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Noble gas and carbon isotope systematics at the seemingly inactive Ciomadul volcano (Eastern-Central Europe, Romania): evidence for volcanic degassing

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Key Points:

- CO_2 emissions at Ciomadul, Eastern-Central Europe, suggest a still-active plumbing system beneath the volcano in spite of long dormancy.
- The CO_2 and He isotope compositions provide evidence for significant contribution of magma-derived volatiles, up to 80%.
- Isotopic signatures of gases indicate that primary magmas could have derived from a mantle source modified by subduction-related fluids.

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Abstract

Ciomadul is the youngest volcano in the Carpathian-Pannonian Region, Eastern-Central Europe, which last erupted 30 ka. This volcano is considered to be inactive, however, combined evidence from petrologic and magnetotelluric data, as well as seismic tomography studies suggest the existence of a subvolcanic crystal mush with variable melt content. The volcanic area is characterized by high CO_2 gas output rate, with a minimum of 8.7×10^3 t yr^{-1}. We investigated 31 gas emissions at Ciomadul to constrain the origin of the volatiles. The $\delta^{13}C$-CO_2 and $^3He/^4He$ compositions suggest the outgassing of a significant component of mantle-derived fluids. The He isotope signature in the outgassing fluids (up to 3.10 R_a) is lower than the values in the peridotite xenoliths of the nearby alkaline basalt volcanic field (R/R_a 5.95Ra±0.01) which are representative of a continental lithospheric mantle and significantly lower than MORB values.
Considering the chemical characteristics of the Ciomadul dacite, including trace element and Sr-Nd and O isotope compositions, an upper crustal contamination is less probable, whereas the primary magmas could have been derived from an enriched mantle source. The low He isotopic ratios could indicate a strongly metasomatized mantle lithosphere. This could be due to infiltration of subduction-related fluids and postmetasomatic ingrowth of radiogenic He. The metasomatic fluids are inferred to have contained subducted carbonate material resulting in a heavier carbon isotope composition ($\delta^{13}C$ is in the range of -1.4 to -4.6 ‰) and an increase of $CO_2/^3He$ ratio. Our study shows the magmatic contribution to the emitted gases.

Plain Language Summary

Determining the fluxes and composition of gases in active and dormant volcanoes could help to constrain their origin. Ciomadul is the youngest volcano of the Carpathian-Pannonian Region, Eastern-Central Europe, where the last eruption occurred 30 ka . Its eruption chronology is punctuated by long quiescence periods (even >100 kyrs) separating the active phases; therefore, the long dormancy since the last eruption (30 ka) does not unambiguously indicate inactivity. Knowing if melt-bearing magma resides in the crust is fundamental to evaluate the nature of the volcano. Isotopic compositions of helium ($^3He/^4He$) and carbon ($\delta^{13}C_{CO2}$) are important tools for the study of the origin of the gases. We show that the isotope variation of the emitted gases suggests a metasomatised lithospheric mantle origin for the primary magmas. This is consistent with a degassing deep magma body existing beneath Ciomadul and that this long-dormant volcano cannot be considered as extinct.

1. Introduction

Gas emissions are often associated with active or dormant volcanic areas and regions affected by extensional tectonics (e.g., O'Nions & Oxburgh, 1988, Oppenheimer et al., 2014). Monitoring of fluids (chemical and isotopic compositions and physical properties) in volcanic regions provides important information concerning the processes occurring at depth (e.g., Edmonds, 2008; Fischer, 2008; Christopher et al., 2010; Mazot et al., 2011; Ruzié et al., 2012; Agusto et al., 2013; Barry et al., 2013, 2014; Caliro et al., 2015; Roulleau et al., 2016; Tassi et al., 2010, 2011, 2016; Wei et al., 2016). The chemical and isotopic composition of the emitted fluids in active volcanoes is primarily controlled by magmatic processes, such as the injection of new magma into the plumbing system or degassing of deep mafic magma in the lower crust, or interaction with the volcanic hydrothermal systems, among others (e.g.,

Caracausi et al., 2003, 2013; Edmonds, 2008; Christopher et al., 2010; Paonita et al., 2012, 2016; Sano et al., 2015). Furthermore , compositional change of the fluids may also correlate with the seismicity at regional scale (e.g., Chiodini et al., 2004; Bräuer et al., 2008; 2018; Melián et al., 2012, Cardellini et al., 2017).

There has been major progress in understanding the factors controlling gas emissions in active and dormant volcanic areas during the last two decades (Aiuppa et al., 2007; Edmonds, 2008; Oppenheimer et al., 2014; Lee et al., 2016; Moussallam et al., 2018); however, much less attention has been given to seemingly inactive volcanic areas (Roulleau et al., 2015). These are volcanoes that last erupted more than 10 ka and at the surface there are no signs of reawakening. The Tatun volcanic complex in Taiwan is an example of such a volcanic system. Although the last eruption occurred 20 ka , geophysical data indicates a still-active magma storage. The composition of emitted gases is consistent with this interpretation, as they contain significant magmatic components (Roulleau et al., 2015). The importance and the potential hazard of such volcanoes are shown by the case of the Ontake volcano in Japan. There were no proven records of historical and even Holocene eruptions before the phreatic eruptive event in 1979 and therefore, there were no detailed studies and monitoring on this volcano. In 2014, another phreatic eruption occurred, causing serious fatalities (Kato et al., 2015) and pointed to the requirement to better understand such long-dormant volcanoes. Sano et al., (2015) demonstrated that regular monitoring of volcanic gases is fundamental to understand the behaviour of these apparently inactive volcanoes. In this regard, detection of a magmatic chamber containing some melt fraction could mean the potential for reactivation even after several tens of kyrs dormancy. Emission of gases with isotopic signatures in the range of magmatic values can be evidence of magma intrusions at depth (Farrar et al., 1995; Sorey et al., 1998; Pizzino et al., 2002; Carapezza et al., 2003, 2012; Carapezza & Tarchini, 2007; Bräuer et al., 2008; 2018; Caracausi et al., 2013, 2015; Fischer et al., 2014; Rouwet et al., 2014, 2017; Sano et al., 2015), in addition to recognition of geophysical anomalies reflecting melt pockets at depth (Comeau et al., 2015; 2016; Harangi et al., 2015a).

Ciomadul is the youngest volcano within the Carpathian-Pannonian Region, Eastern-Central Europe, where the last eruption occurred 30 ka (Harangi et al., 2010; 2015b; Molnár et al., 2019). Thus, it is usually considered as an inactive volcano. In spite of its long dormancy, combined evidence from petrologic and magnetotelluric data (Kiss et al., 2014; Harangi et al., 2015a), as well as seismic tomography (Popa et al., 2012) suggest the presence of a melt-bearing crystal mush beneath the volcano. This is consistent with the local high heat flow (85-120 mW/m^2) compared to the Carpathian Range where this value decreases to 40-60 mW/m^2 (Demetrescu & Andreescu, 1994, Horváth et al., 2006), the high flux of carbon-dioxide of 8.7×10^3 t yr^{-1} (Kis et al., 2017) the presence of mineral and thermal waters up to 78°C (Jánosi, 1980; Rădulescu et al., 1981) and the geodynamically active region (Wenzel et al., 1999; Ismail-Zadeh et al., 2012). The eruption chronology of the Ciomadul lava dome field (Molnár et al., 2018) is characterized by prolonged quiescence periods between the active phases, often exceeding 100 kyrs.

There are a number of sites at Ciomadul, where significant amount of CO_2 gases are emitted (Kis et al., 2017). Althaus et al. (2000),Vaselli et al. (2002), Frunzeti (2013) and Sarbu et al (2018) studied the composition of gases collected from a few locations and concluded that they could indicate a deep-seated magma body below the volcano. Here, we present a comprehensive helium isotope signature (hereafter $^3He/^4He$) and carbon isotope (hereafter $\delta^{13}C_{CO2}$) systematics of the volatile degassing from Ciomadul based on a detailed sampling of all the main known locations of gas emissions to constrain the origin of fluids and to characterize the nature of a seemingly inactive volcano.

2. Geological setting

2.1. Ciomadul Volcanic Dome Field

Ciomadul volcano is located at the southeastern edge of the Carpathian-Pannonian Region, at the southern end of the Călimani-Gurghiu-Harghita volcanic chain (Szakács et al, 1993, Szakács & Seghedi, 1995; Pécskay et al., 2006; **Figure 1**). It is part of a post-collisional volcanic belt, which comprises a series of andesitic to dacitic volcanoes, developed parallel with the Carpathian orogeny. The volcanism occurred well after the continent-continent collision between the Tisza-Dacia microplate and the western margin of the Eurasian plate (Csontos et al., 1992; Matenco and Bertotti 2000, Cloetingh et al, 2004; Seghedi et al., 2004; 2005; 2011; Matenco et al, 2007). Ciomadul is part of a lava dome field and this central volcanic complex involves 8-14 $km^3$of high-K dacitic lavas (Karátson & Timár, 2005, Szakács et al, 2015; Molnár et al., 2019). The volcano developed on the Early Cretaceous clastic flysch sedimentary unit of the Eastern Carpathians that forms several nappes. It consists of binary alternation of sandstones, calcareous sandstones, limestones and clays/marls from the Sinaia Formation of the Ceahlau nappe and the Bodoc flysch (Băncilă, 1958; Ianovici & Radulescu, 1968; Nicolăescu, 1973; Grasu et al., 1996).The flysch unit has a thickness up to 2500 m.

The Ciomadul volcanic complex is made up by amalgamation of several lava domes truncated by two explosion craters called Mohos and Saint Anna (Szakács et al., 2015). This central volcano is surrounded by further isolated lava domes (Baba Laposa, Haramul Mic, Dealul Mare, Büdös-Puturosul and Bálványos; Molnár et al., 2018, **Figure 2**). Volcanism at the Ciomadul volcanic dome field started around 1 Ma, while the most voluminous Ciomadul volcanic structure has developed over the last ca. 160 kyr (Molnár et al., 2018; 2019). During the first volcanic stage, the intermittent lava dome extrusions were separated by relatively long dormant periods even exceeding 100 kyr. The second volcanic stage was characterized by initial lava dome effusion and then, after ca. 40 kyrs of quiescence, a more explosive volcanic activity occurred (from 57 to 30ka, Moriya et al, 1995, 1996; Vinkler et al, 2007; Harangi et al., 2010, 2015b; Karátson et al., 2016; Molnár et al., 2018; 2019). This stage involved lava-dome collapse events, vulcanian and sub-plinian to plinian explosive eruptions (Vinkler et al, 2007; Harangi et al., 2015b; Karátson et al., 2016). The eruptive products are relatively homogeneous K-rich dacites (Szakács and Seghedi, 1987; Szakács et al., 1993; Vinkler et al., 2007; Molnár et al., 2018; 2019). Petrogenetic and thermobarometric studies on amphiboles as well as combined U-Th/He and U/Th zircon dating suggest the presence of a long-lasting (up to 350 kyrs) crystal mush body in the crust. This appears to be mostly at relatively low-temperature just above the solidus (700-750°C) and is periodically partly remobilized by injections of fresh basaltic magmas that could rapidly trigger volcanic eruptions (Kiss et al., 2014; Harangi et al., 2015a; 2015b).

The Ciomadul volcano is located near (~50 km) the Vrancea seismic region (Wenzel et al., 1999; Ismail-Zadeh et al., 2012) located at the arc bend between the Eastern and the Southern Carpathians. Frequently occurring earthquakes have deep hypocentres (70-170 km) delineating a narrow, vertical region. This is consistent with a high-velocity seismic anomaly interpreted as a cold lithosphere slab descending slowly into the asthenospheric mantle (Wortel & Spakman, 2000). Further crustal and subcrustal earthquakes (M<4) occur occasionally around the Perșani basalt volcanic field and the Ciomadul volcano (Popa et al., 2012). The seismic tomographic model indicates a vertically-extended low-velocity anomaly beneath Ciomadul. This can be interpreted as trans-crustal magma storage with an upper melt-dominated magma chamber (Popa et al., 2012). The seismic tomographic model is supported by the result of combined petrologic and magnetotelluric studies which

demonstrated the existence of a low-resistivity anomaly and the depth of 5-20 km beneath the volcanic centers of Ciomadul, inferred to be a melt-bearing crystal mush (Harangi et al., 2015a). In addition, a deeper low-resistivity anomaly was also detected at a depth of 30-40 km, possibly related to a deeper magma accumulation zone at the crust-mantle boundary.

Another Pleistocene monogenetic basalt volcanic field is approximately 40 km from the Ciomadul, at the southeastern part of the Carpathian–Pannonian Region (Figure 1), at the boundary between the Perşani Mts. and the Transylvanian basin (Seghedi & Szakács, 1994; Downes et al., 1995; Harangi et al., 2013; Seghedi et al., 2016). Basaltic volcanism occurred here between 1.14 Ma and 683 ka (Panaiotu et al., 2004, 2013) and formed several volcanic centers accompanied by maars, scoriacones and lava flows. The erupted basaltic magma carried significant amount of ultramafic xenoliths from the lithospheric mantle (peridotites and amphibole pyroxenites) revealing the nature of the uppermost mantle of this region (Vaselli et al., 1995; Falus et al., 2008).

