Eruptive history of the Late Quaternary Ciomadul (Csomád) volcano, East Carpathians, Part I: Timing of lava dome activity

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Abstract

Located at the southern tip of the Intra-Carpathian Volcanic Range in Romania, and composed of a dozen dacitic lava domes, the Ciomadul (Csomád) volcanic complex is the youngest eruptive centre of the Carpatho-Pannonian Region. Whereas, in the last decade, the explosive history of Ciomadul since 50 ka has been well constrained by numerous studies, the chronology of the dome sequence still lacks robust chronological constraints and an extended analysis of all available data. Here, we apply a detailed K-Ar dating approach to refine the chronology of the lava dome eruptions, using the unspiked K-Ar Cassignol-Gillot technique. Our dating focused on the most voluminous central part of the lava dome complex. New eruption ages were determined following a strict separation (of 10 g) of groundmass from about 3 kg of unaltered sample rocks, thereby isolating material whose cooling was contemporaneous with the eruption. The newly applied methodology, mainly consisting of a double full preparation, first at larger grain size (~ 0.4 mm) and then at < 100 µm, provides an appropriate procedure to separate suitable material to obtain the K-Ar age of the eruption, i.e. the sample's groundmass, in which there is no risk of the presence of older, inherited crystals. Our new geochronological data set gives an improved insight into the temporal construction of the Ciomadul volcanic complex, where (due to the method applied here) all ages are younger than those from previous studies that used whole-rock K-Ar ages. Our new results show that Ciomadul's volcanic activity began with the construction of the southeastern, peripheral domes from ca. 850 ka to 440 ka. After a ca. 250 ky long repose period, the activity resumed in the northern part at around 200 ka, with subsequent domes emplaced between 200 and 130 ka, aligned roughly north-south in the western-central part of the complex. Following a 30 ky long quiescence period, the eastern-central domes formed between 100 and 60 ka. In addition to the chronological history of lava dome volcanism, we also investigated the sequence of crystallisation of mineral phases present in the lavas with respect to the modification of eruption ages. Ages obtained on pure minerals (plagioclase, amphibole and biotite) are systematically older than those obtained on groundmass, showing that most of them formed up to 1.85 Myr before eruption in a long-lived, pre-Ciomadul magmatic system. Crystal size distributions (CSD) data support the age contrasts between juvenile groundmass and older inherited minerals. After injection of new magma and convective mixing with crystal clots, ascent of the resulting led to eruptions of material representing contrasting ages.

Keywords

K-Ar geochronology; groundmass; glomerocryst; excess argon; dacitic lava dome; crystal size distributions; Quaternary volcanism

1 Introduction

Accurate, high-temporal resolution data on eruption ages are crucial to better constrain the geochemical and petrological evolution of volcanic systems (e.g. Kersting and Arculus, 1994; Hildenbrand, 2004; Cadoux et al., 2005), as well as to infer hazard parameters such as recurrence rates and repose periods (Marzocchi and Zaccarelli 2006; Damaschke et al. 2018; Reyes-Guzman et al. 2018). The more accurately the volcanic activity is known, the better its recurrence can be documented and its potential risk constrained (Turner et al. 2009). Such ages also allow estimates of magma extrusion rates (Crisp 1984; Singer et al. 1997) and detailed variations of eruption rates through time and space (Hora et al. 2007; Lahitte et al. 2012; Germa et al. 2015). Moreover, eruption ages help identify vent migration patterns (Tanaka et al. 1986; Connor and Hill 1995; Condit and Connor 1996; Heizler et al. 1999) in dispersed, monogenetic volcanic fields (Nemeth and Kereszturi 2015), and volcanic processes, such as magma crystallisation, vesiculation and fragmentation, that are crucial for eruption forecasting in both monogenetic (Kereszturi et al. 2017) and polygenetic volcanic systems (Turner et al. 2011; Damaschke et al. 2018).

During its long-term evolution, the Miocene to Pleistocene volcanic activity of the Inner Carpathian volcanic chain in the Carpathian-Pannonian Region (CPR; Fig. 1) shifted south-eastward (Szabo et al. 1992; Lexa et al. 2010). This migration defined the Călimani-Gurghiu-Harghita (CGH; Kelemen – Görgényi - Hargita) [1] range, East Carpathians, Romania (Pécskay et

[1] Official Romanian names, when mentioned at first, are followed by locally used Hungarian names (in brackets), which is helpful for the reader in finding the names on local maps

al. 1995, 2006). The youngest centre of the CPR, Ciomadul (Csomád) volcano, is located at the south-easternmost tip of the CGH range. It is a dacitic lava domes complex truncated by the well-preserved twin craters of St. Ana (Szent Anna) and Mohoş (Szakács and Seghedi 1995; Karátson et al. 2013). Ciomadul experienced a long-term eruptive history, producing a dozen lava domes emplaced during the last ca. 1 Myr over an area of 70 km² (Pécskay et al., 1995; Szakács et al., 2015). Its latest, mainly explosive, activity has been dated by radiocarbon and luminescence (OSL and post-IR IRSL) methods (Moriya et al. 1996; Vinkler et al. 2007; Harangi et al. 2010, 2015b; Karátson et al. 2013, 2016) around 32 ka. This has great significance for the regional, Late Quaternary tephrostratigraphy considering the areal distribution of these tephra which extend up to 350 km eastward (Karátson et al., 2016; Wulf et al., 2016). However, Ciomadul's whole volcanic history lacks a sufficiently constrained and reliable geochronological framework. Particularly, the recurrence time of the long-lasting dome-forming activity that preceded the explosive events is still poorly constrained. Previously obtained ages based on conventional K-Ar dating of the Ciomadul lava domes suffer from a lack of analytical accuracy (Pécskay et al. 1995; Szakács et al. 2015). An alternative approach, U-Th/He dating of zircon (Molnár et al. 2018), focused mostly on the onset of Ciomadul volcanism (around 1 Ma), without targeting the main area of the central dome complex.

Even Ciomadul have experienced a long dormant period to present , with no eruption in the past 10,000 years, it is susceptible to erupt again (Szakács et al. 2015). Indeed, magneto-telluric surveys suggest the presence of conductivity variations at various levels beneath Ciomadul that have been attributed to the presence of a partially molten magma body below the volcano (Harangi et al. 2015b). These authors interpreted these anomalies as a result of the presence of crystal-mush bodies containing about 5–15% melt fraction at depths of 5-25 km and 30-40 km. These depths coincide with a low velocity seismic zone located by crustal tomography (Popa et al. 2012).

This paper aims to constrain the main history of extrusive activity of Ciomadul, focusing on the central dome complex and its peripheral lava domes. Due to the very young eruption ages (in the 100 ka range), apart from the $^{40}Ar/^{39}Ar$ method, the unspiked Cassignol-Gillot technique (Cassignol and Gillot, 1982; Gillot et al., 2006), which uses the K-Ar radioactive chronometer, is arguably the most precise radiometric argon dating technique that can be applied to Ca-rich volcanic rocks. . The advantage of this technique is that avoids recoil issues of ^{39}Ar, ^{37}Ar, and ^{36}Ar in the reactor that may affect the $^{40}Ar/^{39}Ar$ technique. The method has proven to be well-suited for dating recent up to Holocene lavas (Samper et al. 2009; Germa et al. 2011b; Gertisser et al. 2012). In part 1 of this work, we use this method to obtain precise eruption ages and constrain the geochemical evolution of the system. In part 2 we use the results to also assess the geomorphological evolution and magma output rates that characterized the evolution of Ciomadul's dome complex (Karátson et al., this volume). In this way we build on previous work using high-precision Cassignol-Gillot K-Ar geochronology at, for example, Basse-Terre (Samper et al. 2009), Martinique (Germa et al. 2011b, 2015) or Merapi (Gertisser et al. 2012), in illustrating how a detailed geochronological framework can support studies that also constrain magmatic evolution and time-space eruptive dynamism.

2 Geological background

As volcanic activity migrated south-eastward along the CGH range during the Miocene to Pleistocene (Pécskay et al., 1995, 2006), magma compositions evolved from normal calc-alkaline to high-K calc-alkaline and shoshonitic (Szakács et al. 1993). This evolution was in tandem with a decrease in magmatic output rates (Szakács and Seghedi 1995; Karátson and

Timár 2005). As decrease in the output rate is expressed by the progressive transition from large stratovolcanoes, occasionally with calderas, to smaller, mostly effusive cones and lava domes (Szakács and Seghedi, 1995; Karátson and Timár, 2005; Karátson et al., this volume).

Ciomadul volcano (Fig. 1) represents the best-preserved lava dome complex at the southernmost end of the CGH volcanic range. Its geological setting is presented in Szakács et al. (1993; 2015), Karátson et al. (2013; this volume), Harangi et al. (2015a) and Molnár et al. (2018). A dome complex is a special type of compound polygenetic volcano where an assemblage of nested lava domes, coulees (Blake 1990) and related pyroclastic and epiclastic volcanic rocks are spaced so closely in space and time that they are considered a polygenetic volcano rather than a group of monogenetic volcanoes (Lexa et al. 2010). Mostly high-K dacitic in composition, Ciomadul consists of domes resulting from extrusion of viscous magma and comprises the spatially and volumetrically most significant central dome in this system (Karátson et al., this volume). The system also includes the more isolated southeastern andesitic domes of Dealul Mare (Hegyes-tető) and the Puturosu (Büdös) Hills (Fig. 1), but these are not studied here. To the south, there are two other domes, which have andesitic to shoshonitic composition (Szakács et al., 2015). These latter domes, as well as the adjacent, western Pilişca (Piliske) stratovolcano in the South Harghita range are older than Ciomadul (Szakács et al., 2015; Molnár et al., 2018).

As already described elsewhere, such as at the Okataina Center in New Zeland's Taupo Volcanic Zone (Smith et al. 2004, 2005; Shane et al. 2007; Rubin et al. 2016), the magma batches of Ciomadul's dacites were probably produced as the result of reheating by intrusion(s) of hot mafic magma into a silicic reservoir (Kiss et al. 2014). In particular, crystallisation of amphibole has been related to the storage of a near-solidus silicic crystal mush body at 8 – 12 km depth (Kiss et al. 2014). The remobilization of silicic crystal mush can provide a large amount of xenocrysts, which constitutes up to one third of the volume of the erupted silicic magma of some lava domes as observed, for instance, on Santorini or Montserrat (Zellmer et al. 2000, 2003). At Ciomadul, the role of these xenocrysts has yet to be shown and analysed. The xenocrysts, isolated or as part aggregates of crystals called glomerocrysts (or crystal clots), may have reached the surface with a part of the radiogenic argon ($^{40}Ar^*$) they had accumulated since their formation, making K-Ar dating of the dacitic domes challenging. Indeed, these xenocrysts are carriers of extraneous argon, which are prone to bias K-Ar ages (Dalrymple and Moore 1968; Stipp et al. 1969; Ozawa et al. 2006).

3 Petrology of the Ciomadul lava domes

Detailed petrology of the Ciomadul lava domes was already well established by previous studies ((Kiss et al. 2014; Harangi et al. 2015b; Szakács et al. 2015)). We here only highlight their main characteristics. Ciomadul lava dome rocks are mainly high-K calc-alkaline, poorly vesicular dacites. Mainly porphyritic, these rocks contain 20-35 vol% coarse crystals (most of them being xenocrystic, see below) commonly set in a fine-grained, light-grey groundmass. In order of relative abundance, these include plagioclase ($An_{85–30}$, 10-25 vol%), amphibole (5-13 vol%), biotite (1-4 vol%), orthopyroxene (1-2 vol%), and Fe-Ti oxides (1-2 vol%). Plagioclase occurs as euhedral laths up to 10 mm in size and often exhibits inclusions of green-brown biotite, euhedral amphibole, and sparse equant Fe-Ti oxide crystals. Euhedral crystals include mainly plagioclase, some exhibiting oscillatory zoning and sieve textures, and amphibole. Subhedral biotite is present as red-brown, pleochroic tabular laths up to 5 mm in length (Szakács et al. 2015). Red-brown hornblende (low-Al amphibole with thick breakdown rims) and pargasite (high-Al amphibole with thin reaction rims) are present as rounded, subhedral to anhedral crystals up to 10 mm in size (Kiss et al., 2014;

Harangi et al., 2015b), containing abundant inclusions of Fe-Ti oxides, plagioclase or biotite. From thermobarometrical modelling, formation of amphiboles has been interpreted as bimodal (Kiss et al., 2014); hornblende having formed at lower temperature (< 800°C) and pargasite having formed at higher temperature (950°C).

The dome rocks contain abundant glomerocrysts or crystal clots, which are aggregates of crystals. Importantly for dating, these glomerocrysts consist of remobilised crystals (> 1 mm and up to 15 mm in diameter, Fig. 2) with microdiorite textures, containing mainly rounded and slightly altered plagioclase and amphibole, in addition to Fe-Ti oxides, apatite, biotite and zircon. Such remobilised crystals are here referred to as xenocrysts, whereas the term glomerocryst is used for an aggregate of xenocrysts remobilised from crystal mush. The groundmass of the dome lavas contains plagioclase, hornblende, biotite with occasional orthopyroxene, Fe-Ti oxide and glass.

