen & O'Donnell, 1991). It is worthy of note that deformation and failure of rocks crack mineral grains, causing pervasive microfracturing. Consequently, the rocks can increase their porosities from 20% to as high as 400% prior to failure, opening new microfracture surfaces, and eventually causing macroscopic failure and fracture of rocks (Bräuer et al., 2016). These processes lead to a higher release of volatiles (e.g., He) previously trapped within mineral grains along fracture networks and the pore fluids transport these volatiles through the crust.

Considering that, during the transfer of mantle-derived fluids through the crust, the addition of crustal radiogenic He produces a decrease of the pristine mantle He isotopic ratio, it is possible to assess the flux of mantle-derived He by using the approach proposed by O’Nions and Oxburgh (1988) and making a guess for the crustal He flux range. This method is based on the assumption that, if the degassing of He occurs at steady state, then it is possible to estimate the mantle He flux from the helium isotope composition of the system. This principle is illustrated in Figure 8 that shows the dependence of R/Ra in the surface gas on mantle He flux (for a crustal He flux of 3.3 ± 0.5 × 10$^{20}$ atoms m$^{-2}$ s$^{-1}$). From this, we estimate a mantle-derived He flux in the study area of ~2.1 × 10$^6$ to ~9.0 × 10$^6$ atoms m$^{-2}$ s$^{-1}$, up to 2 orders of magnitude higher than normally found in stable continental areas (<<10$^6$; e.g., O’Nions & Oxburgh, 1988).

Figure 7. Plot of δ$^{13}$C$_{(CO_2)}$ versus CO$_2$/He. The predicted model lines for Rayleigh-type gas dissolution at different pHs are shown as broken lines, while the solid lines are the predicted trend for carbonate mineral precipitation. Changes in δ$^{13}$C$_{(CO_2)}$ are calculated following the method from Gillfillan et al. (2009) using the Rayleigh fractionation equation either for precipitation or for dissolution. In the case of precipitation there is zero He loss from the CO$_2$ phase and CO$_2$/He changes in proportion to the fraction of the remaining CO$_2$ phase while for CO$_2$ dissolution, the change in CO$_2$/He ratio is calculated following the Rayleigh equation.

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However, in active tectonic regions an enhanced release of He from rocks occurs that is up to $10^4$ times higher the steady-state values. Therefore, assuming a $^4$He crustal flux of $10^{-10^4}$ times the average "steady-state" value, the mantle He fluxes increase to between $10^{11}$ and $10^{14}$ atoms m$^{-2}$ s$^{-1}$ (Figure 8). These are typical He fluxes encountered in active tectonic regions and/or in volcanic systems (Figure 9; Torgersen, 2010).

Active fault zones are regions of advanced permeability that permit a fast transfer of volatiles through the crust, and seismicity is a strong evidence of the capacity of faults to transfer fluids through the crust. However, the mechanisms that control the migration of fluids in the deep crust (e.g., ductile layers) are still not well recognized (e.g., Caracausi & Sulli, 2019; Kulogoski et al., 2005). In active tectonic regions, fluids can move via developing fault-fracture meshes with a mechanism analogous to the fault valve model that drives flow by fluid over-pressurization and stress switching (compression to extension) (Newell et al., 2015; Sibson, 2013, 2020), or by creep cavitation that can establish a dynamic granular fluid pump in ductile shear zones (i.e., Fusseis et al., 2009). Therefore, considering: (a) that the study area is affected by extensional tectonics and active seismicity down to the crust-mantle boundary (Faccenna et al., 2014; Marović et al., 2007; Metois et al., 2015); (b) the high regional heat flow (up to 130 mW/m$^2$) due to the up-rise of the asthenosphere up to 50–60-km depth at regional scale (Horváth et al., 2015), (c) the presence of inherited lithospheric tectonic discontinuities that allowed the up-rise of magmas since the Jurassic (Zelić et al., 2010), and that can still work today as pathways for the transfer of deep volatiles through the crust, (d) the computed high fluxes of mantled derived He, we conclude that the mantle below Serbia is the most obvious source of the surface-released heat and fluids.

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**Figure 8.** Helium isotope composition versus the flux of mantle-derived He. The lines are computed by using the approach proposed by O’Nions and Oxburgh (1988) that is based on the progressive addition (as a mixing) of a crustal He component that dilute the mantle He component producing a decrease of the He isotopic signature from the typical mantle-derived component ($6.1$ Ra; Gautheron & Moreira, 2002) to the radiogenic signature ($0.02$ Ra; Ballentine & Burnard, 2002). The solid curve refers to an average continental crust $^4$He steady-state flux of $3.3 \pm 0.5 \times 10^{10}$ atoms m$^{-2}$ s$^{-1}$ (Buttitta et al., 2020). The dotted curves refer to 10× and 100× the average continental crust steady-state He flux. The blue dotted line corresponds to minimum and dark blue dashed line to maximum R/Ra values in our samples, and are used to infer the mantle He flux range in Serbia region.
6. Conclusions

We investigated the chemical and isotopic composition of natural gas manifestations along the Serbian Vardar zone, a mega-suture zone between the Eurasia and the African plate. Gas compositions are very heterogeneous and cluster into the groups of CO\(_2\)-dominated, N\(_2\)-dominated, and CH\(_4\)-dominated gases. Based on their He isotope compositions (<1.19 Ra), the CO\(_2\)-rich samples are interpreted as mixtures of crustal CO\(_2\)-rich gas (from limestones and organic matter) and mantle-derived components. The latter accounts for up to 20% of He (Figure 10). N\(_2\)-dominated samples are more atmospheric/crustal in nature (mantle He, <5%), and are inferred to have experienced extensive chemical and isotopic fractionations during water-rock interactions in shallow crustal layers (Figure 10).

We estimate a mantle-derived He flux of \(\sim 2.1 \times 10^8\) to \(\sim 9.0 \times 10^8\) atoms m\(^{-2}\) s\(^{-1}\), or 2 orders of magnitude higher than normally found in stable continental areas. This elevated transport of mantle-derived volatiles in the Serbian crustal sector is interpreted to occur through lithospheric faults that work as regions of enhanced permeability and favor the migration of fluids thought the whole crust (Figure 10). Our study thus confirms that elevated outgassing of mantle-derived fluids can occur in tectonically active continental regions, even far from active volcanism (e.g., Caracausi & Sulli, 2019; Chiodini et al., 2004; Lee et al., 2019; Tamburello et al., 2018). Finally, we recognize that at regional scale the mantle volatiles are sourced directly from the mantle together with heat and this scenario supports the asthenosphere up-rise and delamination processes at the mantle-crust boundary recognized by recent regional geophysical investigations (Belinić et al., 2021).
Data Availability Statement

Randazzo et al. (2021, http://doi.org/10.26022/IEDA/112164).

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