2.2 Gas emissions and mineral water springs at Ciomadul volcanic area

Gas emanations in the form of bubbling pools and low-temperature (T~8-10°C) dry mofettes are characteristic of the Ciomadul volcano. CO_2-bubbling peat bogs can be also found, mainly at the north-eastern (Buffogó peat bog) and southern parts of the Puturosul Mts. (Zsombor-Valley, Jánosi et al., 2011). The minimum total CO_2 flux was estimated to be 8.7×10^3 t yr^{-1} (Kis et al., 2017). The aquifers of this area are represented by CO_2-rich sparkling mineral water, with temperature up to 22.5 °C (Berszán et al., 2009; Jánosi et al., 2011; Italiano et al., 2017).

3. Sampling and analytical methods

A total of 31sites were selected for this study , including bubbling pools, dry gas emissions (mofettes) and one drilling (**Figure 2 and Table 1**). We collected fluids during two field campaigns carried out in the spring and autumn of 2016 respectively. In the 1st field campaign, gas samples were collected for $\delta^{13}C$-CO_2 and $^3He/^4He$ composition in 1l evacuated Pyrex glass tubes with a vacuum stop-cock, while for chemical composition, gas samples were collected in 150 ml glass tubes with two vacuum stop-cocks. Chemical compositions were analyzed at the Istituto Nazionale di Geofisica e Vulcanologia, Rome, Italy, whereas chemical and isotopic composition of water, noble gas compositions (He, Ne) and $\delta^{13}C$-CO_2 of gas samples were measured at the Isotope Climatology and Environmental Research Centre (ICER), Institute for Nuclear Research, Hungarian Academy of Sciences, Debrecen, Hungary. During the 2nd field campaign, the samples were collected in glass and steel samplers equipped with two valves. These samples were analyzed for their elemental composition (He, Ne, Ar, H_2, O_2, N_2, CO, CH_4 and CO_2), $\delta^{13}C$ (CO_2), $^3He/^4He$ ratios and, ^{20}Ne abundances at the Istituto Nazionale di Geofisica e Vulcanologia, Palermo, Italy.

We also separated clinopyroxene mineral grains (> 3 g in weight) from one of the lherzolite xenoliths collected at the foot of the Gruiu scoria cone, in the Perşani volcanic field. The noble gas composition of the fluid inclusions were analysed at Istituto Nazionale di Geofisica e Vulcanologia, Palermo, Italy.

3.1 Chemical and isotopic composition of gases

The chemical composition of the samples from the 1st campaign was analysed with a Portable Varian CP4900 Micro Gas Chromatograph. This Micro GC is configured for the analysis of He, Ne, H_2, O_2, N_2 by means of a molecular sieve 5A (20 meter unheated) column and CO_2, CH_4 and H_2S by means of a PoraPlot (PPQ 10 meter heated) column. The instrument is equipped with a micro thermal conductivity detector (TCD) responding to the difference in thermal conductivity between the carrier gas (argon) and the sample composition. The detection limit is 1 ppm, operating range is from 1 ppm to 100% level concentrations, and repeatability is < 0.5% RSD in peak area at constant temperature and pressure.

For the analysis of $\delta^{13}C_{CO2}$, carbon dioxide was cryogenically removed from the gas samples by liquid nitrogen and measured by Thermo Finnigan Delta ^{PLUS} XP isotope ratio mass spectrometer. Isotope ratios are given in the standard δ notation in permil (‰) versus VPDB. Errors for $\delta^{13}C$ are 0.5‰.

Noble gas isotopic ratios ($^3He/^4He$ and $^4He/^{20}Ne$) were measured from each gas sample that was inserted into the preparation line of the VG5400 noble gas mass spectrometer. The argon and the other chemically active gases (N_2, CO_2 etc.) were separated in a cryogenic cold system consisting of two cold traps and were adsorbed in an empty trap at 25K. The Ne and He were adsorbed in a charcoal trap at 10K. He was desorbed at 42K and neon at 90K and measured sequentially. The measurement procedure was calibrated with known air aliquots. The analytical uncertainties are 1% for He concentrations and 5% for Ne concentrations and 2.5% for $^3He/^4He$. $^3He/^4He$ ratio is expressed as R/Ra (being Ra the He isotope ratio of air and equal to $1.384 \cdot 10^{-6}$. He isotopic composition was corrected for the atmospheric He contamination (R/R_{ac}) considering the $^4He/^{20}Ne$ ratio; $R/R_{ac} = [R/R_a*(X-1)]/(X-1)$ where X is the air-normalized $^4He/^{20}Ne$ ratio taken as 0.318 (Sano & Wakita, 1985).

For the samples of the second analysis campaign, the chemical and isotopic composition of He-Ne and $^{13}C_{CO2}$ was determined in the laboratories of INGV-Palermo.

The concentrations of CO_2, CH_4, O_2 and N_2 were analysed using an Agilent 7890B gas chromatograph with Ar as carrier and equipped with a 4-m Carbosieve S II and PoraPlot–U columns. A TCD detector was used to measure the concentrations of He, O_2, N_2 and CO_2 and a FID detector for CO and CH_4. The analytical errors were 10% for He and 5% for O_2, N_2, CO, CH_4 and CO_2. More details on the analytical procedures used during this analysis are given in Liotta & Martelli (2012).

The carbon isotopic composition of CO_2 ($\delta^{13}C_{CO2}$) was determined using a Thermo Delta XP IRMS equipped with a Thermo Scientific™ TRACE™ Ultra Gas Chromatograph, and a 30 m Q-plot column (i.e. of 0.32 mm). The resulting $\delta^{13}C_{CO2}$ values are expressed in ‰ with respect to the international V-PDB (Vienna Pee Dee Belemnite) standard and analytical uncertainties are ±0.15‰. The method for the $\delta^{13}C$ determination of Total Dissolved Carbon (TDC) is based on chemical and physical CO_2 stripping (Capasso et al., 2005a). Isotopic ratios were measured using a Finnigan Delta Plus Mass Spectrometer. The results are expressed in ‰ of the international V-PDB standard. The standard deviations of the $^{13}C/^{12}C$ ratios are ±0.2‰.

^3He, ^4He and ^{20}Ne and the $^4He/^{20}Ne$ ratios were determined by separately inserting He and Ne into a split flight tube mass spectrometer (GVI-Helix SFT, for He analysis) and into a multi-collector mass spectrometer (Thermo-Helix MC plus, for Ne analysis), after standard purification procedures (Rizzo et al., 2015). The analytical reproducibility was <0.1% for ^4He and ^{20}Ne. However, the estimation of He and Ne concentration agrees within 10% uncertainty respect to GC measurements. In this study, the time from sampling to analysis was lower than

two weeks and results are fully reliable. The analytical error for He and Ne concentration measurements is generally below 0.3%.

3.2 Noble gas isotope data for the Perşani clinopyroxene

The chosen xenolith is a fresh spinel lherzolite with about 12% clinopyroxene content. Here, we performed new noble gas analyses. The preparation, single-step crushing and analysis of fluid inclusions was the same as described by Correale et al. (2012) and references therein. Helium (^{3}He and ^{4}He) isotopes were measured separately by two different split-flight-tube mass spectrometers (Helix SFT-Thermo). The analytical uncertainty of the determination of the TGC and the He, Ne, abundances was ~10%. Error in the ^{3}He/^{4}He ratios is reported at the 1σ level.

4. Results

The site, sample names and geographical locations with their GPS coordinates (WGS84, Geographical Coordinates), source type (mofettes or bubbling pools), temperature, pH and electrical conductivity for bubbling pool samples are presented in **Table 1**, chemical and isotopic composition are listed in **Table 2 and 3**. Noble gas isotopic compositions of clinopyroxenes from mantle xenoliths are shown in **Table 4.**

4.1 Chemical and isotopic composition of gases

The CO_2 concentration in the collected gases ranges from 6.40 to 98.36%. Besides CO_2, H_2S (2.7×10^{-4} to 1.72×10^{-1} %), He (5.91×10^{-5} to 1.66×10^{-2}%), Ne (6.39×10^{-7} to 5.80×10^{-3}%), H_2 (1×10^{-5} to 2.3×10^{-1}%) CO (6×10^{-5} to 5×10^{-4}%), CH_4 (3.5×10^{-2} to 1.69%), N_2 (1.5×10^{-1} to 74.5%), and O_2 (2×10^{-3} to 18.99) are present in the gas samples. The ternary diagram CO_2/50-N_2-O_2 (**Figure 3**) shows a progressive enrichment in N_2 and O_2 of the samples, indicating a variable amount of air.

The ^{3}He/^{4}He ratios range between 0.77 to 3.10 R_a and the ^{4}He/^{20}Ne ratios from 0.36 and 1700, which show that some of the collected gases are affected by air contamination (**Table 3**). The ^{3}He/^{4}He ratios after corrections for the air contamination (R/R_{ac}) are up to 3.25. The $\delta^{13}C_{CO2}$ ranges between -1.40‰ and -17.2‰ vs. V-PDB (**Table 3**).

4.2 Noble gas ratios of fluid inclusions from Persani clinopyroxenes

Helium content in the fluid inclusions in clinopyroxenes ranged between 4.06×10^{-12} and 3.81×10^{-12} mol/g, Ne content between 2×10^{-15} and 2.74×10^{-15}mol/g, so the He/Ne ratios ranged between 1390 and 2030. The He isotopic signature in fluid inclusions was 5.95 Ra ± 0.01 (**Table 4**).

5. Discussion

5.1 Crustal assimilation vs. mantle metasomatism

Helium comes from three different sources (mantle, crust and air), which can be readily distinguished based on their characteristic isotopic ratios (Sano & Wakita, 1985). Helium

isotopes are useful tracers for detecting deep fluids and their possible origin (crust, mantle or atmosphere) (Ozima and Podosek 2002). It has been demonstrated that in the case of quiescent volcanoes, the active degassing of deep volatiles can occur for a long time after the last volcanic activity (Carapezza et al., 2007; Tassi et al., 2013; Caracausi et al., 2009 and 2015).

The last eruption in Ciomadul occurred 30 ka (Harangi et al., 2010; 2015b; Molnár et al., 2019), yet there is an intense CO_2 degassing with a minimum flux of 8.7 x 10^3 t yr^{-1} (Kis et al., 2017), which is comparable to other dormant volcanic areas such as Panarea (1.72 x 10^4 t yr^{-1}) and Roccamonfina (7.48 x 10^3 t yr^{-1}) from Italy or Jefferson (7.92 x 10^3 t yr^{-1}) from the USA.

In addition, previous investigations (Althaus et al., 2000; Vaselli et al., 2002) highlighted the outgassing of mantle-derived volatiles at Ciomadul volcano. He isotopic ratios in the fluids collected in this study are up to 3.1R_a similar to those obtained from previous studies (**Figure 4, Table 3**). These values are higher than those obtained from the surrounding areas such as in the Carpathian Foredeep and the Transylvanian Basin where He isotopic ratios are between 0.02 and 0.03R_a (Vaselli et al., 2002; Italiano et al., 2017; Baciu et al., 2017, **Figure 4**). These latter values are typical of crustal fluids dominated by ^{4}He produced by decay of U and Th (e.g., Ozima and Podosek, 2002). The higher R_a values measured at Ciomadul could imply a higher contribution of magmatic He. Nevertheless, the 3.1 R_a value is significantly lower than the MORB and SCLM value (Sano & Marty, 1995) requiring addition of radiogenic ^{4}He that decreased the pristine isotopic signature.

The mantle xenoliths of the Perşani volcanic field (ca. 40 km from the Ciomadul area) could provide the He isotopic signature of the lithospheric mantle beneath the region. The He isotopic ratios in fluid inclusions of the Persani clinopyroxenes are 5.95±0.01 (**Table 4**) and these are lower than those of of previous measurements, from 6.5 to 7.3R_a, obtained by Althaus et al. (1998), but consistent with the values of the Subcontinental Lithospheric Mantle (SCLM, $R/R_a = 6.1 \pm 0.9\ R_a$, Gautheron & Moreira, 2002). The continental crust (R/R_a=0.02, Ozima and Podosek, 2002) and atmosphere (R/R_a=1) have distinct isotopic values and $^4He/^{20}Ne$ can be used to infer how mixing between the three possible end-members can support the He isotopic signature of the fluids that outgass in the Ciomadul region (**Figure 4**). Most Ciomadul samples indicate a possible trend between air and a magmatic source, where the He ratio of the magmatic end-member (3.1R_a) is lower than that of the ECLM and the Perşani clinopyroxene. This is also supported by the trend line in the $^3He–CO_2–^4He$ ternary diagram (**Figure 5**), where the Ciomadul samples are along a trend showing variable amounts of CO_2 and R/R_{ac} values between 2 and 3. This trend reflects the dominance of radiogenic He in the fluids outgassing from the Ciomadul volcano. We have now to assess the possible processes that can add the radiogenic He component to the mantle component.

Such a relatively low He isotope ratio of the magma source is not uncommon in volcanic arc settings (e.g., Hilton et al., 1992; Allard et al., 1997; Inguaggiato et al., 1998; Martelli et al., 2004) and can be due to several processes involving the addition of radiogenically-produced ^{4}He, such as magma aging, crustal assimilation, mixing between mantle and crustal-derived fluids, among others (Torgersen et al., 1995; Kennedy et al., 2006). Unfortunately, there are no undifferentiated mantle-derived mafic rocks in the region of the Ciomadul volcano, so we cannot investigate the He isotope composition of the mantle directly below the volcano. In Ciomadul, only high-K dacitic volcanic products are found (Mason et al., 1996; Vinkler et al., 2007; Molnár et al., 2018; 2019), although occurrence of high-Mg minerals such as

olivine and clinopyroxene in the dacites suggest involvement of primitive mafic magmas in the magma evolution of Ciomadul (Vinkler et al., 2007; Kiss et al., 2014).