4 Methods

4.1 Applying the unspiked Cassignol–Gillot K-Ar technique

The unspiked Cassignol-Gillot technique allows the accurate detection of low percentages of radiogenic ^{40}Ar (Quidelleur et al., 2001). It has been applied to the dating of young (< 100 ka) volcanic events and successfully compared with other dating methods such as ^{14}C, ^{36}Cl exposure and thermo-luminescence (Lahitte et al. 2001; Gillot et al. 2006; Germa et al. 2010; Schimmelpfennig et al. 2011). The technique was also favourably compared with the $^{40}Ar/^{39}Ar$ method and gave similar results when applied to groundmass samples (Coulie et al. 2003; Calvert et al. 2006; Hildenbrand et al. 2014).

4.1.1 The unspiked Cassignol–Gillot technique

Independent K and Ar measurements were performed in the Laboratoire GEOPS (GEOsciences Paris-Sud, Orsay, France). Following dissolution using a mixture of HF, nitric and perchloric acids to destroy the silicate network, potassium (K) was measured by flame emission spectroscopy. Ar isotopic measurements were performed using a 180°-sector mass spectrometer (Cassignol and Gillot 1982; Gillot et al. 2006). This technique has a limit of detection for the radiogenic Ar content ($^{40}Ar^*$) of only 0.1% of the total extracted argon (Quidelleur et al. 2001). Details of the Ar isotopic approach are given elsewhere (Cassignol and Gillot 1982; Gillot and Cornette 1986; Gillot et al. 2006) and are summarized in the Supplementary Material. To minimize the effect of mass-discrimination, the amount of radiogenic argon (%$^{40}Ar^*$) was calculated from a direct comparison between the instrumental $^{40}Ar/^{36}Ar$ sample ratio and the instrumental $^{40}Ar/^{36}Ar$ atmospheric ratio at identical pressure. Unlike the conventional K-Ar technique, this direct quantification does not add a ^{38}Ar spike and is made possible by the very stable analytical conditions. Average relative uncertainties of the $^{40}Ar/^{36}Ar$ ratios and on the amount of radiogenic argon (%$^{40}Ar^*$) are 0.045% and 1.533%, respectively. The technique relies on the assumption that all the measured $^{40}Ar^*$ comes from the in-situ radioactive decay of ^{40}K.

4.1.2 Sample preparation

Extraneous argon, i.e. argon not generated by *in situ* decay of potassium, originates from inherited argon and excess argon, and may bias K-Ar ages (Dalrymple and Moore 1968; Stipp et al. 1969; Ozawa et al. 2006). Inherited argon consists of the contamination by older minerals incorporated into the juvenile magma before eruption, whereas excess argon is introduced from outside the system, commonly from fluid circulations (Kelley, 2002). Our sample preparation procedure (from fieldwork sampling to the sample separation) aims at isolating the groundmass from such a source of extraneous argon. Given the incompatible nature of argon, mineral/fluid and mineral/melt partition coefficients range from 0.01 to as low as 7×10^{-6}, and excess argon remains a relatively uncommon phenomenon (Kelley, 2002).

On the other hand, extraneous argon may result from the contamination by older country rock (inherited argon in xenoliths), or by excess argon present either in inclusions of glass within phenocrysts (Dalrymple and Moore 1968) or in hydrous fluid in the grain boundary network (Kelley 2002). As K-Ar ages do not give spectra to check the presence of inherited argon, dates may be erroneously too old due to such contamination sources. However, accurate sampling, sample separation, and very strict selection of a narrow density range of pure groundmass greatly minimizes the risk of contamination due to the presence of extraneous argon.

4.1.3 Sample selection

During two field campaigns (in October 2015 and June 2016), 25 samples (about 3 kg-weight each), were collected from Ciomadul's lava domes. The sample locations are shown in Figure 1 with the UTM coordinates listed in Table 2. Some of the sampled domes were assumed to be coeval with the late-stage (<50 ka) pyroclastic (fall and flow) deposits (Harangi et al., 2010, 2015a, Karátson et al., 2013, 2016; Wulf et al., 2016). In the field, only samples without visible obvious traces of alteration (calcite, zeolite, or any secondary minerals) and fluid circulation were collected. An additional inspection of thin sections, and checking the freshness of the groundmass, reduced the number of samples to be dated to 18, representing nine individual lava domes. The low loss-on-ignition (LOI) values (less than 1.6 wt%, Table 3) indicate that secondary weathering processes have not significantly affected the selected samples. These criteria reduce the possible bias of K-Ar ages related to K loss or gain via alteration.

4.1.4 Sample separation

One of the main issues in determining the eruption age of the xenocryst-bearing lavas from the Ciomadul domes is to separate pure groundmass aliquots from numerous xenocrysts and phenocrysts, which are potential carriers of extraneous argon. The probability of extraneous argon increases with the range of the groundmass density. Indeed aliquots having a large range of density may contain significant amounts of xenocryst and phenocryst fragments together with the groundmass. In our work, we lowered the relative density range to less than 0.05 (dimensionless quantity). To separate the groundmass as much as possible from inherited minerals, we applied a two-step procedure.

First, the whole-rock sample was crushed and sieved to the 250–500 µm size fraction and then ultrasonically washed in 10% nitric acid solution in order to remove any traces of alteration (clay, sulphur, carbonate, etc.) and hydrothermal products (zeolites, salt containing chlorine compounds, some of them being that isobar to argon isotopes). Finally, the sample was rinsed with water, ethanol and acetone, and ca. 200 g clean material was obtained. Neither HF nor HCl acid were used during sample cleaning in order to avoid 36 mass isobaric contamination (by HCl) that could bias the ^{36}Ar detection or induce dissolving and loss of K (HF and HCl) as was observed in the study of Balogh et al. (2010). Groundmass aliquots were separated by means of heavy liquids (bromoform progressively diluted in ethanol) and, if necessary, by magnetic separation (Gillot et al. 1992). This procedure was efficient in separating the mixed grains of biotite/groundmass or amphibole/groundmass from the pure groundmass, although, in some cases, it was not possible to eliminate the mixed plagioclase/groundmass grains.

This first preparation step was followed by additional crushing to the 62.5-125 µm size fraction (Fig. 3b). After cleaning, a second density separation was performed to isolate the groundmass fraction (Fig. 3c) from the remaining plagioclase crystals (Fig. 3d). Following the density separation, magnetic separation and handpicking were performed to guarantee the absence of plagioclases in the aliquots to be dated.

Pure phenocrysts and xenocryts (K-feldspar, plagioclase, biotite and amphibole) were separated from the 250-500 µm fraction in an attempt to estimate the contribution of inherited argon in whole-rock dating. We also separated plagioclase microphenocrysts from samples 16CIO01 and 16CIO04 as their groundmass was slightly altered.

4.2 Crystal size distribution analysis

In order to highlight the petrographical properties of the Ciomadul dacitic lavas and, and determine its impact on the ideal fraction for K-Ar dating, crystal size distribution (CSD) analyses were obtained on representative samples, following standard methods (Higgins 1996). High-resolution photomicrographs were taken and digitally merged together to create single large thin-section images. These images (6400 × 4800 pixels) were imported into ImageJ software, where contrast and brightness were adjusted to highlight crystal boundaries. For each crystal population, including plagioclase (selected by white and/or bright zones) and mafic crystals (amphibole and biotite, orange to dark brown zones), colour histogram analyses and thresholding were applied to outline crystals. Small crystals (< 10 pixels) were removed from these binary images. Best-fit ellipses were applied to determine long- and short-axis measurements. Mean crystal aspect ratios were calculated using the CSDSlice methodology (Morgan and Jerram 2006). For all grain categories, the number of measurements was at least 10 times higher than the minimum recommended (Mock and Jerram 2005; Morgan and Jerram 2006). Intersection lengths were converted to 3-D CSDs, using the CSDCorrections 1.6 software (Higgins 1996, 2002, 2006). L_{max} is calculated by averaging the four largest crystals within each identified population. The lower limit of the CSD was 0.010 mm (which is not necessarily the smallest crystal in the rock). Samples were classified as massive and approximate crystal roundnesses of 0.3 for plagioclase and 0.6 for mafic crystals (on a scale of zero, angular, to one, spherical) were used. Logarithmic length intervals were used, with each bin $10^{0.2}$ times the size of the previous bin. Bins with less than three crystals were removed from the CSD analysis. Where CSD slopes were curved or kinked, individual segments were interpreted using least squares regression.

4.3 Petrographical and geochemical analyses

To highlight the importance of the main mineral phases, a petrographical analysis was performed in order to estimate the relative proportion of the main phenocrysts (plagioclase, biotite, and amphibole), xenocrysts, glomerocrysts and groundmass. Major-element whole-rock analyses were also performed on the newly dated lava rock samples by ICP-AES to assess the geochemical evolution through time. The samples were analysed at Bureau Veritas Minerals, Vancouver, Canada, following standard sample preparation and analytical techniques.

5 Results

5.1 Crystal size distribution analysis and justification of the groundmass separation process

Crystal size distribution data based on the major axis of the fitting ellipsoid and results are presented in Table 1. Almost all samples (black curves in Fig. 4a) show CSD plots for both plagioclase and mafic mineral phases that exhibit kinked profiles, allowing each to be divided into two individual segments. On the other hand, sample 16CIO08 differs with its much more linear CSD profile (coloured curves in Fig. 4a), particularly for the mafic minerals. A downturn in the smallest crystal sizes can appear either from real population proportions or from analytical bias (Higgins 1996, 2002). Considered as representing a left-hand truncation effect, these bins were removed from analyses.

Plots for plagioclase show the most prominent kinked CSDs (black curve, Fig. 4b). Each curve can be divided into two distinctive segments, defined by sizes <0.125 and > 1 mm. Volumetric plagioclase proportions range from 29.5 to 38.0 vol% and maximum length (L_{max} in Table 1) from 2.93 to 4.79 mm. Average characteristic length values, defined as the opposite of the inverse of the slope (Marsh 1988), are around 0.02 mm for the smaller populations and range from 0.65 to 2.12 mm for the larger ones.

Mafic mineral (biotite) CSDs show concave-upward patterns that are smoother than those for plagioclase (grey curve, Fig. 4c) but kinked enough to divide trends into two slopes (<0.125 and > 1 mm). Volumetric mafic mineral proportions range from 7.9 to 12.3 vol% and L_{max} from 1.39 to 2.08 mm. Average characteristic length values range from 0.016 to 0.025 mm for the smaller mafic populations and from 0.32 to 0.50 mm for the larger ones.

Using the method of Marsh (1988), and from the growth rates of plagioclase microphenocrysts estimated at around 1×10^{-10} mm s^{-1} (Higgins and Roberge 2007), residence times for these populations are around six years. Such delay cannot be related to the magma ascent (estimated at 12 days by Kiss et al., 2014), but to the magma storage preceding eruption (Kiss et al., 2014; Harangi et al., 2015b).

CSD plots do not take into account more than 50 % of the total crystal volume (grey in Fig 4A insets). This is the population corresponding to grains smaller than 0.010 mm, and constitutes the microlitic groundmass. This population represents material that crystallised during the eruption.

As the microlitic fraction and microphenocrystic populations not contain pre-eruption inherited argon that may bias results, it represents the ideal fraction for eruption age determination. We hereafter refer to this population as groundmass. The 0.125 – 1 mm fraction corresponds to the juvenile magma groundmass and the smaller phenocrysts, possibly inherited as xenocrysts. As a result, this population is not suitable for determining an eruption age. The > 1 mm fraction is mostly made up of pre-eruptive and, possibly, inherited-argon-rich minerals. As crushing would reduce the larger minerals into grains having the same size and almost the same density as the smaller minerals, simply crushing and separating them in a single-step procedure is not suitable. Groundmass aliquots were thus obtained during the two-step procedure described above (see also Fig. 3), with each separation step contributing to the maximum possible purification of the originally <0.125 mm fraction by removing grains considered to have originated from phenocrysts or glomerocrysts, i.e. from any crystals initially larger than 0.125 mm.

5.2 K-Ar ages

K-Ar ages are reported in Table 2, with all uncertainties quoted at the one-sigma (1σ) level. Age calculations are based on the ^{40}K abundance and decay constants recommendedby Steiger and Jager (1977). The argon content is calculated from two independent measurements. As a higher abundance of radiogenic $^{40}Ar^*$ means a lower uncertainty on the age, the average age and its 1-σ uncertainty have been calculated by weighting each independent age measurement with its amount of radiogenic $^{40}Ar^*$. Percentages of $^{40}Ar^*$ range from 1.03% to 34.3 vol%, with respective relative uncertainties between 6.48% and 0.27%. Relative errors of the ages are between 12.6% and 1.44%, the latter value being near the limit of our method set at 1.42% for a 100% radiogenic sample, i.e. when only the relative uncertainties on K-content (1%) and argon calibration (1%) affect the result. With the exception of sample 16CIO04, all Ar analyses were successfully duplicated at the 1-σ level (Table 2). The poor reproducibility of sample 16CIO04 may reflect grain heterogeneity within the sample. In this case, the uncertainty of the age was calculated as the standard deviation of the duplicated age measurements.

Even if our strict selection effectively removed phenocrysts, glomerocrysts and their fluid inclusions, greatly minimizing the risk of biasing ages by excess argon, we have to consider that the elimination of excess argon might not have been perfect. Such cases would induce eruption ages that are slightly younger than our results.

5.2.1 South-eastern and northern domes

Three new K-Ar ages constrain the emplacement time of the peripheral domes of the Ciomadul area (Table 2, Fig. 1 and Fig. 5) in addition to the somewhat older Dealul Mare. The radiogenic argon content ($^{40}Ar^*$) of the dated samples varies from 4 to 35 vol%, this latter value being related to the exceptional freshness of the sample, yielding very low atmospheric contamination. The groundmass K content is homogenous, from 3.23 to 3.59 wt%.

The two south-eastern peripheral domes of Muntele Puturosu (Büdös Hill) and Balvanyos (Bálványos Hill) represent relicts of apparently heavily eroded domes that cut through the Cretaceous flysch (Szakács et al., 1993, 2015). Muntele Puturosu was dated at 704 ± 18 ka (16CIO08). The Balvanyos dome, which is the south-easternmost volcanic extrusion of the Ciomadul area (Fig. 1), is dated at 641 ± 9 ka (16CIO07) and 440 ± 12 ka (16CIO06). Based on the more proximal position of 16CIO07 the 641 ka age may better constrain the emplacement age of the Balvanyos dome, and the younger sample could be linked to another, nearby eruption source no longer morphologically visible. Due to the small error even at the 2σ level, it can be concluded that the two samples are from successive, adjacent eruptions separated by a long time gap.

In the north, the groundmass separated from the sample collected from the Haramul Mic (Kis-Haram) dome (16CIO01) shows very high atmospheric contamination. Therefore, no trustworthy age could be obtained on the groundmass. Instead, plagioclase microphenocrysts, which crystallized shortly before eruption were processed, giving an age of 245 ± 24 ka. However, due to presence of glomerocrysts, the probability that the aliquots of plagioclase microphenocrysts contain inherited grains is not zero. As a consequence, the K-Ar age has to be considered a maximum value. Because Haramul Mic is the oldest part of the main dome complex, this age implies that most of the extrusive dome activity of Ciomadul was constrained within the past 250 ky.

5.2.2 Western-central part of the dome complex

The most important results of our work are related to the western-central main part of the dome complex, which represents the largest volume of Ciomadul (Karátson et al., this volume). Of these domes, only Haramul Mare (Nagy-Haram), Dealul Cetăţii (Vár-tető), Dealul Taca (Fáca) and Piscul Pietros (Köves Ponk) have been dated by applying the conventional K-Ar technique (Pécskay et al. 1992, 1995; Szakács et al. 2015). In addition, Piscul Pietros was also dated by the U-Th/He method (Harangi et al. 2015a), whereas Dealul Cetăţii (Vár-tető) and Haramul Lerbos (Fű-Haram) were dated using uncorrected U-Th/He measurements (Karátson et al. 2013), only providing age ranges.

The obtained ages define a 50 ky time span from about 184 ka to 133 ka (Table 2, Fig. 1 and Fig. 5), showing that the majority of the Ciomadul domes were formed in a relatively short time interval. The K-content varies from 1.39 wt% (on plagioclase microphenocrysts) to 3.72 wt% (groundmass), whereas radiogenic argon contents ($^{40}Ar^*$) range from 1.2 to 4.4 vol%, inducing relative uncertainties between 3 and 14%. The Dealul Cetăţii (Vár-tető) dome in the north has been dated at 184 ± 5 ka (sample 15CIO01), whereas the Vârful Comlos

(Komlós-tető) dome (sample 16CIO02) yielded an age of 144 ± 4 ka. Adjacent to Vârful Comlos, the dome of Ciomadul Mare (sample 16CIO04) represents the northern rim of the twin-craters of St. Ana and Mohoş, and may morphologically correspond to an older, larger explosion crater (Karátson et al. 2013; Szakács et al. 2015) created during the early Mohoş explosive eruptions. To minimize risk of contamination by gas released during the last explosive phase from the younger craters, and because the St. Ana crater area is still experiencing gas emanation, the material retained to date this dome consisted of plagioclase microphenocrysts. These were separated by the two-step procedure from the 40 – 80 µm grain size fraction obtained after crushing the 80 - 160 µm groundmass fraction. The very small grain size used in both steps allowed minimization of the traces of inherited minerals. The extracted plagioclase microlite fraction, which is expected to be contemporaneous with the eruption, provided an age of 133 ± 18 ka (Table 2), indistinguishable from the Vârful Comlos data, even at 1σ level.

5.2.3 Eastern-central part of the dome complex

After a quiescence lasting tens of thousands of years, volcanic activity resumed at around 100 ka to form the eastern-central domes (Fig. 1). The Haramul Mare dome (sample 15CIO09), has been dated at 96 ± 2 ka (Table 2). At the southern rim of the Mohoş crater, a rock sampled on the active face of a quarry offered access to a fresh sample of the Piscul Pietros (Köves Ponk) dome, which is morphologically truncated by the Mohoş crater. It has been dated at 60 ± 5 ka (sample 16CIO09, Table 2).

5.3 Geochemistry of the lava domes

Representative chemical analyses of the dated samples are given in Table 3. Concentrations of SiO_2 for the Ciomadul lava domes range between 62.8 and 68.4 wt%, and belong to the high-K calc-alkaline (HKCA) series. There is a dacitic composition for all but two samples of the Balvanyos dome (16CIO06 and 16CIO07), the latter straddling the boundary with the high-K andesite field (Fig. 6a). We note that the southern Dealul Mare dome, not studied here, also falls in this latter andesite field (Szakács et al., 2015).

Major element contents (using SiO_2 as a differentiation index; Fig. 6b) show that MgO, CaO, Al_2O_3, MnO, Fe_2O_3, P_2O_5 and TiO_2 decrease with SiO_2, whereas K_2O slightly increases; as does Na_2O but with a more scattered distribution. These evolutionary trends are consistent with fractional crystallization of plagioclase, amphibole, pyroxene, biotite and Ti-Fe oxides. Specifically, the decreasing trends of CaO and Al_2O_3 as SiO_2 increases, for all samples but 16CIO08, are explained by predominantly plagioclase fractionation.

6 Discussion

6.1 Timing of lava dome activity

Our new K-Ar ages for the extrusive products of the Ciomadul lava dome complex allow better constraints on its dynamism. In particular, they reduce the age range previously suggested by Pécskay et al. (1995) and Szakács et al. (2015), showing that the mainly extrusive, dome-building activity occurred in two main stages and is younger than 1 Ma.

Our derived ages indicate that two stages can be distinguished in the construction of the Ciomadul system. The first stage (Table 2) produced the south-eastern peripheral domes of Muntele Puturosu and Balvanyos (Figure 1). In addition to the somewhat older Dealul Mare (Szakács et al. 2015; Molnár et al. 2018), the duration of this stage is constrained between around 850 and 440 ka. The second, and volumetrically most significant, stage of Ciomadul, began around 200 ka with the Haramul Mic dome-forming eruption. This stage built the northern and central portions of the dome complex. In turn, the main lava domes that form this second stage can be divided into two phases, an older phase between 200 and

130 ka and a younger phase beginning around 100 ka. Within the second phase, the 60 ka age of Piscul Pietros roughly coincides with the onset of the late-stage explosive eruptions (Harangi et al. 2015a; Karátson et al. 2016). Overall, the activity of the Ciomadul lava-dome complex is aligned approximately north-south, sub-parallel to a local fault (Matenco et al. 2007). This suggests a tectonic control on magma extrusion which was characterized by two stages, separated by a long repose of ca. 440-200 ka. Dome eruptions over the main eruptive stage of Ciomadul (< 200 ka) point to a recurrence time of ca. 30 ka. Such an interval is in the same order of magnitude as the age of the latest volcanic event (Karátson et al., 2016), confirming the dormant (i.e. not extinct) status of the volcano as also suggested by fumarole activity (Vaselli et al. 2002; Kis et al. 2017), seismic tomography (Popa et al. 2012), and magnetotelluric surveys (Kiss et al. 2014; Harangi et al. 2015b).

6.2 Comparison with previous radiometric results

The issue of obtaining radiometric ages from whole-rock has been demonstrated elsewhere as possibly inducing biased results (Hofmann et al. 2000; Samper et al. 2007; Germa et al. 2011a). For instance, $^{40}Ar/^{39}Ar$ dating of lava domes on Montserrat yielded an age of 223 ± 7 ka using whole rock, whereas groundmass measurements produced an age of 155 ± 5 ka (Harford et al. 2002). The same study on the active dome obtained a surprisingly old age of 426 ± 95 ka on pure plagioclase and only 21 ± 22 ka on the groundmass fraction. This bias is particularly significant for young samples where any contamination effect would be magnified proportionally to the small amount of in-grown radiogenic Ar. In contrast to various crystal phases, the groundmass is the last phase to crystallize when the lava cools upon eruption. It is thus enriched in incompatible elements, including potassium, and in elements which are in equilibrium with the atmosphere. Hence the initial argon isotopic ratios in the groundmass are atmospheric, and are devoid of radiogenic argon ($^{40}Ar^*$).

Szakács et al. (2015) excluded the possibility of overestimated ages as they considered quartz phenocrysts as the most likely source of excess argon, which are very uncommon in the Ciomadul lavas (Kiss et al., 2014). However, as seen in Table 4 and Fig. 4, our groundmass ages contrast with those obtained from whole rock analyses by applying the conventional K-Ar method (Pécskay et al. 1995; Szakács et al. 2015). Only one sample (16CIO08, M. Puturosu dome) has an age (704 ± 18 ka); compatible at 1-σ level with that obtained from whole rock by the conventional K-Ar technique (710 ± 40 ka, Table 4). For the remaining samples, considering the 2-σ level, only two out of the seven ages match, but these agreements are mostly due to the large uncertainties on conventional K-Ar results (Fig. 5; Table 4).

Biotite from the Piscul Pietros dome, which was dated by both techniques, gave comparable ages of 290 ± 110 ka by conventional K-Ar (Szakács et al. 2015) and 196 ± 4 ka by the unspiked Cassignol-Gillot technique (this work); again the overlap of the ranges is only due to the very large error of the former. On the other hand, neither of these two ages are consistent with the age of 560 ± 110 ka initially proposed by Pécskay et al. (1992).

Our groundmass dating of the Balvanyos dome, the south-easternmost Ciomadul dome (Fig. 1), yielded ages of 641 ± 9 ka (16CIO07) and 440 ± 12 ka (16CIO06), in contrast to previous ages of 920 ± 180 ka and 1020 ± 150 ka obtained by whole-rock K-Ar dating (Pécskay et al. 1995). Again, the minimal overlap (at 2σ) with the age obtained by the unspiked Cassignol-Gillot technique is only due to the very large error. Consequently, it is likely that these ages would not be coeval, if measured with the same range of uncertainties. It thus involves a possible shift toward older ages for the whole-rock K-Ar measurements, mostly induced by inherited argon.

One of the most controversial ages of Ciomadul was assigned to the northernmost dome, Haramul Mic (Kis-Haram), with an unpublished K-Ar age of 0.85 Ma (without reported uncertainties by Casta (1980), quoted in Szakács et al. 2015). Karátson et al. (2013) argued that the recent "pancake" shape of the dome (which is in contrast to other, high and steep-sided Peléan domes and coulées of Ciomadul) is not due to the old age, but simply reflects the original flat dome shape. Indeed, we dated this dome at 245 ± 24 ka using plagioclase microphenocrysts, which provides a maximum age. Szakács et al. (2015) also reported a K-Ar age of 210 ± 50 ka obtained from a block 2 km west of the dome. In agreement with this date, our dating confirms that, after at least a ca. 250 ky-long quiescence, extrusive activity resumed at Haramul Mic less than 250 ka ago.

The systematic offset between groundmass and whole rock ages can be related to an extraneous ^{40}Ar component in the whole rock measurement, which comes from the inclusion of xenocrystic minerals. To evaluate the effect of extraneous ^{40}Ar on age results, we conducted a component analysis on a thin section of sample 15CIO01 (Fig. 3a), whose groundmass was dated at 184 ± 5 ka. Our aim was to calculate a whole-rock age by combining ages of the groundmass and the plagioclase fraction (the two dominant phases) with respect to their proportions in the sample. For the calculation, the thin section image was converted to a black and white image by setting a threshold. Below a value of 20% on the gray scale pixel is converted in black, otherwise is converted in write. This allows us to distinguish plagioclase (in white in Fig. 7a) from groundmass (in black). Because of the sample grain size (200 µm), the composition was next simulated by averaging the tone of each 200 µm-wide subset (i.e. 40 pixel-wide square zones on the image). The composition was then defined on the grey scale, from a material of pure plagioclase (100% on grey scale, i.e. white on Fig. 7a), to one fully composed of groundmass (0% on grey scale, i.e. black on

Fig. 7a), including mixed material defined by an intermediate tone on grey scale (Fig. 7a). In order to highlight the composition of each grain, a colour map is also proposed (Fig. 7b). Pure plagioclase and pure groundmass grains are coloured in yellow and blue, respectively. Mixed grains are illustrated by variation of red lightness: black for grain having a composition almost similar of a groundmass grain, red for the perfectly intermediate composition (50% groundmass - 50% plagioclase), white for grain having a composition almost similar of a plagioclase grain (Fig. 7b). The age of each grain population was then modelled by considering its plagioclase/groundmass ratio (dotted black curve in Fig. 7c). The thin section reveals a composition of about 11 vol% of pure plagioclase dated at 1.1 Ma (Table 5), 60 vol% of pure groundmass dated at 184 ka (Table 1), and 29 vol% of mixed grains with mixed ages (Fig. 7c). Applying the mixing theory to our multiphase and multi-age sample (Boven et al. 2001), the whole rock age can be constrained by weighting each grain population age by its proportion of the total:

$$A = (\Sigma\, a_i \times p_i \times K_i) / (\Sigma\, p_i \times K_i) \qquad \text{(Eq. 1)}$$

where a_i, p_i and K_i are ages (right Y-axis values in Fig. 7c), proportions, and K-contents of each grain population i, respectively. Such a calculation using a whole rock age model gives 320 ± 8 ka, 74% older than the groundmass age of 184 ± 5 ka, and in agreement with the 400 ± 160 ka age previously obtained from whole rock data for the same dome (Szakács et al. 2015). The whole rock model age shows the effect of only superficially removing the inherited xenocrysts from groundmass, as performed in the previous K-Ar studies.