Magma aging and crustal assimilation are two mechanisms that could account for the addition of the radiogenic He component to the mantle-derived melts. Both these processes have been invoked to explain low He isotopic ratios (< MORB and SCLM) in different volcanic regions, worldwide, such as Aeolian Island, Italy (Mandarano et al., 2015) and Iceland (Condomines et al., 1993). The magma-aging mechanism considers an addition of ^{4}He by radiogenic decay in the magma itself. In constrast, crustal assimilation furnishes ^{4}He by interaction between magma and the whole rock. First, we investigated the likelihood that the magma aging model can interpret the low He isotopic signature in the fluids that outgas at Ciomadul volcano.

The ^{3}He/^{4}He ratio of the fluid inclusions of the Persani clinoproxene (5.95Ra ±0.01) can be assumed to represent the mantle end-member value beneath of the region. Thus, the primary magmas of Ciomadul could be also characterized by such isotope ratio. The Ciomadul dacites have U and Th concentrations of 3 and 15 ppm respectively (Vinkler et al., 2007; Molnár et al., 2018; 2019). Using these data, the magma-aging model calculation yield ^{3}He/^{4}He ratio around 4.65R_a after 30 kyr (**Figure 6**). Thus, this process alone cannot be responsible for the low He (ca. 3.1R_a) isotopic signature of the Ciomadul fluids. Furthermore, if we assume the U (1.5ppm) and Th (5.5 ppm) contents of the Persani basalts (Harangi et al., 2013), the magma-aging model is still not a viable process to provide the required ^{4}He addition and generate the low ^{3}He/^{4}He for Ciomadul gases.

The relatively low He isotopic ratio can also be explained by high-level crustal assimilation (e.g., van Soest et al., 2002), which has to also be evaluated. Assuming the U and Th amount of the typical upper crust, 2.7 and 10.5 ppm, respectively (Rudnick and Gao, 2014) and an age of 5Ma, 3% of crustal assimilation could be sufficient to achieve the observed low He isotopic ratios. The Sr-Nd-O isotope compositions of the erupted magmas sensitively reflect such a process. Mason et al. (1996) published isotopic data for three samples of the Ciomadul volcanic system. They have distinct isotopic features compared to the calc-alkaline volcanic suite of the Calimani-Gurghiu-Harghita chain. Although the Sr-Nd isotopic data could suggest an AFC process with 10-35% assimilation of flysch sediment, such a high crustal contamination is not feasible, based on the fairly low δ^{18}O values (6.3-7.1 per mil) of the phenocrysts from the dacites (Mason et al., 1996). Instead, they suggested that these isotopic characteristics could also be explained by source contamination from subduction-related fluids. In fact, the bulk-rock composition of the Ciomadul dacites has unique characteristics with high Sr, Ba (both showing typically >1000 ppm) and high K compositions and low concentrations of heavy rare-earth elements (Seghedi et al., 1987; Vinkler et al., 2007; Molnár et al., 2018; 2019). Furthermore, the high-Mg pargasitic amphiboles thought to have derived from the less differentiated magmas have also relatively high Ba content (Kiss et al., 2014). Thus, these peculiar compositional characters can be due to the nature of the magma source rather than magma differentiation processes. The elevated K, Sr and Ba contents of the assumed mantle source of the Ciomadul primary magmas can be due to metasomatism and this is in contrast what the peridotite xenoliths from the Persani volcanic field show (Vaselli et al., 1995). In fact, the He signature of the outgassed volatiles at Ciomadul resembles the values in fluids from other subduction-related volcanic systems (i.e., Italy, Greece, Indonesia; Hilton et al., 1992; Martelli et al., 2004; Shimizu et al., 2005), where the mantle source regions seem to be contaminated by crustal material which added radiogenic ^{4}He and decreased the pristine He isotopic signature (Hilton et al., 2002).

Such a small-scale spatial heterogenity of the lithospheric mantle beneath this area can be explained by the closer location of Ciomadul to the collision front, where subduction is

expected to have occurred during the Miocene up to around 11 Ma (Royden et al., 1982; Cloetingh et al. 2004; Matenco et al., 2007; Seghedi et al., 2011). Such a scenario is not unique, Martelli et al. (2004) suggested that the relatively low He isotopic ratio in the volcanic rocks of Central Italy can be explained by magma source features (i.e., contribution of radiogenic He from metasomatic, subduction-related fluids and ingrowth of ^{4}He in the lithospheric mantle). We note that the ^{87}Sr/^{86}Sr isotopic ratio of the Ciomadul dacites and the highest ^{3}He/^{4}He isotopic values of the emitted gases plot into the same trend (Figure. 5 in Martelli et al., 2004) what the Central Italian volcanic areas form.
In summary, considering the petrology of the Ciomadul volcanic products, the relatively low He isotope magmatic end-member of the Ciomadul gases can be interpreted as due to magma-source characteristics, where the radiogenic He was added via subduction-related fluids and increased radioactive ingrowth following the metasomatism. However, a mixing between mantle-derived fluids with and SCLM He isotopic signature and ^{4}He-rich crustal fluids coming from shallow crustal layers should still be further explored as a possible process responsible of the low He isotopic ratios in the Ciomadul fluids. This likelihood will be discussed in the next section.

5.2 Sources and origin of carbon-dioxide

The carbon isotopic composition of CO_2 ($\delta^{13}C_{CO2}$) from the studied fluids range between -1.40‰ and -4.61‰ vs. VPDB, consistent with previous measurements in the area (-2.77 to -4.70‰; Vaselli et al., 2002; Frunzeti, 2013; Sarbu et al., 2018). In the Pannonian Basin (central Europe), the carbon isotopic composition of CO_2 gases shows values in a narrow range between -3 to -7‰ with an average value of -5‰ V-PDB based on hundreds of measurements (Cornides, 1993; Sherwood-Lollar et al., 1997; Palcsu et al., 2014; Bräuer et al., 2016). These values are consistent with a mantle origin. In contrast, crustal-derived CO_2 is characterized by a $\delta^{13}C$ of about -25‰ in case of biogenic sedimentary source and around 0 ‰ considering thermo-metamorphism of limestone (Sano&Marty, 1995 and references therein). The Ciomadul gases overlap the range of mantle composition, even if some samples have more positive values that cannot be explained by the addition of a crustal biogenic component **(table 3 and Figures 7 and 8**). To constrain the origin of CO_2 in the fluids emitted by the Ciomadul volcano, we used the relationship between the elemental ratio $CO_2/^{3}He$ and the isotopic signature $\delta^{13}C_{CO2}$ (Sano and Marty, 1995; **Figure 7)**.
The $CO_2/^{3}He$ ratios of the Ciomadul gases are higher than 2×10^{9}, the expected mantle ratio (Marty and Jambon, 1987) and which suggests an addition of a crustal component. It is interesting that these ratios fall into the same trend as shown by volcanic and fumarolic gases measured at volcanic arcs, worldwide (Mason et al., 2017; **Figure 8a and b**). Almost all the Ciomadul samples fall close the mixing line between a mantle component and a limestone end-member suggesting that mixing of the two sources could be the main process that controls the CO_2-^{3}He systematics in these fluids. In contrast, CO_2 fluids in the Transylvanian Basin, (Baciu et al., 2007, 2017) west of the volcano have distinct character and fall closer to the mantle – organic sediment mixing line. Rayleigh-type fractionation due to gas exsolution from water is not a plausible process to produce the carbon isotopic signature and the $CO_2/^{3}He$ of the studied fluids (**Figure 7**) (Holland&Gilfilland, 2013; Roulleau et al., 2015). However, the $^{13}C_{CO2}$ values of most of the samples fall in the narrow range of -2 and -5‰, which is a typical signature for mantle-derived carbon. We obtain the same trend in the He isotopic ratios (R/R_a) vs.$^{13}C_{CO2}$ (V-PDB) plot (**Figure 8a and b),** where the Ciomadul samples clearly approach the mantle end-member and overlap the isotopic values of many other volcanic systems related to subduction areas. Remarkably the Ciomadul samples show

similarities in He-C isotopic composition with active and dormant volcanic regions (e.g., Italy and Indonesia).
The involvement of carbonatic component can be explained by mixing with fluids derived from thermometamorphic decomposition of carbonates in the flysch sedimentary pile or by mantle source contamination via subducted carbonatic material The mantle source of the Ciomadul magmas is considered to be a metasomatic lithospheric mantle based on the compositional features of the dacitic rocks. The relatively low He isotopic ratio can due to these source characteristics, whereas metasomatism was the result of slab-derived fluids during the Miocene subduction along the Eastern Carpathians followed by ingrowth of radiogenic He by radioactive decay. The Sr-Nd-O isotope data of the volcanic rocks do not support significant upper-level crustal contamination, but rather crustal component addition to the source region via slab-derived fluid metasomatism (Mason et al., 1996). The combination of He and C isotopic data suggests that this crustal component consisted of decomposed subducted carbonate material as suggested also for the volcanic rocks in Italy, although addition of fluids from carbonate decomposition at shallow crustal level cannot be unambiguously excluded.

5.3 Relationship with the deep magmatic system

Dormant volcanoes pose a particular hazard to society since there is much less awareness about a possible eruption event. However, the scientific community is giving increased attention to these volcanoes and the surrounding areas that are generally characterized by intense gas emissions (Burton et al., 2013 and references therein). Recent investigations highlighted the presence of an active plumbing system even below volcanoes which last erupted >10 kyr (e.g., Colli Albani, Italy; Trasatti et al., 2018; Uturuncu, Bolivia; Sparks et al., 2008; Comeau et al., 2015; Tatun, Taiwan; Konstantinou et al., 2007; Lin & Pu, 2016). Harangi et al. (2015a) suggested the term PAMS volcano, i.e. volcano with Potentially Active Magma Storage for these long-dormant volcanoes, which have clear implication for a subvolcanic melt-bearing magma plumbing system. Ciomadul belongs to this category, since there are a number of observations suggesting that a melt-bearing magma body could still exist beneath it (Popa et al., 2012; Szakács and Seghedi, 2013; Harangi et al., 2015a). The isotopic composition of the emitted gases coupled to the high localized heat flow in the area of the Ciomadul vocano gives additional support to this interpretation.
This involves the similarities in the isotope composition of CO_2, and He of the gases emitted at the Ciomadul with those found in other active and dormant volcanic arc systems worldwide and their proposed high magmatic component. Furthermore, the Ciomadul volcanic system is characterized by relatively high CO_2 gas fluxes (Kis et al., 2017). This is consistent with the presence of a still-degassing magma below the Ciomadul system as inferred by geophysical investigations that recognized a low-resistivity and low-velocity anomaly in the crust, below the volcano (Popa et al., 2012; Harangi et al., 2015a) as well as petrologic observations suggesting the involvement of a mafic magma in the petrogenesis of the erupted dacite (Kiss et al., 2014). The measurements of U-Th and U-Pb spot ages on zircons suggest a long-standing magma storage that could go back as far as about 350 ka (Harangi et al. 2015b; Lukács et al., 2018). Molnár et al. (2018; 2019) presented a detailed eruption chronology for the Ciomadul lava dome field involving the Ciomadul volcanic complex and emphasized that volcanic activity could be renewed even after long (>100 kyr) repose times. Several 10's kyr quiescence periods between the active phases have also been pointed out also during the evolution of the Ciomadul volcanic complex (Harangi et al., 2015b; Molnár et al., 2019). However, the zircon U-Th and U-Pb ages suggest that

crystallization was on-going also during the long quiescence periods, i.e. there was an active magma storage beneath the apparently inactive volcano This suggests a long-standing felsic upper-crustal crystal mush system underlain by a mafic hot zone in the lower crust, as has already been suggested by petrologic interpretations (Kiss et al. 2014). The diverse amphibole compositions in the dacites are consistent with a polybaric magma evolution, i.e. with transcrustal magma storage (Cashman et al., 2017; Sparks & Cashman, 2017) comprising ephemeral melt-dominated bodies, i.e. magma chambers at various depths. In addition, fluid-gas accumulation zones can also have developed within this magma storage (Christopher et al., 2015; Sparks & Cashman, 2017). Thus, a possible source of the CO_2 gases could be these fluid entrapment zones within the crystal mush during quiescent period. However, gas emission is more common around the Ciomadul volcanic complex and significantly lower within the volcano itself (Kis et al. 2017). Allard et al. (1991) and Edmonds (2008) pointed out that stronger degassing around the volcanic edifice is not uncommon in volcanic regions. An alternative source of the CO_2 gases could be mafic magma residing at deeper level, possibly at the lower crust. Indeed, the occurrence of high-Mg minerals, such as olivine, clinopyroxene and orthopyroxene in the dacites (Vinkler et al., 2007; Kiss et al., 2014) suggests that mafic magma also played an important role in the magma evolution. Harangi et al. (2015a) detected a lower crustal low resistivity anomaly, which might represent the mafic magma accumulation. Thus, we propose that most of the CO_2 gases could come directly from the presumed mafic-magma accumulation zone at the lower crust through fractures (Kis et al., 2017), whereas only limited amount of gases are derived from the mushy magma storage.

Vaselli et al. (2002) already suggested that the emitted gases in Southern Harghita could have a magmatic component. Based on our new measurements, we support this interpretation, particularly in the area of Ciomadul volcano. Assuming that a deep-seated mafic magma body can be the main source of the CO_2 gases and considering that it is characterized by relatively low $^3He/^4He$ isotope signature ($3.1R_a$) inherited by the mantle source region, we can use this value to calculate the relative magmatic component of the emitted gases (Sano & Wakita, 1985). If no interaction with crustal fluids occurred, the magmatic component in the gases could exceed even the 80%. Remarkably, we obtained such high values for the areas having a larger diffusive CO2 flux. This high magmatic He content of the gases is not unique and resembles what Trasatti et al. (2018) proposed for Colli Albani volcanic complex, another long-dormant volcanic field, where they assumed more than 80% mantle-derived component in the emitted CO_2 gases. However, the magmatic component can be lower, if interaction between the ascending gases with crustal gases occurred at shallow crustal depth, a possibility what we cannot test at this stage, but requires further studies.

Conclusions

We investigated 31 gas emissions at the Ciomadul volcano, a long-dormant PAMS volcano in eastern-central Europe, to constrain the origin of the emitted volatiles and the possible processes that modify their chemistry during the transfer of these fluids towards the surface. The carbon and helium isotopic compositions provide evidence for a significant magmatic component. Our study shows a clear magmatic component in the emitted fluids and the highest values correspond to the area characterized by the highest CO_2 flux from soil, so the high fluxes can be associated with the highest contribution of volatiles derived from a magma body.

The relatively large CO_2 gas emission and significant magmatic component of the gases are consistent with geophysical and petrologic models (Popa et al., 2012; Harangi et al., 2015a, 2015b), that a degassing magmatic intrusion could still exist beneath Ciomadul. A long-

standing silicic crystal mush body should be developed in the shallow crust, while a mafic magma accumulation zone is inferred at the lower crustal level. The magmatic gases could be derived either from a deep mafic magma and/or from the volatile accumulation zones developed in the shallow crustal felsic-crystal mush body. Petrology and geochemistry of the erupted dacitic magma imply that upper crustal contamination played no or subordinate role and the primary magmas could have derived from a mantle source contaminated by subduction-related fluids that is consistent with the He and C isotope composition of the gases emitted at Ciomadul volcano. Thus, a magma source with relatively low He isotope value (3.10 R_a), similar what was proposed for volcanic systems in central Italy and Greece seems to be viable beneath Ciomadul. This differs from the SCLM value detected at the nearby Persani volcanic field (Althaus et al. 1998; this study) and also in the Pannonian basin (Cornides, 1993; Palcsu et al., 2014; Bräuer et al., 2016) and requires a spatially-variable modified lithospheric mantle even a small scale. The isotopic composition (He and CO_2) of the emitted volatiles implies interaction of crustal gases to varying degrees, although some of them could reach the surface without major modification.

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Table 1. *List of the sites investigated including location names, geographical position (geographical coordinates in WGS84), type of manifestation (mofetta, bubbling pool, drilling), type of sample (free gas) and field data (temperature, pH and EC-expressed in µS/cm) where available.*

No.	Site	N	E	Type of manifestation	Sample type	T^0C	pH	EC (µS/cm)
1	Torjai Stinky Cave	46.1198	25.9488	mofetta	free gas	nd	nd	nd
2	Timsós cave	46.1191	25.9495	mofetta	free gas	nd	nd	nd
3	Gyilkos cave	46.1218	25.9494	mofetta	free gas	nd	nd	nd
4	Buffogó peat bog pool	46.1279	25.9504	bubbling pool	free gas	1	3	472
5	Buffogó peat bog	46.1283	25.9504	bubbling pool	free gas	nd	nd	nd
6	Várpad - Ibolya pool	46.1134	25.9600	bubbling pool	free gas	7.1	6.46	3220
7a	Bálványos mofetta	46.1118	25.9579	bubbling pool	free gas	9.7	4.99	3722
7b	Bálványos mofetta	46.1118	25.9579	bubbling pool	free gas	9.7	4.99	3722
8	Bálványos pool	46.1095	25.9590	bubbling pool	free gas	5	6.54	9360
9	Csiszárfürdő - Iker pool white	46.1063	25.9514	bubbling pool	free gas	1.2	5.12	741
10	Csiszárfürdő - Hammas pool	46.1065	25.9504	bubbling pool	free gas	3.6	5.29	2040
11	Csiszárfürdő - Timsós pool	46.1063	25.9504	bubbling pool	free gas	4.7	5.9	1274
12	Csiszárfürdő - Csokoládés pool	46.1059	25.9508	bubbling pool	free gas	2.7	4.2	837
13	Mikesfürdő - Vallató pool	46.1170	25.9281	bubbling pool	free gas	5	6.16	2300
14	Mikesfürdő - Vallató mofetta	46.1180	25.9283	mofetta	free gas	5	2.72	1620
15	Mikesfürdő - Hammas pool	46.1168	25.9340	bubbling pool	free gas	1.9	2.96	968
16	Mikesfürdő - Bükkös pool	46.1161	25.9349	bubbling pool	free gas	2.3	3.6	584
17	Apor lányok feredeje - Small pool	46.1150	25.9496	bubbling pool	free gas	4.8	1.71	3620
18	Apor lányok feredeje -spring on fault 2	46.1148	25.9496	bubbling pool	free gas	6.9	2.2	7100
19	Apor lányok feredeje - Szemvíz 4	46.1148	25.9496	bubbling pool	free gas	4.2	2.6	2080

20	Gyógyvizek	46.1133	25.9504	bubbling pool	free gas	3.7	1.85	2780
21	Bálványos Sósmező drilling 1	46.1159	25.9424	drilling	free gas	nd	nd	nd
22	Bálványos Sósmező drilling 2	46.1159	25.9424	drilling	free gas	nd	nd	nd
23	Bálványos Sósmező drilling 3	46.1159	25.9424	drilling	free gas	nd	nd	nd
24	St Anna crater rim	46.1310	25.8936	mofetta	free gas	nd	nd	nd
25	Jajdon pool	46.0701	25.9538	bubbling pool	free gas	4.6	7.3	1489
26	Jajdon mofetta	46.0699	25.9538	mofetta	free gas	nd	nd	nd
27	Băile Tuşnad mofetta	46.1421	25.8518	mofetta	free gas	nd	nd	nd
28	Lăzăreşti Nyírfürdő mofetta	46.1831	25.9520	mofetta	free gas	nd	nd	nd
29	Lăzăreşti Nyírfürdő pool	46.1831	25.9518	bubbling pool	free gas	6.6	5.96	768
30	Lăzăreşti Nyírfürdő pool 2	46.1829	25.9519	bubbling pool	free gas	nd	nd	nd
31	Ciucsângeorgiu mofetta	46.3363	25.9642	mofetta	free gas	nd	nd	nd

Note. nd=not determined.

Table 2.. *Chemical composition of the different gas samples, expressed in %.*

No.	Site	Campaign	Laboratory	H_2S	He	Ne	H_2	CO	CH_4	N_2	O_2	CO_2	Source
1	Torjai Stinky Cave	1st Campaign	Debrecen	nd	6.3 x10-4	3.5 x10-5	nd	nd	nd	nd	nd	nd	this work
	Torjai Stinky Cave		Rome	5.2x10-2	7.0 x10-4	4.0 x10-4	2.0 x10-5		8.4 x10-1	1.6 x101	4.9E+00	78.09	this work
	Torjai Stinky Cave	2nd Campaign	Palermo	1.8 x10-2	6.1 x10-4	6.4 x10-7	nd	5.0 x10-4	8.9 x10-1	1.2 x101	2.9E+00	82.68	this work
2	Timsós cave	1st Campaign	Debrecen	nd	6.9 x10-4	2.9 x10-5	nd	nd	nd	nd	nd	nd	this work
	Timsós cave		Rome	6.8 x10-2	7.0 x10-4	3.0 x10-4	3.0 x10-5		8.4 x10-1	1.2 x101	3.8E+00	83.05	this work
	Timsós cave	2nd Campaign	Palermo	nd	6.3 x10-4	4.8 x10-5	nd	1.0 x10-4	9.3 x10-1	2.1E+00	7.3 x10-2	95.24	this work
3	Gyilkos cave	1st Campaign	Debrecen	nd	5.6 x10-4	4.0 x10-4	nd	nd	nd	nd	nd	nd	this work
	Gyilkos cave		Rome	nd	6.0 x10-4	1.0 x10-3	4.0 x10-5	nd	1.1 x10-1	3.8 x101	9.5E+00	52.54	this work
4	Buffogó peat bog pool	1st Campaign	Debrecen	nd	6.7 x10-4	8.8 x10-7	nd	nd	nd	nd	nd	64.98	this work
	Buffogó peat bog pool		Rome	nd	8.0 x10-4	5.0 x10-4	4.0 x10-5	nd	9.7 x10-1	2.6 x101	7.6E+00	64.98	this work
	Buffogó peat bog pool	2nd Campaign	Palermo	5.0 x10-4	7.1 x10-4	7.9 x10-4	nd	nd	1.3E+00	1.9E+00	1.5 x10-1	95.50	this work
5	Buffogó peat bog	1st Campaign	Debrecen	nd	9.4 x10-4	2.0 x10-6	nd	nd	nd	nd	nd	nd	this work
6	Várpad - Ibolya pool	1st Campaign	Debrecen	nd	5.9 x10-5	1.4 x10-4	nd	nd	nd	nd	nd	75.97	this work
	Várpad - Ibolya pool		Rome	nd	2.0 x10-4	5.0 x10-4	2.0 x10-5	nd	2.2 x10-1	1.8 x101	5.7E+00	75.97	this work
7a	Bálványos mofetta	1st Campaign	Debrecen	nd	8.3 x10-4	1.8 x10-6	nd	nd	nd	nd	nd	nd	this work
7b	Bálványos mofetta	1st Campaign	Debrecen	nd	4.6 x10-4	1.8 x10-4	nd	nd	nd	nd	nd	94.87	this work
	Bálványos mofetta		Rome	nd	5.9 x10-3	4.1 x10-3	3.4 x10-2	nd	6.4 x10-1	3.7E+00	8.2 x10-1	94.87	this work
	Bálványos	2nd	Palermo	nd	1.0 x10-3	2.5 x10-4	1.4 x10-3	nd	1.3E+00	2.2 x101	6.1E+00	68.25	this work

	mofetta	Campaign											
8	Bálványos pool	1st Campaign	Debrecen	nd	1.7 x10-3	1.7 x10-4	nd	nd	nd	nd	nd	63.84	this work
	Bálványos pool		Rome	nd	1.7 x10-2	5.8 x10-3	2.3 x10-1	nd	1.7E+00	2.6 x101	8.4E+00	63.84	this work
9	Csiszárfürdő - Iker pool white	1st Campaign	Debrecen	nd	1.3 x10-3	1.0 x10-5	nd	nd	nd	nd	nd	nd	this work
	Csiszárfürdő - Iker pool white	2nd Campaign	Palermo	nd	9.5 x10-4	1.1 x10-5	nd	nd	1.7E+00	1.8E+00	1.7 x10-1	94.73	this work
10	Csiszárfürdő - Hammas pool	1st Campaign	Debrecen	nd	1.1 x10-3	6.4 x10-7	nd	nd	nd	nd	nd	96.72	this work
			Rome	1.1 x10-1	1.0 x10-2	2.3 x10-3	9.0 x10-4	nd	1.2E+00	9.8 x10-1	3.5 x10-1	96.72	this work
	Csiszárfürdő - Hammas pool	2nd Campaign	Palermo	nd	6.9 x10-4	5.5 x10-6	nd	nd	1.2E+00	8.8 x10-1	3.0 x10-2	94.81	this work
11	Csiszárfürdő - Timsós pool	1st Campaign	Debrecen	nd	1.1 x10-3	1.2 x10-3	nd	nd	nd	nd	nd	11.23	this work
	Csiszárfürdő - Timsós pool		Rome	nd	6.0 x10-4	1.0 x10-3	4.0 x10-5	nd	1.7 x10-1	7.0 x101	1.9 x101	11.23	this work
12	Csiszárfürdő - Csokoládés pool	1st Campaign	Debrecen	nd	9.4 x10-4	7.8 x10-4	nd	nd	nd	nd	nd	89.49	this work
	Csiszárfürdő - Csokoládés pool		Rome	1.7 x10-2	1.3 x10-2	4.6 x10-3	2.3 x10-3	nd	1.5E+00	7.4	1.6E+00	89.49	this work
	Csiszárfürdő - Csokoládés pool	2nd Campaign	Palermo	nd	8.7 x10-4	1.6 x10-5	nd	9.0 x10-5	1.5E+00	1.5E+00	1.4 x10-1	94.51	this work
13	Mikesfürdő - Vallató pool	1st Campaign	Debrecen	nd	4.5 x10-4	8.5 x10-6	nd	nd	nd	nd	nd	41.34	this work
	Mikesfürdő - Vallató pool		Rome	nd	5.9 x10-3	nd	6.0 x10-4	nd	5.5E-01	4.6 x101	1.3 x101	41.34	this work
	Mikesfürdő - Vallató pool	2nd Campaign	Palermo	nd	4.3 x10-4	1.4 x10-5	nd	nd	1.2E+00	1.8E+00	1.8 x10-1	93.95	this work
14	Mikesfürdő - Vallató mofetta	1st Campaign	Debrecen	nd	3.0 x10-4	4.0 x10-5	nd	nd	nd	nd	nd	91.86	this work
	Mikesfürdő - Vallató mofetta		Rome	2.7 x10-2	3.0 x10-4	2.0 x10-4	1.0 x10-5	nd	9.6 x10-1	5.2E+00	1.9E+00	91.86	this work
15	Mikesfürdő - Hammas pool	1st Campaign	Debrecen	nd	7.2 x10-4	2.7 x10-6	nd	nd	nd	nd	nd	87.67	this work
	Mikesfürdő - Hammas pool		Rome	nd	7.0 x10-4	2.0 x10-4	4.0 x10-5	nd	9.9 x10-1	8.5E+00	2.9E+00	87.67	this work