A relationship between the volume percentages of glomerocrysts and inherited radiogenic argon was also assessed (Table 4). To apply this, the volume percentage of glomerocrysts is obtained from thin section analysis, and a proxy of inherited radiogenic argon is calculated as follows:

$$^{wr}Ar_i = (^{wr}Age - {}^{gm}Age) / {}^{wr}A \qquad \text{(Eq. 2)}$$

where $^{wr}Ar_i$ is the percentage of radiogenic argon assumed to have originated from inherited minerals, and ^{wr}Age and ^{gm}Age are the ages obtained from whole rock and groundmass analyses, respectively. All samples dated by both techniques were considered. The sample with no glomerocrysts (16CIO08, M. Puturosu dome) is the only one that does not display inherited argon as the whole rock and groundmass ages are coeval. It is also the sample where the CSD plot presents the most linear relationship. This can be taken as a sign of a single crystal population, or a minimal proportion of inherited crystals (coloured curves in Fig. 4a). On the other hand, sample 15CIO09 (Haramul Mare dome) has a 25 % glomerocrysts content by volume, and 84 ± 35 % of its radiogenic argon originates from inherited argon (Table 4). A good correlation (Pearson correlation coefficient R ~ 0.95) exists between glomerocryst abundance and inherited radiogenic argon (Fig. 7). This correlation remains good even if the glomerocryst-free sample (of M. Puturosu) is omitted. The correlation between glomerocryst abundance and inherited radiogenic argon allows a corrected age for the Dealul Taţa dome to be derived. Thin section analysis of the same dome lava, as dated on whole rock at 430 ± 50 ka by Szakács et al. (2015), displays a 23 vol% glomerocryst content. It contains 85 ± 20 % of inherited argon (blue thin lines in Fig. 8) which implies an age of 64 ± 61 ka. This age is still poorly constrained but is consistent with those obtained here for the same area across which are younger than 144 ka (Fig. 1).

Some of our new K-Ar ages are in good agreement with published (U–Th)/He ages (Karátson et al. 2013; Harangi et al. 2015a; Molnár et al. 2018). For the M. Puturosu dome, the (U–Th)/He age of 642 ± 44 ka (Molnár et al. 2018) is similar to both the conventional K-Ar age of 710 ± 40 ka (Szakács et al. 2015) and our new K-Ar age of 704 ± 18 ka, which are all coeval at 2σ. Also, our new ages for the Balvanyos dome, 641 ± 9 ka and 440 ± 12 ka, are similar to the 583 ± 30 ka (U-Th)/He age of Molnár et al. (2018). Note, however, that there is a strong alteration of the dome rocks of the Balvanyos summit, close to where the (U-Th)/He age was obtained (Molnár et al. 2018). Instead, both our dated samples were taken at the periphery of the dome from talus debris containing fresh rocks. Of these samples, the position of 16CIO07 is the most proximal to the dome, and therefore the 641 ± 9 ka date is that proposed to constrain the Balvanyos dome extrusion; overlapping with the 583 ± 30 ka (U-Th)/He age at 2σ.

The Haramul Mic dome was dated at 163 ± 11 ka by (U–Th)/He by Molnár et al. (2018). This is only slightly different (at 2σ) from our age obtained from plagioclase microphenocrysts (245 ± 24 ka). In this case, because our age was considered as a maximum, the younger (U–Th)/He age is more likely. The similar age obtained by both methods confirms the conclusion that the main lava dome activity of Ciomadul started at around 200 ka.

On the other hand, there are also a number of (U–Th)/He ages which are not in agreement with our dates. Of these, the results proposed for the Dealul Cetăţii dome are not coeval even at 2σ: 184 ± 5 ka (this study) and ca. 116 – 142 ka (Karátson et al., 2013). Also, the Piscul Pietros (Köves Ponk) dacitic dome yielded an age of 60 ± 5 ka (this study), which is older than the (U–Th)/He age obtained from zircon (42.9 + 1.4 - 1.5 ka) by Harangi et al. (2015b). In this latter case, that the (U–Th)/He age is possibly too young could be due to three reasons. First, the (U–Th)/He age is significantly lower than the 380 ka-long U–Th secular equilibrium (Farley et al. 2002), consequently it correction of the U-Th concentration at the scale of each dated zircon (Schmitt et al. 2010; Danisik et al. 2012), making the ages very sensitive to the accuracy of such a correction. Secondly, for the Piscul Pietros dome, only four zircons were dated, and only the three oldest are coeval, thus the youngest age should not be considered when calculating the average age. Using only the 3 coeval zircon ages yields an age of about 46 ± 4 ka which is closer to, and compatible with, our K-Ar age at 2σ. Thirdly, extraneous argon from an incomplete removal of xenocrysts for the overestimation of the K-Ar age, as well as partial loss of helium for the underestimation of the (U–Th)/He age, cannot be totally excluded. However, extraneous Ar effects, based on the careful sample preparation are considered minor, if not negligible.

6.3 Difference between groundmass and xenocryst mineral ages

To demonstrate the occurrence of inherited argon, a whole-rock age determination was carried out for the Haramul Mare dome (sample 15CI009, Table 4) following our unspiked K-Ar technique. Several K-bearing phases were also dated to identify which of them were the most susceptible to bias by inherited argon (Table 5 and Fig. 8). With the exception of plagioclase from M. Puturosu dome, all ages were significantly older than the groundmass ages (Tables 2 and 5). Consequently, the younger the juvenile lava of the dome is, the more important the influence of the xenocrysts is on the biased whole-rock age.

The effect of single-step or two-step separation has been assessed by processing two aliquots of sample 15CIOO1. The groundmass obtained from single-step separation gave an age of 202 ± 6 ka, whereas an age of 184 ± 5 ka (i.e. 10% younger) was obtained from the two-step separation (Fig. 10). This age difference can be related to inherited argon from the plagioclase fraction remaining after the single-step separation, assuming that the crystals originate from grains larger than 0.125 mm, i.e. from the size range on the CSD plot that corresponds to the mixing between grains from both grain-size populations (Fig. 4b). As the plagioclases from the glomerocrysts are significantly older (~ 1.4 Ma, see below) than the eruption age (184 ± 5 ka), even a tiny remnant of them within the dated groundmass will produce an overestimated age.

The same issue of inherited glomerocrysts can also be encountered for the late-stage pyroclastic deposits that drape the lower flanks of the Ciomadul dome complex (Karátson et al., 2016). The BIX-2 block-and-ash flow deposit, ~3 km south of Lake St. Ana and ~1 km east of Bixad village (Fig. 1), for instance, is considered younger than 50 ka (Vinkler et al., 2007; Harangi et al., 2010; Karátson et al., 2016), whereas biotite phenocrysts contained within the sample of lava-dome rock yielded an age of 561 ± 19 ka (15CIOX2), categorizing them as xenocrysts. We note that this age is coeval with the age obtained from biotite xenocrysts (569 ± 9 ka, Table 5) from the Dealul Cetăţii dome (184 ± 4 ka, Table 1 and Fig. 1) located 4 km to the north, suggesting that for both eruptions (BIX-2 block-and-ash flow and Dealul Cetăţii dome) the xenocrysts were inherited material originating from the same crystal mush.

The most extreme shift is encountered for the plagioclase glomerocrysts of the Vârful Comlos dome (16CIO02, Table 5). These were dated at 1848 ± 27 ka, compared to 144 ± 4 ka from the groundmass. Considering the freshness of the sample, the loss of potassium (which would increase the age) can be ruled out and, consequently, these plagioclases are considered as the oldest inherited phase incorporated in any rock sample of Ciomadul. Notably, their old age is in the range obtained for the adjacent Pilişca volcano (Pécskay et al., 1995; Szakács et al., 2015; Molnár et al., 2018; Karátson et al., this volume).

The presence of inherited glomerocrysts indicates that the dated lava dome samples do not have a single crystallization age. Furthermore, theses lavas contain minerals having experienced a multi-stage crystallization history, as also confirmed by the abundance of oscillatory zoning in the larger plagioclase population (see, for instance, those in Fig. 3a). Similar assimilation of inherited argon in plagioclase, hornblende and biotite has been reported for the Youngest Toba Tuff eruption (74 ± 4 ka), where these minerals show K-Ar ages predating the eruption by as much as 1.5 Ma (Gardner et al. 2002). In the context of Ciomadul, it has previously been suggested that the crystal mush residing beneath the volcano was rapidly (in < 100 y) remobilized by mafic magmas prior to the latest eruptions after tens of thousands of years of quiescence (Harangi et al. 2015a), as also observed in New Zealand at Taupo (Cole et al. 2014).

The following two arguments suggest that the older ages are due to the presence of argon inherited from the most retentive mineral phases: (1) the rather good correlation between K-Ar ages from the groundmass and the (U-Th)/He ages, and (2) the contrast between groundmass ages and pure mineral phase ages. This latter contrast would not be so important in case of a generalized contamination of the magma by excess argon. Indeed, excess argon tends to be relatively uncommon in minerals from silicic volcanic rocks largely because argon is highly incompatible in all major igneous minerals (Kelley 2002). As already described for Ciomadul (Kiss et al. 2014) and elsewhere (Singer et al. 1998; Stewart 2010; Doherty et al. 2012), the presence of glomerocrysts suggests a long-residence storage of silicic crystal mush in an upper crustal storage zone about 8-12 km below the surface. This may have been remobilized by any subsequent eruption of the dacitic magma (Kiss et al. 2014). At Ciomadul, our geochronological data show that a significant proportion of the 'phenocrysts' in the porphyritic dacites of Ciomadul are in fact old glomerocrysts.

Magma mixing is a widespread igneous phenomenon of variable importance, particularly evident in systems where a vapor-saturated magma reservoir occurs (Anderson 1976). Such mixing between highly crystallized remnant magma of preceding activity with newly injected hot magma prior to eruption has been observed in other volcanic settings such as Unzen (Nakamura 1995), the Mascota - Amatlán de Cañas volcanic fields (Luhr et al. 1989; Gomez-Tuena et al. 2011) and the Palma Sola volcanic field (Gomez-Tuena et al. 2003) in the Trans-Mexican Volcanic Belt volcanism. Of these cases, the Los Azufres volcanic field (Mexico) shows evidence of the presence of a quartzo-feldspathic crystal-mush, located at a depth of around 5 – 10 km (Rangel et al. 2018). Large sanidine, quartz, plagioclase, and amphibole phenocrysts and mineral clots were assimilated from this mush by a melt extraction process, probably triggered by the arrival of a hotter magma at the base of the crystal-mush. This juvenile magma in turn caused reheating and partial melting of the quartzo-feldspathic crystal-mush (Rangel et al. 2018).

The size effect of the analysed minerals has also been checked by dating of plagioclases from samples 16CIO02, 16CIO04 and 16CIO09 (250-500 µm fraction from single-step preparation and 63-125 µm fraction from two-step separation). In all cases (Table 5 and Fig. 8), the larger-sized fraction size gave the oldest ages. This systematic shift toward older ages of large grains substantiates that the population of large plagioclase crystals contains inherited glomerocrysts. The case of sample 16CIO09 is extreme, as the small plagioclase grains gave an age of 201 ± 5 ka, three times older than the groundmass age (60 ± 5 ka) but also five times younger than that obtained on large plagioclase xenocrysts (981 ± 15 ka). This finding implies that in the two-step fraction a significant amount of inherited plagioclase remained in addition to juvenile minerals that crystallised during lava dome cooling. These inherited minerals are either anhedral glomerocrysts (Fig. 3a), or euhedral and zoned individual phenocrysts of plagioclase (Fig. 3a) that must have formed in the magma storage system prior to eruption. Unfortunately, because of the contrast between eruption and inherited mineral ages (which has a difference by a factor of up to 16 in sample 16CIO09), even a small portion of inherited plagioclase remaining in the microphenocrystic fraction extracted from the two-step separation will significantly increase the age obtained. This is the reason why we suggest considering the ages obtained on plagioclase microphenocrysts as maximum ages (16CIO01 on Haramul Mic and 16CIO04 on Ciomadul Mare domes). A similar age range (1 Ma) between multiple dated fractions has been observed on a single basaltic lava sample (from the Tihany Maar Volcanic Complex, Western Hungary) from eight groundmass aliquots showing various density and magnetic properties (Balogh and Nemeth 2005). In this later case, due to a much older eruption age (7.92 ± 0.22 Ma), the difference between the different dated fractions shows less contrast (only 20% of excess). However, as in our study, the oldest age comes from aliquots showing the highest contamination by inherited minerals, while the groundmass aliquot, whose age is closest to that of the eruption, i.e. almost free of inherited minerals, is light and magnetic.

6.4 Magmatic origin of inherited minerals

The apparent presence of inherited argon in the minerals of Ciomadul leads to questions regarding their origin with respect to the argon diffusion law in silicate minerals. Closure temperatures calculated for volume diffusion (e.g. Dodson, 1973) predict that at supra-solidus temperatures, and with extended residence time (> 1 ky), every major mineral phase in these magmas should have remained fully open to argon loss prior to eruption. To explain the presence of inherited argon in magmas, it has been suggested that the incompletely reset minerals were xenocrysts with short (~ 10 years) residence times (Gansecki et al., 1996; Singer et al., 1998; Gardner et al., 2002). This mechanism is particularly likely for relatively small (< 10 km^3) magma bodies (Singer et al. 1998), such as those of Ciomadul. Similar processes operating over similar time scales has been observed at different volcanic context, for instance : (1) the Taupo Volcanic Zone, New Zealand, where a large variations in crystallinity and long magma time residence (up to 250 ky, i.e. same order of magnitude as in Ciomadul) are shown (e.g. Brown et al., 1998; Brown and Fletcher, 1999; Matthews et al., 2012); (2) ongoing eruption of Unzen (Japan) where dacite is formed by mixing of relatively high- and low-temperature end-member magmas (Nakamura 1995; Nishimura et al. 2005). Thermo-mechanical considerations suggest that an effective reactivation of crystal mush is possible when the melt content in the magma reservoir increases to ~60%, allowing eruptible magma to coalesce (Bachmann and Bergantz 2004; Huber et al. 2011).

At Ciomadul, the source of glomerocrysts may be from previous crystallised magma of Ciomadul, i.e. from a disrupted crystal mush (Kiss et al., 2014). The thermobarometrical analysis of amphibole (hornblende and pargasite) crystallisation present in Ciomadul rocks shows that hornblende is xenocrystic, despite the importance of this phase in some domes (Kiss et al. 2014). Plagioclase is present both as inherited glomerocrysts and phenocrysts, because it displays ages either older than (samples 15CIO01, 16CIO02, 16CIO09) or similar (16CIO08) to the groundmass ages. Crystal clots of hornblende and plagioclase observed in some domes (samples 15CIO01, 16CIO02, 16CIO03, 16CIO04, and 16CIO09) suggest that the glomerocrystic material came from sources up to 1.85 Ma old (the oldest age obtained at Ciomadul). Such populations of older crystals contain variably argon-inherited content, explaining spuriously old ages that are common in differentiated lava domes in an arc context (Harford et al. 2002; Zimmerer et al. 2016).

The dominant mechanism for the generation of kinked CSD profiles is magma mixing. This preserves a steep slope for small-sized grains and adds a gentler slope for larger sized crystals, regardless of their proportions (Higgins, 2006). The larger population (phenocrysts/glomerocrysts) can be identified as crystals inherited from one of the parental magmas (crystal mush), whereas the finer population (microphenocrysts) originated from the juvenile parent magma, in addition to the microlitic groundmass. Profiles of CSD data that are particularly kinked validate such a scenario. The fact that both mafic mineral phases and plagioclase show exceedingly similar kinked CSD spectra (i.e. an abnormally large amount of coarse grains) in the Ciomadul lavas strongly supports deep-seated storage as a common feature of this magmatic contribution (Armienti et al. 1994).

The oldest reliable eruption age of the dacitic domes of Ciomadul is around 700 ka (Muntele Puturosu dacitic dome). Another Ciomadul-type dacite dome adjacent to the Pilişca volcano, Bába Laposa (942 ± 65 ka), and the andesitic dome of Dealul Mare (842±53 ka), both dated by (U-Th)/He method (Molnár et al., 2018), are just slightly older. Therefore, the old age obtained on the inherited plagioclase phase (1.85 Ma) points to assimilation of xenocrysts from earlier magmatism, possibly that of the Pilişca volcano itself (Fig. 1). Incorporation of quite old xenocrysts from a crystal mush into dacitic magmas similar to those of Ciomadul has been observed in other volcanic systems. For instance, Nevado de Toluca (Mexico) experienced an eruption at ~13 ka where biotite, up to 4 Ma old, was incorporated and resided in the magma for only a short period of time before it erupted (Arce et al. 2006). One can note that in this example, as well as at Ciomadul, mafic-intermediate magma replenished the system since ∼ 1 Ma and contributed to the eruption of new domes as well as effusive-explosive activity (Torres-Orozco et al., 2017a).

From amphibole thermobarometrical studies, Kiss et al. (2014) suggested a complex and multi-zonal context of polybaric crystallization of amphibole in the mid- to upper crust beneath Ciomadul. Crystallisation of these minerals occurred in a long-lived shallow storage zone (possibly shared with the neighbouring Pilişca volcano) filled with a cold crystal mush

(Kiss et al. 2014) that was subsequently remobilized by the injection of a hot mafic magma, as observed at Unzen, Montserrat or Ruapehu volcanoes (Nakamura 1995; Murphy et al. 2000; Gamble et al. 2003).

Repose periods as long as those occurring between Ciodamul eruptions are frequently observed at these volcanoes fed by intermediate magmas. Illustrated by zircon crystallization ages ranging from 10s to 100s of thousands of years, these volcanoes have experienced prolonged and recurrent presence of melt-bearing magma (Cooper and Reid 2008; Schmitt et al. 2010; Reid et al. 2011; Rubin et al. 2016). The operation of such volcanic plumbing systems generates a large amount of glomerocrystic aggregates made up of minerals, which begin to store radiogenic argon prior to eruption. At Ciomadul, at the depth of 8-12 km proposed by Kiss et al. (2014), the expected crystal-mush temperatures (240 – 300 °C) are in the same order of magnitude as the closure temperature for argon gas in the mineral constituting the crystal clots: ~ 225-300 °C for plagioclase, ~ 350 °C for biotite and K-feldspar, and ~ 600 °C for hornblende (assuming a cooling rate of 10°C/Ma; e.g. McDougall and Harrison, 1999; Cassata et al., 2009; Baxter, 2010). Consequently, these minerals likely began to store radiogenic argon in the crystal mush prior to the eruption. The newly injected magma batches of Ciomadul’s eruptions, provided the heat to remobilise the crystal mush and its constituent mineral phases that had crystallised earlier from an evolved (silica-rich) magma. The biotite ages are significantly younger than those obtained on plagioclase and amphibole (Fig. 9). This can be interpreted as reflecting either a difference in the crystal clot ages from which the mineral originated (younger for biotite than plagioclase/amphibole). Alternatively, it may reflect a different behaviour of these minerals which come from a single source but which have a contrasting response to argon degassing when they are in contact with the replenishing magma. The former hypothesis is more speculative as incorporation of xenocrysts would include all mineral phases present in the crystal mush without segregation, whereas the latter is easily obtained by consideration of diffusion processes.

The coexistence of hornblende and plagioclase in the crystal clots support the interpretation that the xenocrysts came from the same-aged source, and the diffusional Ar loss model implies a complete reset of radiogenic argon in the plagioclases (Gardner et al., 2002). Such results from the 74 ka Toba Tuff were interpreted incompatible with a long storage of xenocrystic minerals in the magma reservoir but, instead, were explained by contamination of the plutonic crystals, preceding the eruption by only a few years (Gardner et al. 2002). Models of diffusion in similar contexts (Gansecki et al. 1996; Gardner et al. 2002; Bachmann et al. 2007) suggest that the magma of most Ciomadul monogenetic domes assimilated the solidified and cooled crystal-mush material (with trapped argon) shortly before extrusion. Consequently, the more than doubling of the xenocryst volume in the Ciomadul lava domes with time (from an average of 7% at 700 ka to ~ 17% at 60 ka, Fig. 11) can be interpreted as increasing assimilation of crystal mush, as it became increasingly fragmented and remobilised (Fig. 11).

6.5 Geochemical evolution of the Ciomadul lava domes

With regard to the new geochronological constraints, we can consider the main petrological and geochemical features of magma evolution through time. Samples with ages > 450 ka seem to be characterized by a higher concentration (~23 vol.%) of plagioclase crystals, whereas their concentration slightly decreases toward the younger domes (~ 15 %) (Fig. 11). This can be attributed to shorter magmatic storage for the progressively younger rocks, limiting the growth of large plagioclase phenocrysts. On the other hand, over the 700 ky long history of Ciomadul's effusive volcanism, the proportion of xenocrysts or glomerocrystic aggregates slightly increases with time (Fig. 11).

While small groundmass microlites grew from their carrier liquid during the final phase of pre-eruptive or post-eruptive crystallization, large glomerocrysts were entrained from a crystal mush. Material erupted in later episodes contains proportionally more mush-derived material (Fig. 11), in relation to a larger amount of assimilation of the silicic crystal mush located beneath the volcano (cf. Kiss et al., 2014). Changes in phase proportions (Table 4 and Fig. 11) between Ciomadul eruptions highlight an increase of the glomerocryst entrainment efficiency during the whole Ciomadul history. With time, the proportion of crystal mush, fragmented during interaction with the new magma, increases. This induces an increasing mobility of the glomerocrysts, allowing them to be more readily remobilised, and eventually assimilated, during the injection of fresh magma. Such a scenario would explain the inherited argon increase through time as more and more inherited crystals are incorporated into the magma reaching the surface (Fig. 11).

Since 250 ka (i.e. over the main phase of Ciomadul dome activity), a temporal evolution in major element oxide concentrations can be seen (Fig. 12). With time, SiO_2 and Na_2O concentrations significantly increase, as does, to a lesser extent, K_2O. On the other hand, elements such as Fe_2O_3, MgO, as well as Al_2O_3, CaO and TiO_2 concentrations slightly decrease. The evolution through time for these oxides highlights the effect of fractional crystallization and the increase of the influence of crystal mush assimilation since 250 ka. The relatively good correlation between the degree of differentiation and time, as well as the general trends in the major element data, support a dual control by crystal-melt fractionation and crystal mush assimilation. Slightly decreasing of the plagioclase content through time as well as the concentrations of CaO and Al_2O_3 could be considered as paradoxical. However, geochemical data provided here are from whole-rock, i.e. from crystal-rich lavas where both plagioclase phenocrysts and xenocrysts influence element oxide concentration. Consequently, the total concentration of plagioclase (phenocryst + xenocryst) present in the lavas increases through time, which is in accordance with the expected behaviour of CaO and Al_2O_3.

7 Conclusions

New unspiked K-Ar dates acquired mostly from the groundmass of lava samples, complemented by major elements geochemistry, provide new insights into the geochronological evolution of the extrusive history of the Late Quaternary Ciomadul volcano. Our dating effort mainly focused on the central, most voluminous, part of Ciomadul, which was hitherto poorly constrained. Following a rigorous process of sample selection and preparation by a two-step separation, we managed to obtain groundmass aliquots avoiding any traces of xenocrysts. Most ages obtained on these groundmass fractions contradict those obtained by whole-rock K-Ar dating reported in previous studies and largely agree with (U-Th)-He ages. Based on the new results, the timing of the extrusive activity at Ciomadul can be summarised as follows: 1) a first stage from ca. 850 ka to 440 ka during which minor extrusive activity occurred in the area of the Puturosu Hills; followed by 2) a shorter but more voluminous second stage from ca. 200 ka to 30 ka. During this second stage, volcanism began (between ca. 200 ka to 130 ka) when the northern and western-central parts of Ciomadul were constructed. Then, after a few tens of thousands of years of quiescence, predominantly effusive activity resumed at ~ 100 ka when the eastern-central part of the dome complex grew. This second phase of activity partly overlapped with the final, highly explosive eruptive phase that began at ~ 51 ka and ended around 29 ka

(Karátson et al. 2016). As the current quiescence period of the volcano is shorter than quiescence periods occurring in its earlier history, Ciomadul cannot be considered extinct.

In addition to the groundmass ages presented here, dating efforts focussing on pure mineral phases highlight that a large amount of inherited argon is responsible for the obvious shift from the systematically older whole-rock to the younger groundmass ages, showing a more or less linear relationship between excess argon and the abundance of inherited crystals. These crystals are more abundant in the younger rocks, indicating increasing contamination of magma by inherited crystals from a crystal mush during volcanic activity at Ciomadul. Some of the inherited crystals must have formed up to 2 Ma ago and may be associated with the neighbouring Pilişca volcano. Such a dual source of composition for the erupted material is noticeable on the kinked CSD plots of the Ciomadul dacitic lavas. Contrasting behaviour of the mineral phases during partial degassing inside the crystal mush, from their formation to the eruption and during their incorporation into the juvenile magma, can explain the wide range of ages obtained in a single sample. Comparison with the geochemical data suggests a magmatic evolution towards more SiO_2-rich products and increasing assimilation and incorporation with time of an earlier-formed crystal mush.

In summary, Ciomadul's initial, sporadic dome extrusions in the SE of the volcanic complex were followed by much larger scale extrusive activity in the central part. The good spatial resolution of the obtained ages provides the basis for an assessment of magma extrusion volumes through time (Karátson et al., this volume). The rigorous sample preparation methodology, the small errors, and a complete analysis of all previously published radiometric ages, validates the reliability of the newly obtained K-Ar ages. This approach, when coupled with CSD and geochemical studies, demonstrates how such an integrated approach can inform on the evolution of magmatic systems, the activity they feed, and the time scales of evolution over hundreds to hundreds-of-thousands of years

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Figure captions

Fig. 1 A) DEM in shaded relief of Eastern Carpathian; B) Location of the main East Carpathian volcanic massifs; C) Ciomadul dome complex. Sample locations (squares) are color-coded according to their sector: red squares: peripheral south-eastern and northern domes; green squares: western-central part of the dome complex; purple squares: eastern-central part of the dome complex. Ages and uncertainties are in ka. St. Ana and Mohoş: uneroded twin craters.