	Mikesfürdő - Hammas pool	2nd Campaign	Palermo	nd	5.9 x10-4	7.9 x10-6	nd	nd	1.1E+00	1.1E+00	2.0 x10-3	94.83	this work
16	Mikesfürdő - Bükkös pool	1st Campaign	Debrecen	nd	8.0 x10-4	6.7 x10-4	nd	nd	nd	nd	nd	82.58	this work
	Mikesfürdő - Bükkös pool		Rome	nd	7.0 x10-4	4.0 x10-4	2.0 x10-5	nd	9.0 x10-1	1.3 x101	4.0E+00	82.58	this work
	Mikesfürdő - Bükkös pool	2nd Campaign	Palermo	nd	7.7 x10-4	3.9 x10-4	nd	1.0 x10-4	1.1E+00	9.9E+00	2.4E+00	84.33	this work
17	Apor lányok feredeje - Small pool	1st Campaign	Debrecen	nd	1.2 x10-3	5.0 x10-6	nd	nd	nd	nd	nd	58.09	this work
	Apor lányok feredeje - Small pool		Rome	nd	8.0 x10-4	7.0 x10-4	3.0 x10-5	nd	7.7 x10-1	3.2 x101	9.4E+00	58.09	this work
17	Apor lányok feredeje - Small pool	2nd Campaign	Palermo	2.7 x10-4	8.3 x10-4	6.5 x10-5	nd	9.0 x10-5	1.2E+00	1.1E+00	2.8 x10-3	97.15	this work
18	Apor lányok feredeje -spring on fault 2	1st Campaign	Debrecen	nd	7.8 x10-4	6.6 x10-5	nd	nd	nd	nd	nd	98.36	this work
	Apor lányok feredeje -spring on fault 2		Rome	1.7 x10-1	9.7 x10-3	2.2 x10-3	3.2 x10-3	nd	1.2E+00	1.5 x10-1	1.2 x10-1	98.36	this work
	Apor lányok feredeje -spring on fault 2	2nd Campaign	Palermo	3.5 x10-4	6.5 x10-4	7.8 x10-7	nd	nd	1.2E+00	8.6 x10-1	nd	96.38	this work
19	Apor lányok feredeje - Szemvíz 4	1st Campaign	Debrecen	nd	1.2 x10-3	2.8 x10-6	nd	nd	nd	nd	nd	36.24	this work
	Apor lányok feredeje - Szemvíz 4		Rome	2.0 x10-2	7.0 x10-4	1.0 x10-3	2.0 x10-4	nd	4.4 x10-1	5.0E+01	1.4 x101	36.24	this work
	Apor lányok feredeje - Szemvíz 4	2nd Campaign	Palermo	nd	nd	nd	nd	6.0 x10-5	9.2 x10-1	2.0E+01	5.0E+00	74.99	this work
20	Gyógyvizek	1st Campaign	Debrecen	nd	8.1 x10-4	1.6 x10-6	nd	nd	nd	nd	nd	97.62	this work
	Gyógyvizek		Rome	1.1 x10-1	1.1 x10-2	2.6 x10-3	9.0 x10-4	nd	1.3E+00	5.3 x10-1	4.9 x10-1	97.62	this work

	Gyógyvizek	2nd Campaign	Palermo	nd	7.5 x10-4	8.6 x10-4	2.0 x10-3	1.5 x10-4	8.9 x10-1	1.4 x101	3.5E+00	78.42	this work
21	Bálványos Sósmező drilling 1	1st Campaign	Debrecen	nd	2.6 x10-4	6.4 x10-4	nd	nd	nd	nd	nd	79.78	this work
	Bálványos Sósmező drilling 1		Rome	nd	2.0 x10-4	5.0 x10-4	3.0 x10-5	nd	3.5 x10-2	1.5 x101	4.9E+00	79.78	this work
22	Bálványos Sósmező drilling 2	1st Campaign	Debrecen	nd	4.4 x10-4	5.4 x10-4	nd	nd	nd	nd	nd	80.62	this work
	Bálványos Sósmező drilling 2		Rome	nd	2.0 x10-4	4.0 x10-4	3.0 x10-5	nd	8.9 x10-2	1.5 x101	4.6E+00	80.62	this work
23	Bálványos Sósmező drilling 3	1st Campaign	Debrecen	nd	6.2 x10-4	4.7 x10-4	nd	nd	nd	nd	nd	nd	this work
24	St Anna crater rim	1st Campaign	Debrecen	nd	8.2 x10-4	1.0 x10-3	nd	nd	nd	nd	nd	22.74	this work
	St Anna crater rim		Rome	nd	6.0 x10-4	1.0 x10-3	4.0 x10-5	nd	1.1 x10-1	6.1 x101	1.6 x101	22.74	this work
25	Jajdon pool	1st Campaign	Debrecen	nd	1.0 x10-3	1.1 x10-3	nd	nd	nd	nd	nd	20.50	this work
	Jajdon pool		Rome	4.1 x10-2	8.6 x10-3	nd	4.0 x10-4	nd	4.0 x10-1	6.2 x101	1.7 x101	20.50	this work
26	Jajdon mofetta	1st Campaign	Debrecen	nd	5.9 x10-4	1.7 x10-3	nd	nd	nd	nd	nd	12.11	this work
	Jajdon mofetta		Rome	nd	5.8 x10-3	nd	5.0 x10-4	nd	1.3 x10-1	6.9 x101	1.9 x101	12.11	this work
27	Băile Tuşnad mofetta	1st Campaign	Debrecen	nd	4.1 x10-4	3.2 x10-4	nd	nd	nd	nd	nd	97.97	this work
	Băile Tuşnad mofetta		Rome	nd	4.1 x10-3	2.7 x10-3	7.0 x10-4	nd	5.9 x10-1	9.2 x10-1	5.2 x10-1	97.97	this work
28	Lăzăreşti Nyírfürdő mofetta	1st Campaign	Debrecen	nd	1.3 x10-4	2.0 x10-5	nd	nd	nd	nd	nd	97.99	this work
	Lăzăreşti Nyírfürdő mofetta		Rome	8.4 x10-2	2.2 x10-3	2.4 x10-3	2.0 x10-4	nd	7.8 x10-1	7.1 x10-1	4.3 x10-1	97.99	this work

29	Lăzărești Nyírfürdő pool	1st Campaign	Debrecen	nd	3.7 x10-4	9.7 x10-4	nd	nd	nd	nd	nd	93.14	this work
	Lăzărești Nyírfürdő pool		Rome	5.0 x10-3	3.7 x10-3	4.0 x10-3	1.4 x10-3	nd	1.3E+00	4.8E+00	7.3 x10-1	93.14	this work
	Lăzărești Nyírfürdő pool	2nd Campaign	Palermo	nd	1.1 x10-4	2.7 x10-6	nd	nd	8.1 x10-1	1.7E+00	5.0 x10-2	96.71	this work
30	Lăzărești Nyírfürdő pool 2	1st Campaign	Debrecen	nd	1.3 x10-4	2.7 x10-5	nd	nd	nd	nd	nd	97.66	this work
	Lăzărești Nyírfürdő pool 2		Rome	5.9 x10-2	1.9 x10-3	2.9 x10-3	9.0 x10-4	nd	7.9 x10-1	8.6 x10-1	6.2 x10-1	97.66	this work
31	Ciucsângeorgiu mofetta	1st Campaign	Debrecen	nd	5.9 x10-4	1.5 x10-3	nd	nd	nd	nd	nd	6.40	this work
	Ciucsângeorgiu mofetta		Rome	nd	5.4 x10-3	nd	5.0 x10-4	nd	6.4 x10-2	7.5 x101	1.9 x101	6.40	this work
32	Csiszárfürdő Băile Reci			nd	2.3 x10-3	2.3 x10-3	nd	nd	8.0 x10-3	nd	nd	99.99	Frunzeti, 2013
33	Gyógyvizek Izvoarele Tămăduitoare			nd	3.5 x10-3	4.6 x10-6	nd	nd	1.3E+00	1.4E+00	nd	97.24	Frunzeti, 2013
34	Apor lányok feredeje			nd	3.5 x10-3	1.3 x10-6	nd	nd	1.3E+00	1.9E+00	nd	96.76	Frunzeti, 2013
35	Torjai Büdös Cave (Stinky Cave)			nd	2.7 x10-3	4.6 x10-6	nd	nd	1.2E+00	2.1E+00	nd	96.80	Frunzeti, 2013
36	Mikesfürdő-Hammas			nd	3.3 x10-3	5.0 x10-6	nd	nd	1.3E+00	1.5E+00	nd	97.17	Frunzeti, 2013
37	Buffogó peat bog			nd	3.7 x10-3	1.4 x10-6	nd	nd	1.6E+00	1.6E+00	nd	96.80	Frunzeti, 2013
38	Tusnad			nd	5.3 x10-5	7.3 x10-6	nd	nd	3.0 x10-3	4.4E+00	nd	95.70	Frunzeti, 2013
39	Tusnad Nadas			nd	6.0 x10-6	nd	3.4 x10-5	nd	3.8 x10-3	3.2 x10-1	1.1 x10-1	99.56	Vaselli et al., 2002
40	Lăzărești Nyir			5.0 x10-3	7.8 x10-4	nd	4.0 x10-5	2.2 x10-5	3.4E+00	7.4E+00	1.4 x10-2	89.11	Vaselli et al., 2002
41	Sf Ana			nd	6.9 x10-4	nd	5.0 x10-6	7.0 x10-6	6.5 x10-1	1.6E+00	4.2 x10-2	97.69	Vaselli et al., 2002

42	Puturosul			1.2 x10-2	4.1 x10-4	nd	3.7 x10-5	nd	7.8 x10-1	9.0 x10-1	4.2 x10-2	98.26	Vaselli et al., 2002
43	Puturosul Sud			nd	1.4 x10-3	nd	9.0 x10-6	9.0 x10-6	2.4E+00	2.0E+00	3.0 x10-2	95.63	Vaselli et al., 2002
44	Bálványos			6.0 x10-3	6.3 x10-4	nd	1.5 x10-4	4.0 x10-6	1.1E+00	8.9 x10-1	4.4 x10-2	97.97	Vaselli et al., 2002
45	Torjai Büdös Cave (Stinky Cave)			nd	1.1 x10-3	nd	nd	nd	8.0 x10-1	9.7 x10-1	6.0 x10-2	98.20	Althaus et al., 2000
46	Apor lányok feredeje-Upper pool			nd	1.3 x10-3	nd	nd	nd	1.2E+00	1.5E+00	1.8 x10-1	97.75	Althaus et al., 2000
47	Apor lányok feredeje-Lower pool			nd	1.3 x10-3	nd	nd	nd	9.4 x10-1	7.3 x10-1	2.0 x10-2	98.16	Althaus et al., 2000
48	Bixad			nd	nd	nd	nd	nd	2.3 x10-1	8.9 x10-1	2.7 x10-1	99.00	Althaus et al., 2000
49	Bixad			nd	nd	nd	nd	nd	nd	nd	nd	nd	Althaus et al., 2000
50	Tusnad Nagy			nd	nd	nd	nd	nd	nd	nd	nd	nd	Althaus et al., 2000
51	Balvanyos Carpatii			nd	nd	nd	nd	nd	nd	nd	nd	nd	Althaus et al., 2000
52	Gyógyvizek			nd	nd	nd	nd	nd	nd	nd	nd	nd	Unpublished data
53	Bancu			nd	nd	nd	nd	1.0 x10-5	7.0 x10-1	2.4E+00	2.0 x10-1	95.88	Unpublished data
54	Lazaresti			nd	nd	nd	nd	nd	8.5 x10-1	2.0E+00	1.8 x10-1	96.4	Unpublished data

Note. Nd= not determined

Table 3. *Isotopic composition of the gas samples.*

No.	Site	Campaign	Laboratory	R/Ra measured	R/Ra corrected	4He/20Ne	δ13C-CO_2	δ18O-CO_2	CO_2/3He	Source
1	Torjai Stinky Cave	1st Campaign	Debrecen	2.67	2.69	18.07	-3.24	-6.74	3.29E+10	this work
		2nd Campaign	Palermo	3.01	3.01	955.55	-3.09	nd	3.24E+10	this work
2	Timsós cave	1st Campaign	Debrecen	2.71	2.73	23.83	-3.36	-6.08	3.17E+10	this work
		2nd Campaign	Palermo	2.90	2.95	13.20	-3.47	nd	3.69E+10	this work
3	Gyilkos cave	1st Campaign	Debrecen	2.12	2.40	1.40	-3.22	-6.63	nd	this work
4	Buffogó peat bog pool	1st Campaign	Debrecen	2.86	2.86	758.43	-2.70	-9.00	2.45E+10	this work
		2nd Campaign	Palermo	2.27	2.95	0.90	-3.15	nd	3.27E+10	this work
5	Buffogó peat bog	1st Campaign	Debrecen	1.78	1.78	477.09	nd	nd	nd	this work
6	Várpad - Ibolya pool	1st Campaign	Debrecen	1.49	2.43	0.44	-3.13	nd	3.81E+11	this work
7a	Bálványos mofetta	1st Campaign	Debrecen	1.13	1.13	456.45	nd	nd	nd	this work
7b	Bálványos mofetta	1st Campaign	Debrecen	2.06	2.19	2.62	-4.20	nd	6.71E+10	this work
		2nd Campaign	Palermo	2.06	2.15	4.0	-17.20	nd	nd	this work
8	Bálványos pool	1st Campaign	Debrecen	2.14	2.17	9.75	-2.84	nd	1.26E+10	this work
9	Csiszárfürdő - Iker pool white	1st Campaign	Debrecen	2.43	2.44	127.86	-3.06	-7.44	nd	this work
		2nd Campaign	Palermo	2.81	2.82	90.4	nd	nd	2.53E+10	this work
10	Csiszárfürdő - Hammas pool	1st Campaign	Debrecen	1.97	1.97	1695.21	-3.59	-8.40	3.23E+10	this work
10		2nd Campaign	Palermo	2.90	2.90	123.8	-3.20	nd	3.43E+10	this work
11	Csiszárfürdő - Timsós pool	1st Campaign	Debrecen	2.46	3.09	0.95	-2.47	nd	2.33E+09	this work
12	Csiszárfürdő -	1st Campaign	Debrecen	2.44	2.90	1.21	-3.40	nd	2.37E+10	this work

	Csokoládés pool									
12		2nd Campaign	Palermo	2.90	2.91	55.00	-2.60	nd	2.68E+10	this work
13	Mikesfürdő - Vallató pool	1st Campaign	Debrecen	2.72	2.73	52.98	-2.28	-6.87	2.42E+10	this work
13		2nd Campaign	Palermo	2.55	2.57	31.4	-2.30	nd	6.18E+10	this work
14	Mikesfürdő - Vallató mofetta	1st Campaign	Debrecen	2.21	2.25	7.43	-2.45	-6.37	9.87E+10	this work
15	Mikesfürdő - Hammas pool	1st Campaign	Debrecen	2.74	2.74	266.70	-3.35	-7.09	3.19E+10	this work
15	1	2nd Campaign	Palermo	3.02	3.03	74.0	-2.90	nd	3.85E+10	this work
16	Mikesfürdő - Bükkös pool	1st Campaign	Debrecen	2.46	2.93	1.19	-2.65	nd	2.52E+10	this work
16		2nd Campaign	Palermo	1.98	2.16	2.0	-3.20	nd	3.64E+10	this work
17	Apor lányok feredeje - Small pool	1st Campaign	Debrecen	1.99	1.99	233.48	-3.09	-5.13	1.81E+10	this work
17		2nd Campaign	Palermo	2.81	2.86	12.8	nd	nd	2.95E+10	this work
18	Apor lányok feredeje -spring on fault 2	1st Campaign	Debrecen	3.10	3.15	11.80	-3.85	nd	2.87E+10	this work
18		2nd Campaign	Palermo	2.90	2.90	836.3	-4.00	nd	3.68E+10	this work
19	Apor lányok feredeje -Szemvíz 4	1st Campaign	Debrecen	1.85	1.85	425.84	-3.52	-2.79	1.20E+10	this work
19		2nd Campaign	Palermo	1.34	1.50	1.00	-2.60	nd	nd	this work
20	Gyógyvizek	1st Campaign	Debrecen	2.73	2.73	497.01	-3.42	-4.58	3.17E+10	this work
20		2nd Campaign	Palermo	1.46	1.73	0.9	-3.30	nd	4.37E+10	this work
21	Bálványos Sósmező drilling 1	1st Campaign	Debrecen	0.78	0.27	0.41	-4.61	-5.44	8.13E+11	this work

22	Bálványos Sósmező drilling 2	1st Campaign	Debrecen	0.82	0.72	0.82	-4.37	-5.30	1.82E+11	this work
23	Bálványos Sósmező drilling 3	1st Campaign	Debrecen	2.43	2.83	1.32	-3.92	nd	nd	this work
24	St Anna crater rim	1st Campaign	Debrecen	1.99	2.58	0.78	-2.80	-9.05	7.78E+09	this work
25	Jajdon pool	1st Campaign	Debrecen	2.30	2.83	0.99	-3.41	nd	5.02E+09	this work
26	Jajdon mofetta	1st Campaign	Debrecen	1.45	3.25	0.36	-3.96	nd	4.51E+09	this work
27	Băile Tușnad mofetta	1st Campaign	Debrecen	2.02	2.32	1.28	-1.50	nd	7.48E+10	this work
28	Lăzărești Nyírfürdő mofetta	1st Campaign	Debrecen	1.43	1.45	6.50	-2.08	nd	3.84E+11	this work
29	Lăzărești Nyírfürdő pool	1st Campaign	Debrecen	1.11	1.46	0.38	-1.40	nd	1.24E+11	this work
29		2nd Campaign	Palermo	1.01	1.01	40.2	-1.50	nd	6.45E+11	this work
30	Lăzărești Nyírfürdő pool 2	1st Campaign	Debrecen	1.30	1.32	4.69	-1.91	nd	4.13E+11	this work
31	Ciucsângeorgiu mofetta	1st Campaign	Debrecen	0.77	0.14	0.39	-2.95	nd	5.50E+10	this work
32	Csiszárfürdő Băile Reci			0.796	0.796	0.99	nd	nd	3.89E+10	Frunzeti, 2013
33	Gyógyvizek Izvoarele Tămăduitoare			2.302	2.302	766.09	-3.25	-7.43	8.62E+09	Frunzeti, 2013
34	Apor lányok feredeje			2.438	2.438	2686.92	-3.72	-4.92	8.17E+09	Frunzeti, 2013
35	Torjai Büdös Cave (Stinky Cave)			2.199	2.199	583.84	-3.15	-7.48	1.17E+10	Frunzeti, 2013
36	Mikesfürdő-			2.242	2.242	656.89	-3.16	-9.87	9.47E+09	Frunzeti,

	Hammas									2013
37	Buffogó peat bog			2.274	2.274	2711.03	-2.77	-9.21	8.31E+09	Frunzeti, 2013
38	Tusnad			0.724	0.724	9.79	-4.7	-8.2	1.79E+12	Frunzeti, 2013
39	Tusnad Nadas			1.66	1.66	1.28	-4.42	nd	7.19E+12	Vaselli et al., 2002
40	Lăzărești Nyir			2.95	2.95	7.7	nd	nd	2.79E+10	Vaselli et al., 2002
41	Sf Anna			3.18	3.18	25	nd	nd	3.20E+10	Vaselli et al., 2002
42	Puturosul			2.29	2.29	10.11	nd	nd	7.53E+10	Vaselli et al., 2002
43	Puturosul Sud			nd	nd	nd	-4.7	nd	nd	Vaselli et al., 2002
44	Bálványos			4.48	4.48	163	nd	nd	2.52E+10	Vaselli et al., 2002
45	Torjai Büdös Cave (Stinky Cave)			3.1	3.100	47.3	nd	nd	2.07E+10	Althaus et al., 2000
46	Apor lányok feredeje-Upper pool			3.12	3.120	151	nd	nd	1.72E+10	Althaus et al., 2000
47	Apor lányok feredeje-Lower pool			3.19	3.190	712	nd	nd	1.70E+10	Althaus et al., 2000
48	Bixad			1.47	1.470	0.67	nd	nd	nd	Althaus et al., 2000
49	Bixad			0.8	0.8	1.3	nd	nd	nd	Althaus et al., 2000
50	Tusnad Nagy			1.2	1.2	6.44	nd	nd	nd	Althaus et

										al., 2000
51	Balvanyos Carpatii			3.04	3.04	1.06	nd	nd	nd	Althaus et al., 2000

Note. $^{3}He/^{4}He$ ratios are normalized to the atmosphere and listed as R/R_a values corrected for the atmospheric He contamination (R/R_{ac}) considering the $^{4}He/^{20}Ne$ ratio; $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2 are expressed in ‰ vs. VPDB. Nd=not determined

Table 4. *Isotopic composition of Persani clinopyroxene.*

Sample	[He] mol/g	[Ne] mol/g	He/Ar	$^{4}He/^{20}Ne$	R/Ra	R/Ra c
Cpx xenolith	4.06E-12	2.00E-15	0.92	2030.46	5.96	5.96
Cpx xenolith 2	3.81E-12	2.74E-15	0.91	1389.41	5.94	5.94

Note. $^{3}He/^{4}He$ ratios are normalized to the atmosphere and listed as R/R_a values ($R=^{3}He/^{4}He$ isotopic ratio of the sample, R_a=atmospheric $^{3}He/^{4}He=1.382\times10^{-6}$) and corrected for the atmospheric helium contamination (R/R_{ac}) considering the $^{4}He/^{20}Ne$ ratio;

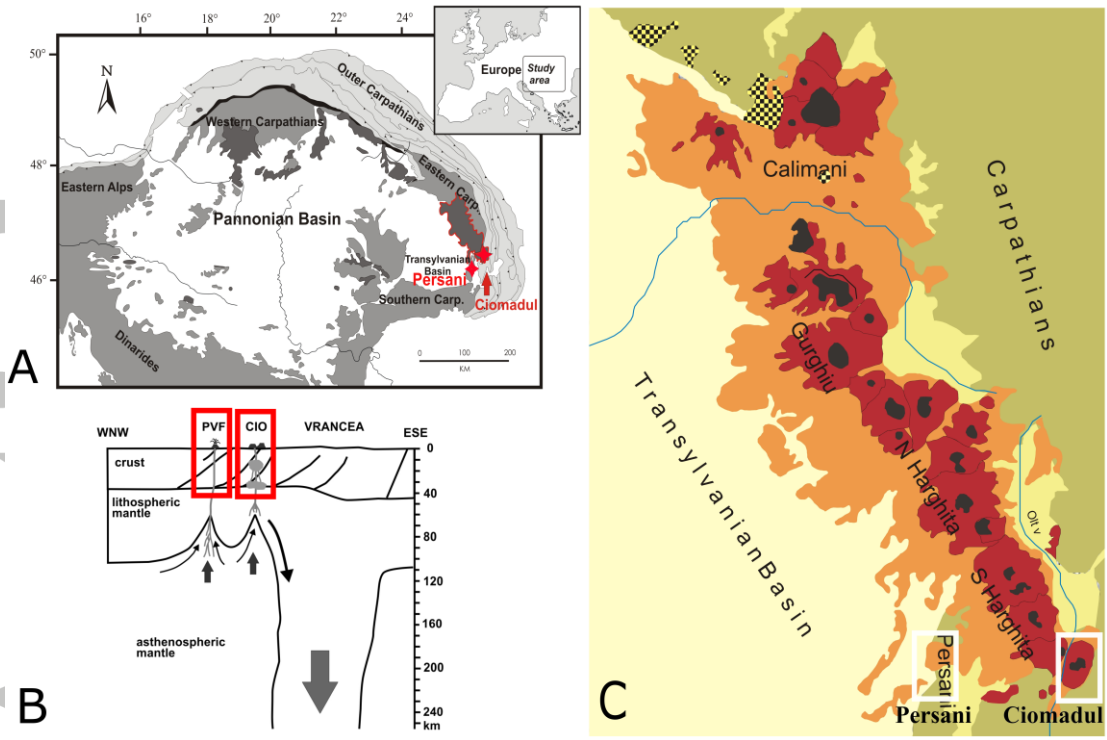

Figure 1a: Location of Ciomadul and Persani volcanoes in the southeastern Carpathian area of the Carpathian-Pannonian Region (after Harangi et al., 2013), **1b:** Geotectonic model of the Persani and Ciomadul volcanic areas, PVF=Persani Volcanic Field, CIO=Ciomadul (after Harangi et al., 2013), **1c:** Location of Ciomadul and Persani volcanoes in the volcanic range of the Eastern Carpathians (modified after Szakács & Seghedi, 1995)

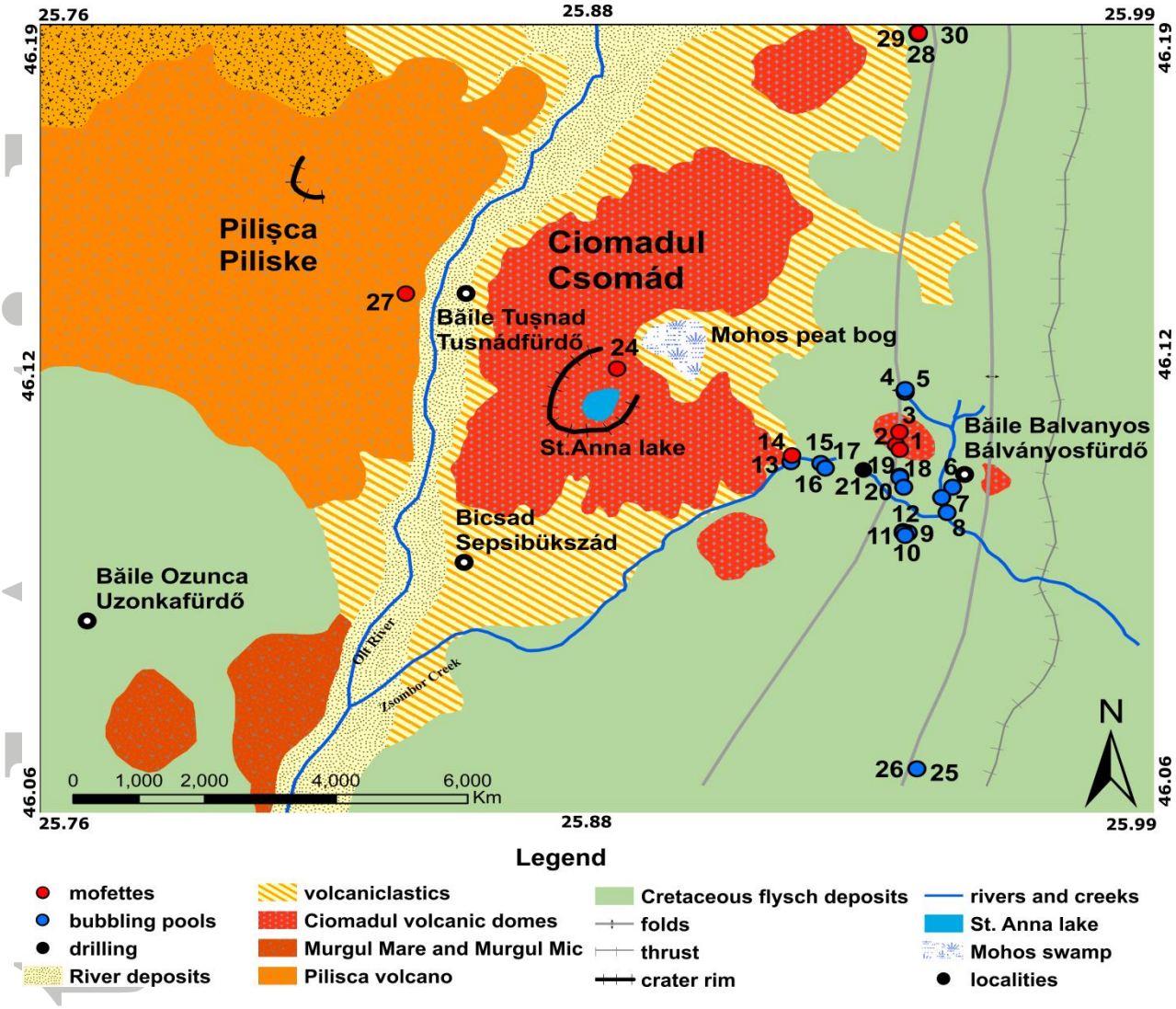

Figure 2: Geological sketch map of the study area. The red, black and blue dots indicate the type of the sampling points: mofette, drilling and bubbling pool respectively. The numbers on the sampling sites are the same as in Tables 1. (Geological map is modified after Ianovici & Radulescu, 1968)