Fig. 2 Photomicrograph of a thin section of the Haramul Mare dome in plane-polarised (A) and cross-polarised (B) view. Plag.: plagioclase; Biot.: biotite; Amp.: amphibole; Glom.: glomerocrysts, mostly composed of plagioclase phenocrysts and small hornblende (Hb.), appear in the upper part as a crystal clot. Width is 10 mm. C) Close-up view of the microlitic groundmass and microphenocrysts.

Fig. 3 Illustration of the procedure of the two-step sample separation from a photomicrograph of sample 15CIO01. Mosaics b, c and d simulate the results of the separation. Each square in these mosaics represents a fraction of the crushed sample that is either kept (visible) or removed (hidden by green squares) during the separation. a) Thin section in cross-polarised light (field of view is 8 mm wide). Labels highlight characteristic anhedral glomerocryst (anh. glom.) and euhedral plagioclase (enh. plag.). b) Grains selected by the first step. Note the small diamond-like phenocryst (at the center left), the peripheral part of large phenocrysts, and the abundance of microphenocrysts (in the upper half) that remain after this first step. c) Grains that remain selected after the second step of preparation. d) Grains that would not be removed from the groundmass in the case of a single-step of separation.

Fig. 4 Semi-log crystal size distribution (CSD) plots for mineral phases in the Ciomadul lava dome A) Plagioclase (black curves) and mafic (amphibole and biotite, grey curves) crystal CSD plot. All but those for sample 16CIO08 (coloured curves) show kinked profiles. Insets show analysed micro-photographs used in the CSD plots in B) and C) (plagioclase in white, mafic crystals in black, groundmass in grey) B) Fitting of a mixture of two magmas with linear CSDs to the observed CSD from samples 16CIO01 and 15CIO09 for plagioclases focussed on the kink zone between the two linear segments for the fine and coarse grains. Regressions though coherent populations, for which assumptions of near-uniform morphologies are valid, are shown as dotted lines. Values for the equation of these regressed lines and R^2 values are given (same box colour as the corresponding line). Inset shows the complete CSD graph. C) Same graph as B) but for mafic (biotite) crystals.

Fig. 5 Graph comparing K-Ar results and those proposed in previous studies. Each dome on this diagram is plotted according to the age obtained by this work (X-axis) vs. the age obtained in previous studies (Y-axis). Error bars and black squares show 2σ (95%) confidence interval.

Fig. 6 A) K_2O vs SiO_2 diagram (Peccerillo and Taylor; 1976), for Ciomadul lava dome samples; B) Harker diagrams showing the variations of major element oxides as a function of SiO_2.

Fig. 7 Whole-rock age model from thin section analysis (sample 15CIO01, same as Fig. 3). a) Upper left: Identification of the mineral phases by binarization; lower right: Mosaicing of previous image to simulate 200 µm grain size. b) Grain composition analysis from their grayscale properties (converted to colour for easier identification). Yellow: pure plagioclase;

blue: groundmass; shaded white to red to black: mixed grains with increasing proportion of groundmass grains. c) Distribution of the grain density proportion (left Y-axis) and ages modelled for each grain composition (dotted black curve scaled on the right Y-axis). Bottom scale defines the expected density of the respective grain populations.

Fig. 8 Graph of the inherited argon abundance (deduced from whole-rock ages) versus abundance of glomerocrysts (in vol%). Heavy lines display a ± 1σ correlation trend. Thin horizontal lines are the estimation (± 1σ) of inherited argon abundance for the Dealul Cetăţii dome obtained from the analysis of its thin section in order to propose a corrected eruption age.

Fig. 9 Compilation of the ages obtained on groundmass and separated minerals. Samples are sorted with respect to the distance to the ~2 Ma old Pilişca volcano.

Fig. 10 Map of the ages (in ka) obtained from the different phases of the Dealul Cetăţii dome (15CIO01). The small and large grids correspond to the two-step and single-step procedure, respectively.

Fig. 11 Graph of the evolution of abundance of phenocrysts, glomerocrysts (in vol% of dome, on left axis) and amount of argon inherited from xenocrysts (in %, on right axis) versus eruption age. Boxes show global trends for each parameter. Schematic cartoon summarizing a scenario for the assimilation of xenocrysts by dacitic magma based on crystal mush disaggregation and increasing incorporation of inherited crystals in juvenile magma trough time (modified from Neave et al., 2017). The figures are not to scale.

Fig. 12 Geochemical evolution of major element oxides (in wt. %) of dacitic domes of Ciomadul through time (eruption ages in ka).

Table_01

Table 1 CSD input parameters and results, including crystal habit and L_{max}.

Sample	Mineral	Count	Crystal Habit				Shape	L_{max}	Phase
			Short	Interm.	Long	R^2 values		(mm)	proportion
16CIO08	Plagioclase	8164	1	1.5	3	0.86	Tabular	2.93	35.2%
16CIO08	Mafic m.	5454	1	1.5	3	0.85	Columnar	1.58	12.3%
15CIO01	Plagioclase	3465	1	1.3	2.1	0.88	Tabular	4.20	29.5%
15CIO01	Mafic m.	2781	1	1.25	2.1	0.83	Columnar	1.39	7.9%
15CIO09	Plagioclase	5720	1	1.25	2.1	0.86	Tabular	4.79	38.0%
15CIO09	Mafic m.	2008	1	1.5	3	0.88	Columnar	2.08	11.3%
16CIO09	Plagioclase	3020	1	1.3	2.2	0.87	Tabular	4.31	33.7%
16CIO09	Mafic m.	3486	1	1.6	2.9	0.88	Columnar	1.55	7.4%

Table_02

Table 2 K-Ar ages obtained in this study for Ciomadul lava domes. (G.M.: groundmass; : Plag. µP.: plagioclase microphenocrysts; D.S.: two-step separation; S.S.: single-step separation); Sample coordinates are projected using the Universal Transverse Mercator (UTM) projection (zone 35 N).

stage	Sample code Dome Name	Easting (in m)	Northing (in m)	Eleva-tion (m asl)	Dated phase	Fraction Size (µm)	K%	$^{40}Ar^*$ ± 1σ (in % of total ^{40}Ar)		$^{40}Ar^*$ relative uncertainty	$^{40}Ar^*$ ± 1σ $\times 10^{11}$ at/g		Age ± 1σ (in ka)		Weighted mean age ± 1σ
1st stage	16CIO08	418645	5107909	1099	G.M.	63-125	3.226	5.233	0.169	0.726%	23.29	0.885	691	17	
	Muntele Puturosu							4.489	0.108	0.446%	24.26	0.485	720	19	**704 ± 18**
	16CIO07	419620	5107472	846	G.M.	63-125	3.585	29.213	0.089	0.373%	23.78	2.592	635	10	
	Balvanyos							34.293	0.065	0.268%	24.19	2.225	646	9	**641 ± 9**
	16CIO06	419673	5107443	856	G.M.	63-125	3.449	4.283	0.043	0.280%	15.45	0.185	429	12	
	Balvanyos							4.488	0.101	0.624%	16.24	0.455	451	12	**440 ± 12**
2nd stage	16CIO01	416986	5114107	866	Plag.	63-125	1.336	1.025	0.201	6.438%	3.127	0.206	224	26	
	Haramul Mic				µP.			1.211	0.076	2.065%	3.680	0.092	264	23	**245 ± 24**
	15CIO01	413713	5110905	994	G.M.	63-125	3.722	4.399	0.084	1.182%	7.139	0.371	184	5	
	Dealul Cetăţii							4.170	0.075	1.055%	7.132	0.314	183	5	**184 ± 5**
	16CIO02	413146	5109912	1242	G.M.	63-125	3.471	4.266	0.055	1.055%	5.220	0.235	144	4	
	Vârful Comlos							4.234	0.016	0.307%	5.209	0.068	144	4	**144 ± 4**
	16CIO04	413873	5109760	1260	Plag.	40-80	1.391	1.209	0.029	1.655%	1.725	0.034	119	10	
	Ciomadul Mare				µP.			1.508	0.049	2.322%	2.102	0.074	145	10	**133 ± 18**
	15CIO09	416664	5111953	902	G.M.	63-125	3.668	6.414	0.042	1.107%	3.754	0.267	98	2	
	Haramul Mare							12.020	0.073	2.005%	3.639	0.877	95	2	**96 ± 2**
	16CIO09	415362	5108313	1101	G.M.	63-125	3.441	1.162	0.058	2.840%	2.042	0.067	57	5	
	Piscul Pietros							1.323	0.063	2.797%	2.239	0.083	62	5	**60 ± 5**

Table_03

Table 3 Major element concentrations for the Ciomadul lava domes (in wt%%).

Sample	15CIO09	16CIO01	16CIO02	16CIO03	16CIO04	16CIO05	16CIO06	16CIO07	16CIO08	16CIO09	16CIO11
SiO2	65.26	66.18	66.59	65.60	66.87	66.50	61.80	61.74	64.68	67.07	67.36
TiO2	0.45	0.35	0.38	0.37	0.32	0.32	0.52	0.53	0.53	0.31	0.29
Al2O3	16.85	16.46	16.62	16.62	16.29	16.20	17.35	17.43	17.82	16.15	16.26
Fe2O3	2.86	2.41	2.47	2.51	2.28	2.28	3.54	3.65	2.22	2.11	1.99
MnO	0.06	0.05	0.05	0.05	0.05	0.05	0.07	0.07	0.04	0.05	0.04
MgO	1.93	1.54	1.64	1.67	1.52	1.51	2.18	2.22	1.33	1.39	1.32
CaO	4.03	3.55	3.66	3.65	3.22	3.26	4.78	4.94	3.56	3.00	2.89
Na2O	4.34	4.07	4.34	4.24	4.30	4.31	4.22	4.33	4.36	4.43	4.67
K2O	3.36	3.46	3.32	3.21	3.61	3.57	3.40	3.20	3.28	3.55	3.50
P2O5	0.20	0.12	0.16	0.14	0.13	0.14	0.18	0.18	0.13	0.11	0.12
LOI	0.3	1.5	0.4	1.6	1.1	1.5	1.6	1.3	1.6	1.5	1.2
Sum	99.64	99.69	99.63	99.66	99.69	99.64	99.64	99.59	99.55	99.67	99.64

Table_04

Table 4 Comparison between new and previously proposed ages. For each dated dome, abundance (in vol%) are given for: K-bearing minerals (P.: plagioclase; B.: biotite; A.: amphibole), total of K-bearing phenocrysts (T. Ph.:); glomerocrysts (Glom.); and groundmass (G.M.);; W.-R. Age: previously proposed age on whole-rock for the same lava dome; $Ar_{inherited}$: fraction (in %) of the total of radiogenic argon assumed to be inherited; Source: references for whole rock and (U–Th)/He ages: 1: Casta (1980); 2: Pécskay et al. (1992); 3: Pécskay et al. (1995b); 4: Karátson et al., (2013); 5 : Szakács et al. (2015); 6: Harangi et al. (2015b); 7: Molnár et al. (2018); 8: this work

Location	**New measurements (this work)**								**Previously proposed ages**				
	Cassignol-Gillot (unspike) method								**Traditional K-Ar method**			**(U–Th)/He method**	
	Sample	**Phenocryst vol%**			**T. Ph. vol%**	**Glom. vol%**	**G.M. vol%**	**Age (in ka)**	**W.-R. age**	**Sour-ce**	**$Ar_{inherited}$ (%)**	**(U–Th)/He Age**	**Sour-ce**
		P.	**B.**	**A.**									
Puturosul	16CIO08	19	2	5	26	1	65	704 ± 18	710 ± 50	5	1 ± 7	642 ± 44	7
Bálványos	16CIO07	25	3	8	36	14	39	641 ± 9	1020 ± 150	3	37 ± 16	583 ± 30	7
Bálványos	16CIO06	23	1	7	31	13	47	440 ± 12	920 ± 180	3	52 ± 22		
Haramul Mic	16CIO01	10	2	7	19	18	54	245 ± 24	850 ± 200	1	71 ± 29	154 ± 16	7
Dealul Cetăţii	15CIO01	11	2	6	19	17	56	184 ± 5	400 ± 160	5	54 ± 45	116 – 142	4
Haramul Mare	15CIO09	12	4	6	22	16	44	96 ± 2	590 ± 160	3			
									231 ± 5	8	58 ± 3		
Piscul Pietros	16CIO09	21	2	8	30	23	47	60 ± 5	560 ± 110	2	89 ± 26	42.9 ± 1.5	6
Vârful Comlos	16CIO02	14	2	8	22	8	59	144 ± 4					
Ciomadul Mare	16CIO04	22	2	10	34	13	41	133 ± 18					

Table_05

Table 5 K-Ar ages obtained on separated pure phases, larger grain size groundmass, and whole rock. Dated phases: Amp.: Amphibole; Biot.: Biotite; Gr.M.: groundmass; Plag. µL.: plagioclase microlites; Plag. Gl.: plagioclase glomerocrysts; W.R.: whole rock