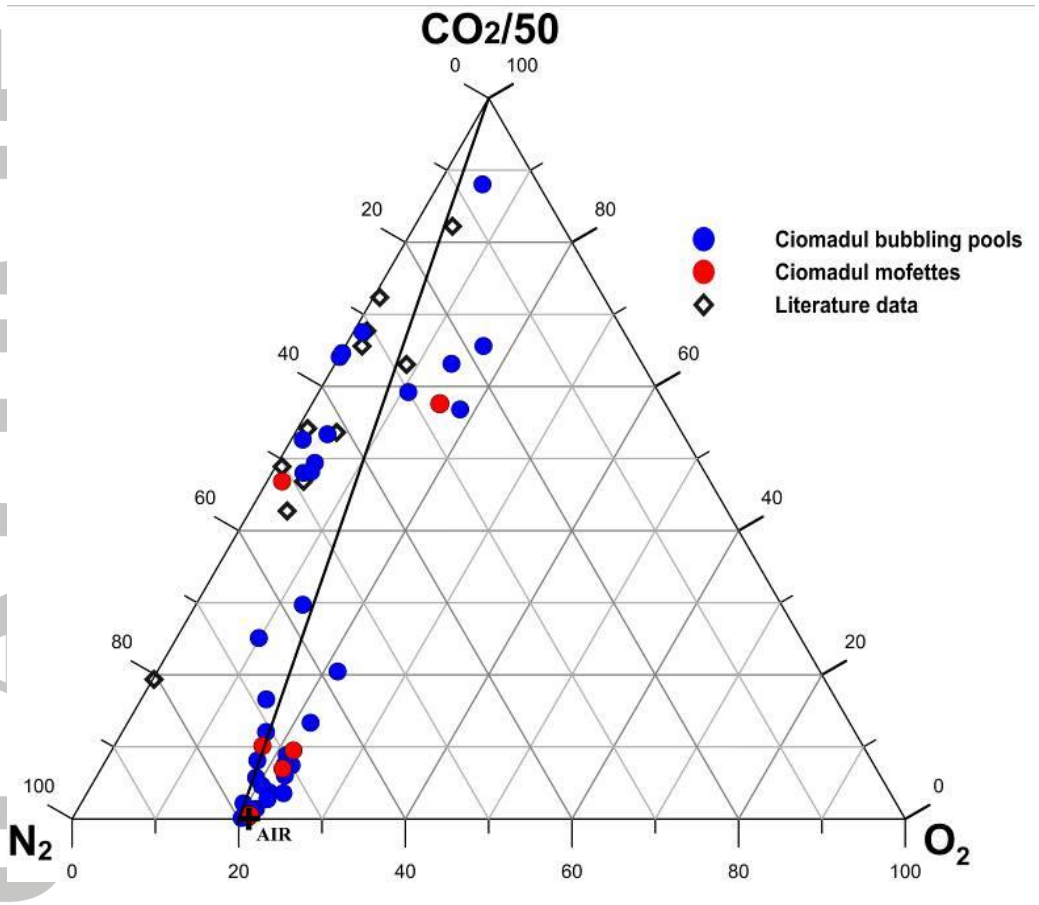

Figure 3: $CO_2/50$ - O_2 - N_2 triangular diagram showing the relative contents of components. The samples distribution highlights mixing between CO_2 and atmospheric gas species. Literature data from Ciomadul area is represented by data from Althaus et al., 2000; Vaselli et al., 2002; Frunzeti, 2013).

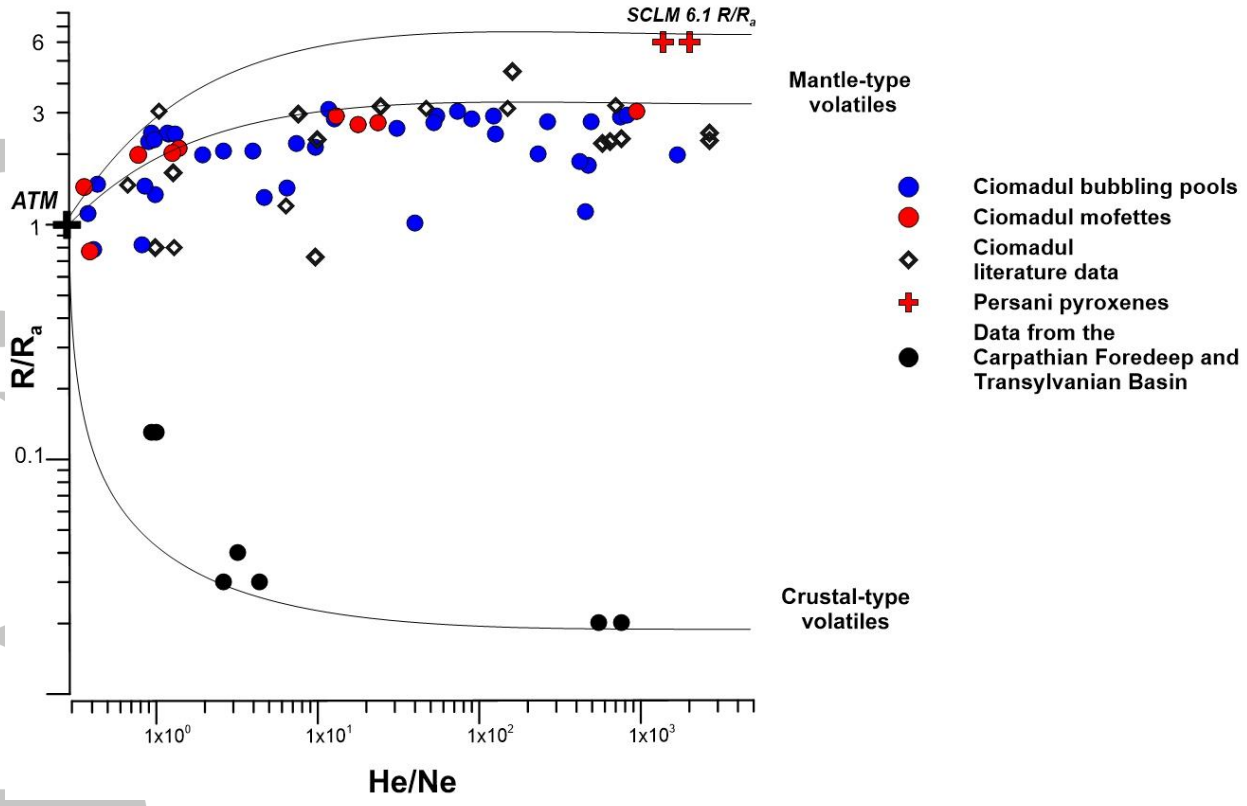

Figure 4: Helium isotopic ratios (R/R_a values) and $^4He/^{20}Ne$ relationships. The theoretical lines represent binary mixings of atmospheric He with mantle-originated and crustal He (Pik & Marty, 2008). The assumed end members for He-isotopic ratios and $^4He/^{20}Ne$ ratios are: ATM (1 R_a, He/Ne=0.318, Sano and Wakita 1985).; Subcontinental European Mantle ($6.1 \pm 0.9 R_a$ and $^4He/^{20}Ne$ ratio=1000; Gautheron and Moreira, 2002); typical crustal end-member is $0.02 R_a$ and $^4He/^{20}Ne$ ratio = 1000 (Sano and Marty, 1995). Literature data for comparison: data after Althaus et al. 2000; Vaselli et al. 2002; Baciu et al., 2007; 2017; Frunzeti et al., 2013).

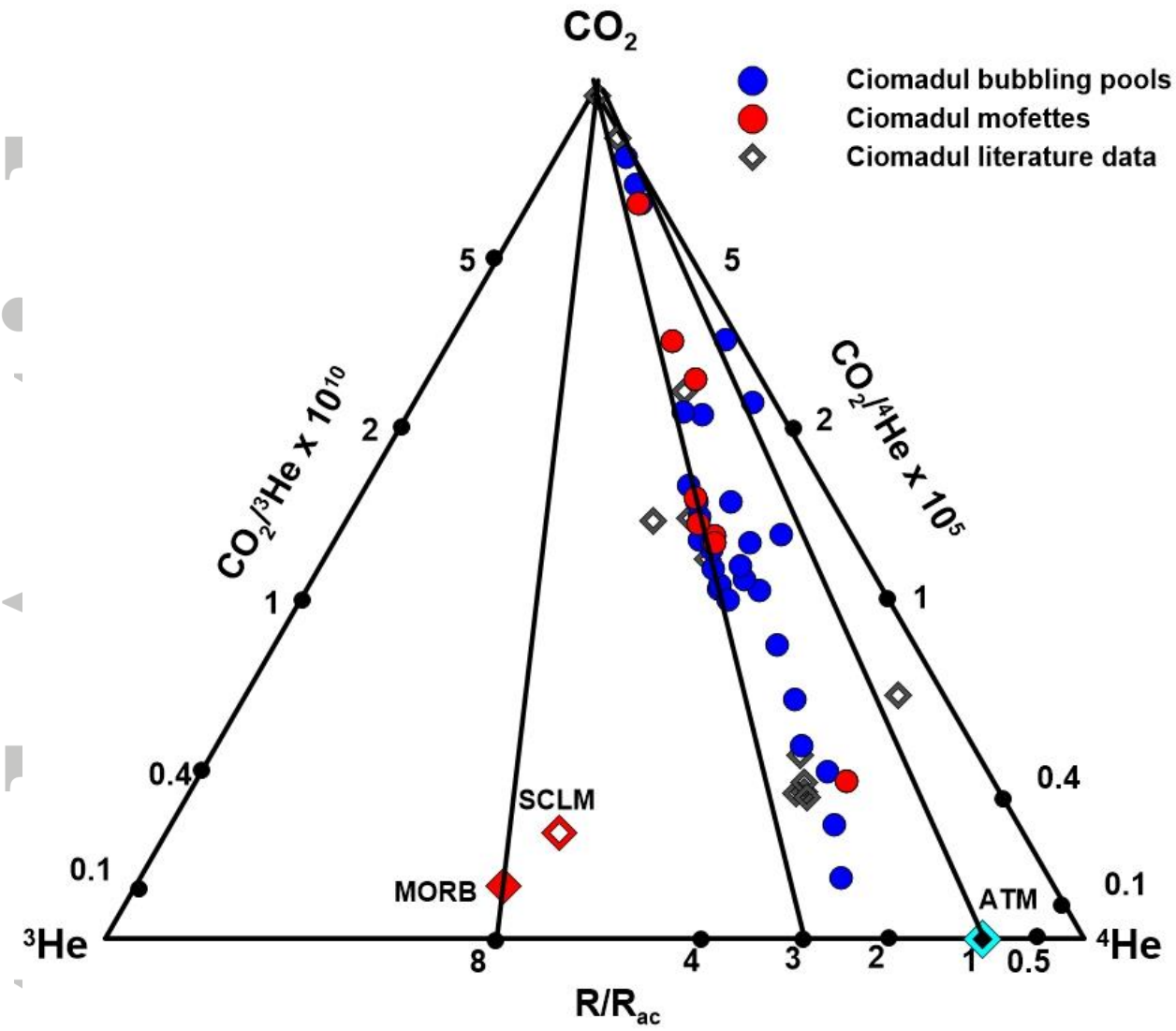

Figure 5: Ternary CO_2-^3He-^4He diagram of Ciomadul gas samples.Ciomadul literature data after Althaus et al. 2000, Vaselli et al. 2002, Frunzeti et al., 2013. For reference, we have plotted the MORB (Marty & Jambon, 1987) and SCLM values (Gautheron and Moreira, 2002)

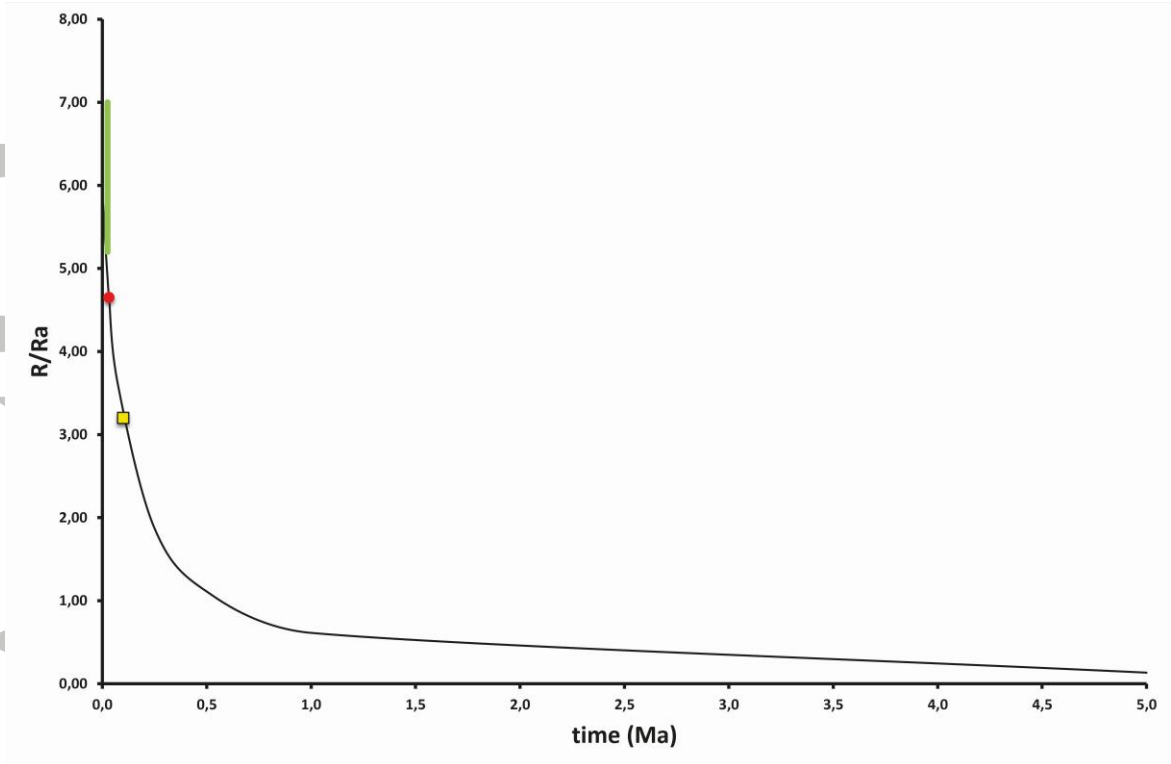

Figure 6 Magma aging evolution over time of the He isotopic signature (as R/R_a). The green bar is the range of the SCLM He isotopic ratio (6.1±0.9; Gautheron and Moreira, 2002). The red circle is the value or the $^3He/^4He$ (4.65Ra) at 30 ka for the magma aging evolution. $^3He/^4He$ =3.2 is at 100ka (yellow square).

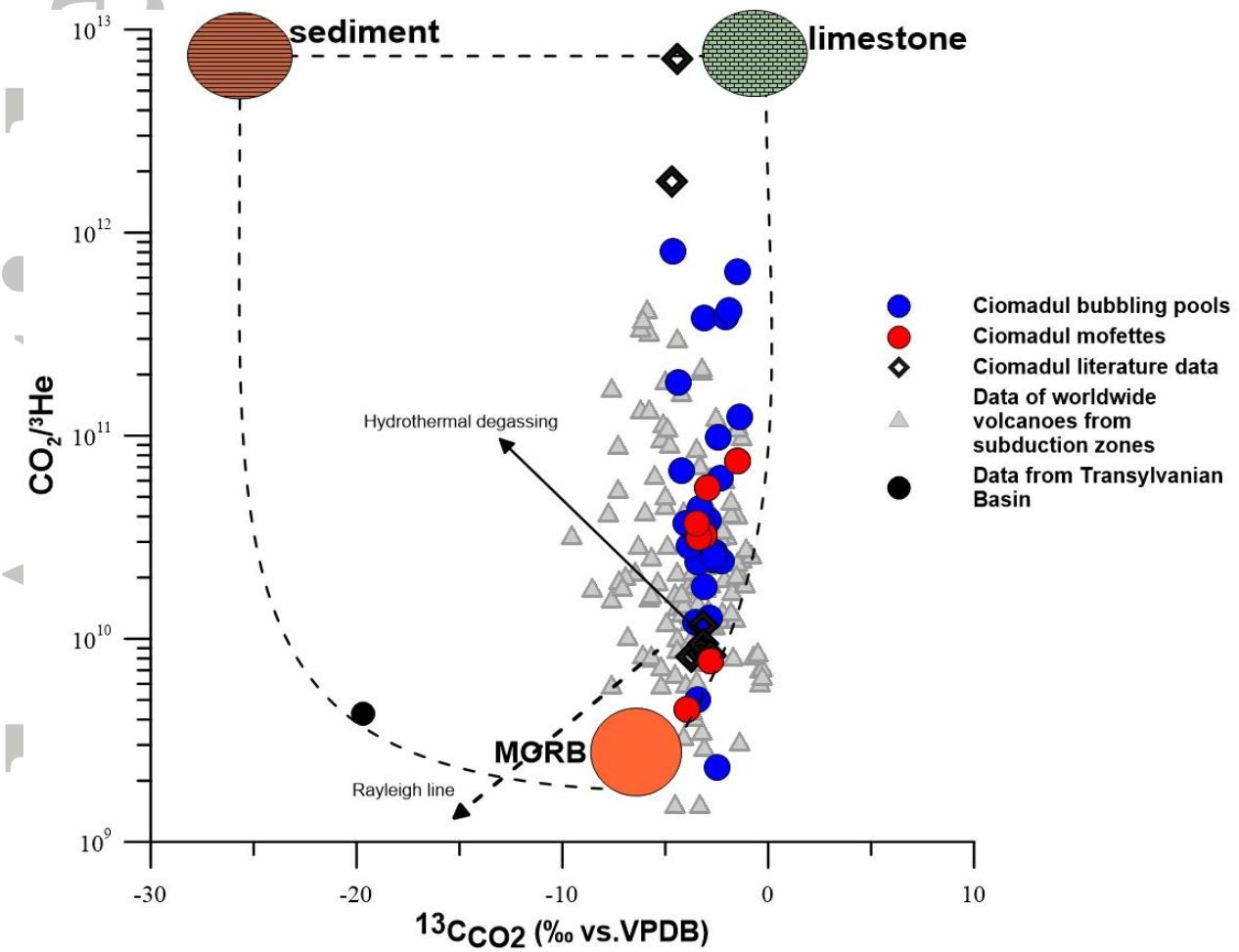

Figure 7: Correlation diagram of Sano and Marty (1995) plotting $CO_2/^3He$ vs. $^{13}C_{CO2}$ (VPDB) of Ciomadul gas emissions. Lines show the theoretical mixing between a mantle end-member and a crustal end-member represented by marine limestone and organic sediment carbon. Ciomadul samples are showing a trend of mixing between fluids of mantle origin and fluids originating from limestone. Literature data for comparison: data after Althaus et al. 2000; Vaselli et al. 2002; Baciu et al., 2007; 2017; Frunzeti et al., 2013.
Data on individual volcanoes worldwide based on the compilation of Mason et al. (2017), by Allard, 1983; Marty & Giggenbach, 1990; Poorter et al., 1991; Varekamp et a., 1992; Sturchio et al., 1993; Sano et al., 1994; Sano & Marty, 1995; Tedesco et al., 1995;Hilton, 1996;Sano&Williams, 1996; Allard et al., 1997; Fischer et al., 1998; Van Soest et al., 1998; Pedroni et al., 1999; Lewicki et al., 2000; Parello et al., 2000; Favara et al., 2001; Snyder et al., 2001; Shaw et al., 2003; Symonds et al., 2003; Jaffe et al., 2004; Capasso et al, 2005b; Carapezza et al., 2007; de Leeuw et a., 2007; Werner et al., 2009; Capaccioni et al., 2011; Tassi et al., 2011; Aguilera. et al., 2012;Melian et al., 2012; Caracausi et al., 2013.

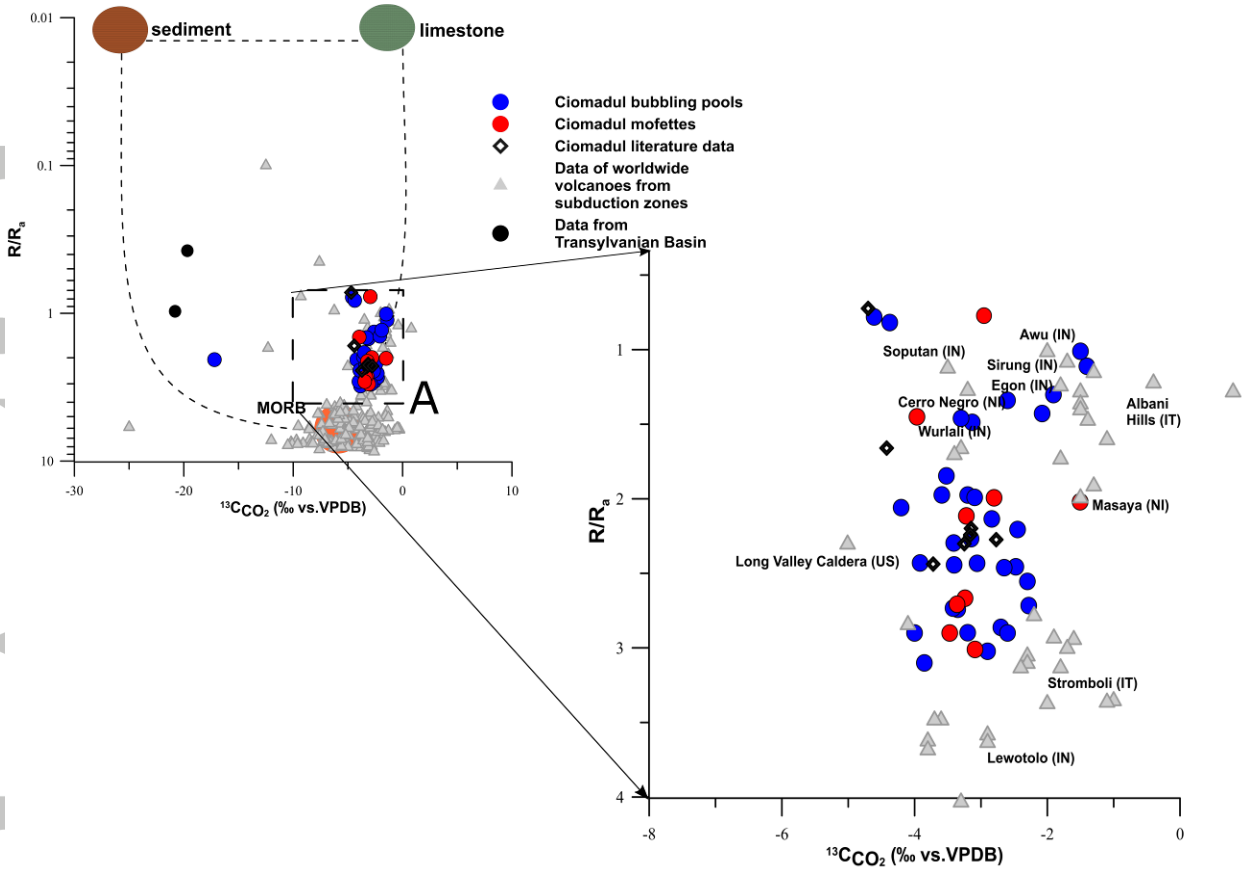

Figure 8a and b Correlation diagram (Ciotoli et al., 2013) plotting He isotopic ratios (R/R_a) vs. $^{13}C_{CO2}$ (VPDB) of Ciomadul gas emissions. Lines show the theoretical mixing between a mantle end-member (MORB) and a crustal end-member represented by marine limestone and organic sediment carbon (Sano & Marty, 1995, Sherwood Lollar, 1997). Literature data for comparison: data after Althaus et al. 2000; Vaselli et al. 2002; Baciu et al., 2007, 2017; Frunzeti et al., 2013. Data on individual volcanoes worldwide based on the compilation of Mason et al. (2017) from the data presented by Allard,., 1983; Marty & Giggenbach, 1990; Poorter et al., 1991; Varekamp et al., 1992; Sturchio et al., 1993; Sano et al., 1994; Sano & Marty, 1995; Tedesco et al., 1995; Hilton, 1996; Sano &Williams, 1996; Allard et al., 1997; Fischer et al., 1998; Van Soest et al., 1998; Pedroni et al., 1999; Lewicki et al., 2000; Parello et al., 2000; Favara et al., 2001; Snyder et al., 2001; Shaw et al., 2003; Symonds et al., 2003; Jaffe et al., 2004; Capasso et al, 2005b; Carapezza et al., 2007; de Leeuw et al., 2007; Werner et al., 2009; Capaccioni et al., 2011; Tassi et al., 2011; Aguilera et al., 2012; Melian et al., 2012; Caracausi et al., 2013.