Sample code	**Dated phase**	**Me-thod**	**Fraction Size (µm)**	**K%**	**^{40}Ar* ± 1σ (in % of total ^{40}Ar)**		**^{40}Ar* relative uncertainty**	**^{40}Ar* ± 1σ ×10^{11} at/g**		**Age ± 1σ (in ka)**		**Weighted mean age ± 1σ**	
15CIO01	Amp.	S.S.	125-250	0.931	11.113	0.030	0.270%	13.85	0.037	1423	24		
					27.431	0.153	0.558%	13.34	0.074	1371	21	**1386**	**37**
15CIO01	Plag. Gl.	S.S.	125-250	0.822	7.353	0.053	0.721%	9.72	0.070	1132	24	**1132**	**24**
15CIO01	Biot.	S.S.	125-250	6.532	20.605	0.024	0.116%	38.88	0.045	570	9		
					16.920	0.029	0.171%	38.81	0.067	569	9	**569**	**9**
15CIO01	Gr.M.	S.S.	125-250	3.612	4.039	0.038	0.941%	7.70	0.072	204	6		
					3.874	0.056	1.446%	7.52	0.109	199	7	**202**	**6**
16CIO02	Plag. Gl.	S.S.	250-500	0.655	24.750	0.087	0.352%	12.66	0.044	1848	28	**1848**	**28**
16CIO02	Plag. µL.	D.S.	63-125	0.654	7.503	0.036	0.480%	7.32	0.035	1071	21	**1071**	**21**
16CIO09	Plag. Gl.	S.S.	250-500	0.757	35.123	0.139	0.396%	7.55	0.030	955	14		
					35.222	0.114	0.324%	7.96	0.026	1007	15	**981**	**15**

16CIO09	Plag. µL.	D.S.	63-125	1.714	6.101	0.039	0.639%	3.60	0.023	201	5	**201**	**5**
16CIO09	Biot.	S.S.	125-250	6.762	8.071	0.037	0.458%	13.87	0.064	196	4	**196**	**4**
16CIO08	Plag. µL.	D.S.	63-125	1.568	4.834	0.031	0.641%	12.01	0.077	733	19		
					4.585	0.047	1.025%	12.19	0.125	744	21	**739**	**20**
16CIO04	Plag. µL.	D.S.	63-125	1.104	1.422	0.039	2.742%	1.96	0.054	170	13		
					1.523	0.042	2.758%	1.84	0.051	160	12	**165**	**12**
15CIO09	W.R.	S.S.	40-500	2.119	7.907	0.120	1.518%	5.10	0.077	230	6		
					7.874	0.036	0.457%	5.11	0.023	231	5	**231**	**5**
15CIOX2	Biot.	S.S.	125-250	5.720	3.242	0.048	1.481%	33.54	0.497	561	21	**561**	**21**

Figure_01

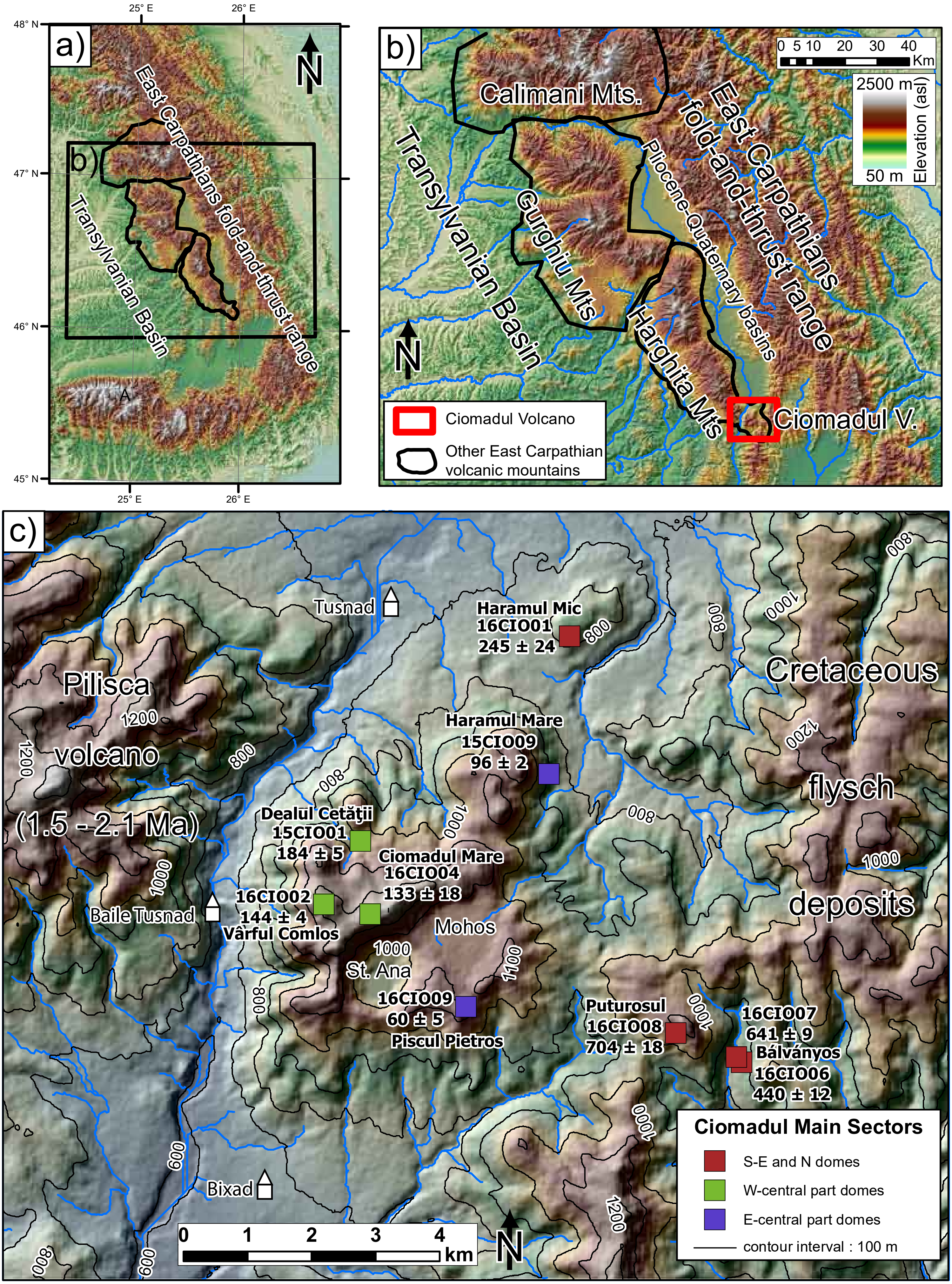
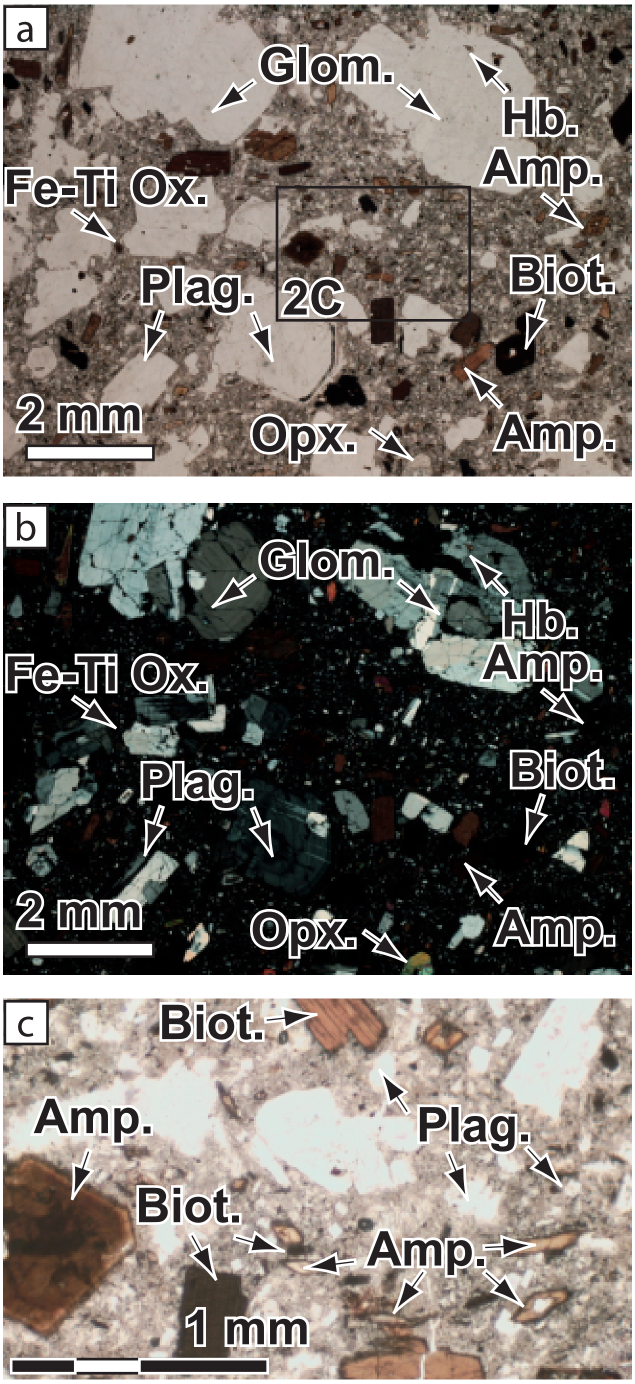

a)
b)
25° E
26° E
48° N
47° N
46° N
45° N
N
East Carpathians fold-and-thrust range
Transylvanian Basin
Calimani Mts.
Transylvanian Basin
Gurghiu Mts
Harghita Mts
Pliocene-Quaternary basins
East Carpathians fold-and-thrust range
Ciomadul V.
0 5 10 20 30 40 Km
2500 m
50 m
Elevation (asl)
Ciomadul Volcano
Other East Carpathian volcanic mountains
c)
Pilisca volcano (1.5 - 2.1 Ma)
Tusnad
Baile Tusnad
Bixad
Haramul Mic 16CIO01 245 ± 24
Haramul Mare 15CIO09 96 ± 2
Dealul Cetății 15CIO01 184 ± 5
Ciomadul Mare 16CIO04 133 ± 18
16CIO02 144 ± 4
Vârful Comlos
Mohos
St. Ana
16CIO09 60 ± 5
Piscul Pietros
Puturosul 16CIO08 704 ± 18
16CIO07 641 ± 9
Bálványos 16CIO06 440 ± 12
Cretaceous flysch deposits
0 1 2 3 4 km
Ciomadul Main Sectors
S-E and N domes
W-central part domes
E-central part domes
contour interval : 100 m

Figure_02



a
Glom.
Hb.
Amp.
Fe-Ti Ox.
2C
Plag.
Biot.
2 mm
Opx.
Amp.
b
Glom.
Hb.
Amp.
Fe-Ti Ox.
Plag.
Biot.
2 mm
Opx.
Amp.
c
Biot.
Amp.
Plag.
Biot.
Amp.
1 mm

Figure_03

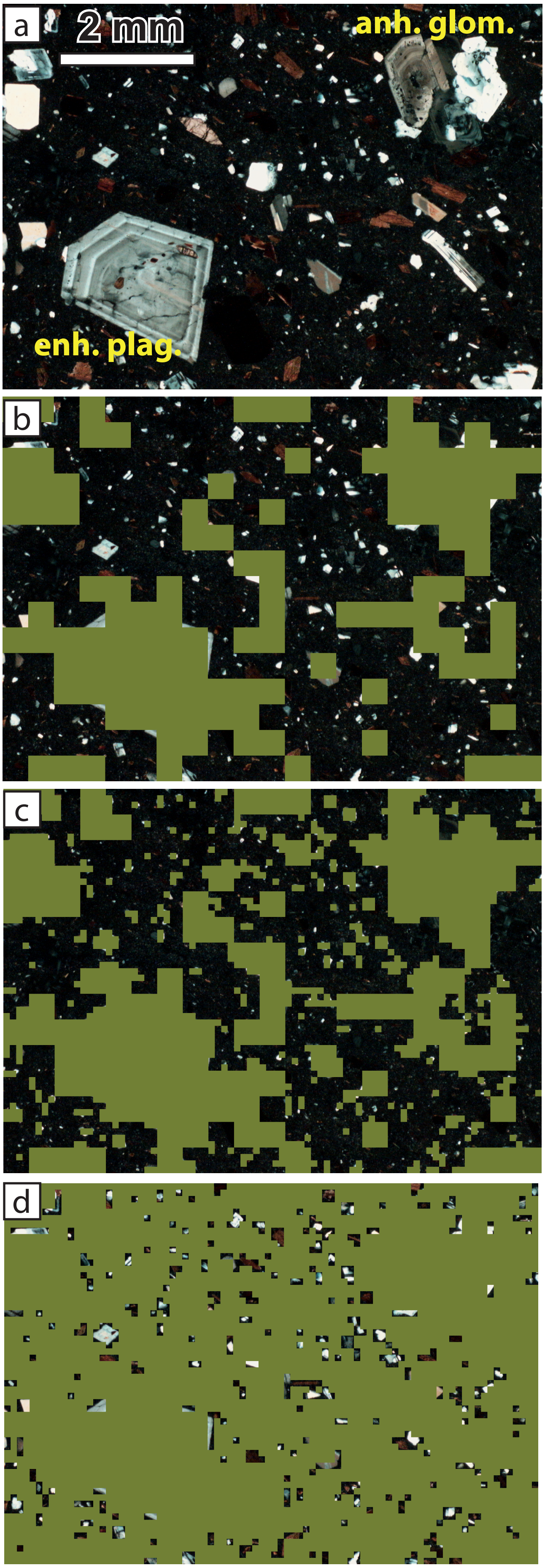
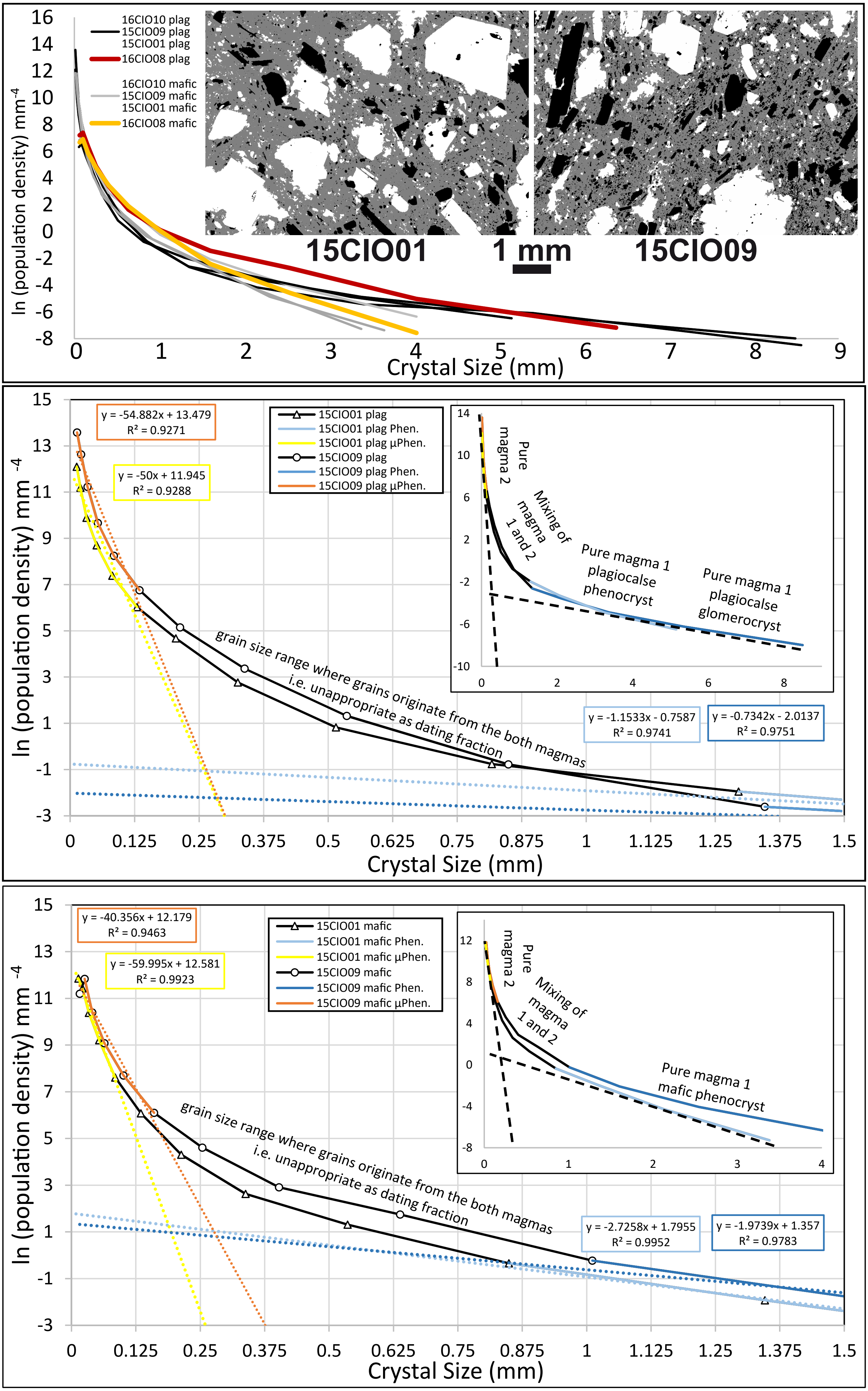
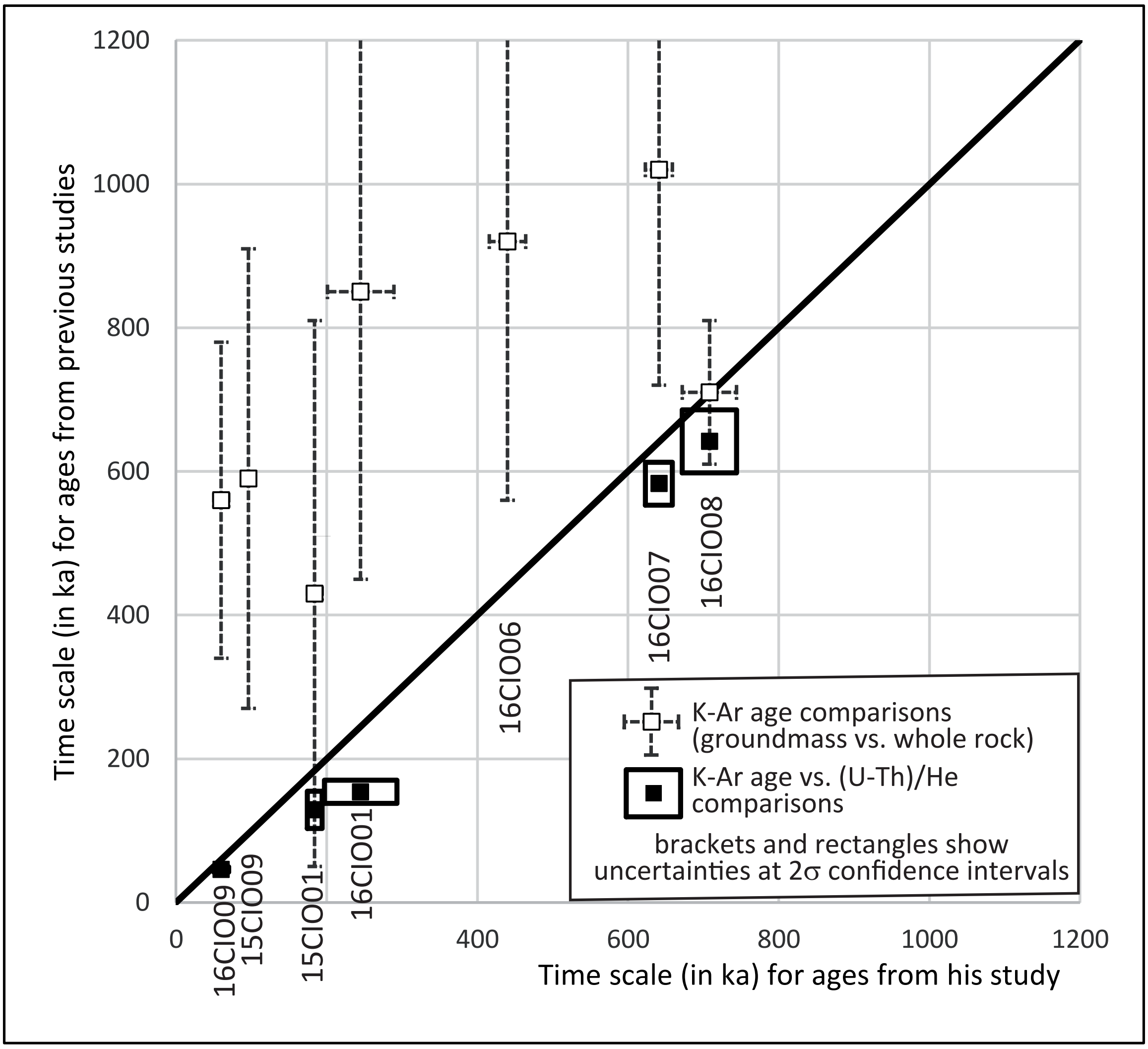


Figure_04



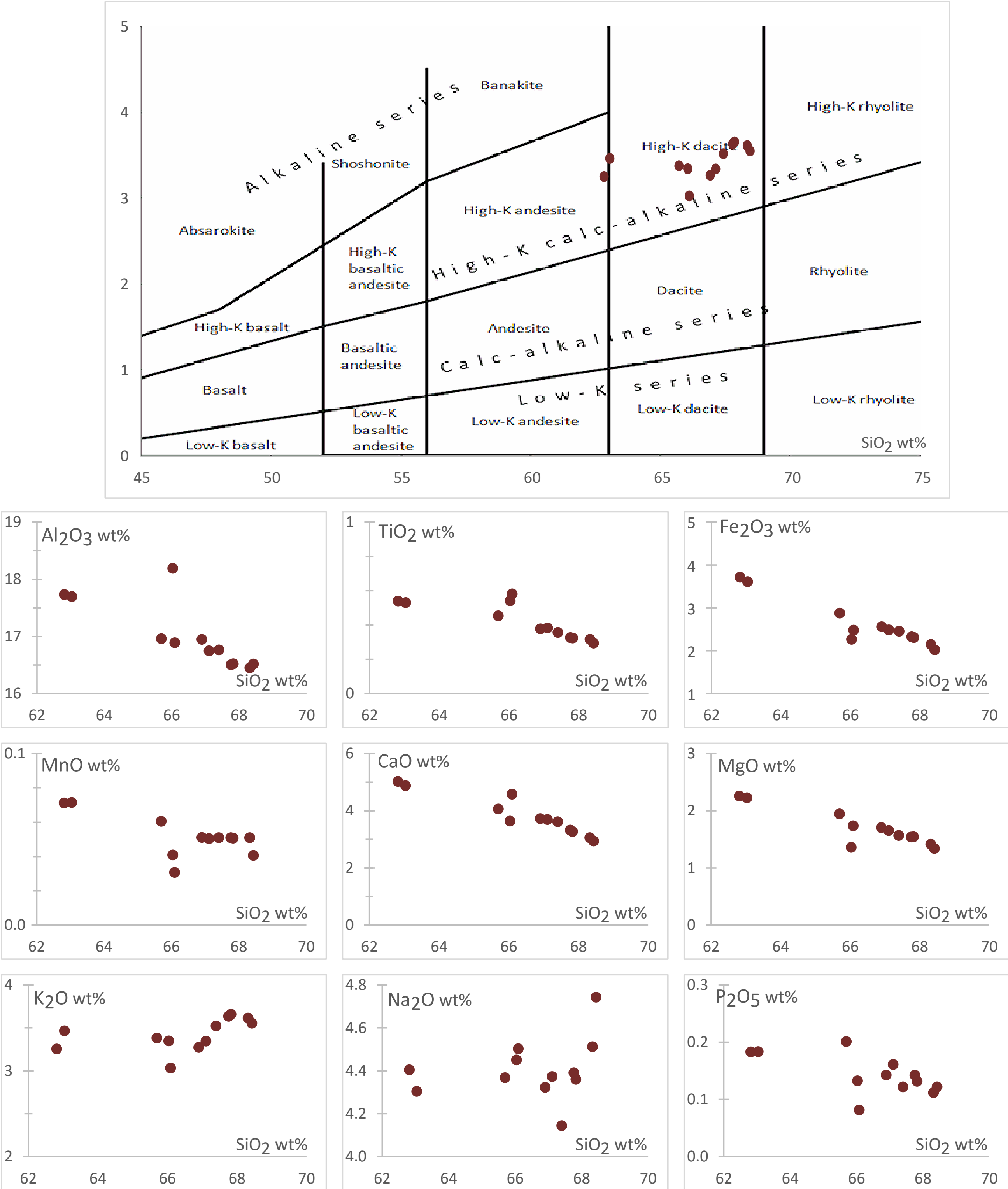
16CIO10 plag
15CIO09 plag
15CIO01 plag
16CIO08 plag
16CIO10 mafic
15CIO09 mafic
15CIO01 mafic
16CIO08 mafic
15CIO01
1 mm
15CIO09
ln (population density) mm-4
Crystal Size (mm)
y = -54.882x + 13.479
R² = 0.9271
y = -50x + 11.945
R² = 0.9288
15CIO01 plag
15CIO01 plag Phen.
15CIO01 plag µPhen.
15CIO09 plag
15CIO09 plag Phen.
15CIO09 plag µPhen.
Pure magma 2
Mixing of magma 1 and 2
Pure magma 1 plagiocalse phenocryst
Pure magma 1 plagiocalse glomerocryst
grain size range where grains originate from the both magmas
i.e. unappropriate as dating fraction
y = -1.1533x - 0.7587
R² = 0.9741
y = -0.7342x - 2.0137
R² = 0.9751
y = -40.356x + 12.179
R² = 0.9463
y = -59.995x + 12.581
R² = 0.9923
15CIO01 mafic
15CIO01 mafic Phen.
15CIO01 mafic µPhen.
15CIO09 mafic
15CIO09 mafic Phen.
15CIO09 mafic µPhen.
Pure magma 1 mafic phenocryst
y = -2.7258x + 1.7955
R² = 0.9952
y = -1.9739x + 1.357
R² = 0.9783

Figure_05



1200
1000
800
600
400
200
0
0
400
600
800
1000
1200
Time scale (in ka) for ages from previous studies
Time scale (in ka) for ages from his study
16CIO09
15CIO09
15CIO01
16CIO01
16CIO06
16CIO07
16CIO08
K-Ar age comparisons
(groundmass vs. whole rock)
K-Ar age vs. (U-Th)/He
comparisons
brackets and rectangles show
uncertainties at 2σ confidence intervals

Figure_06



Alkaline series
Banakite
High-K rhyolite
High-K dacite
Shoshonite
Absarokite
High-K andesite
High-K calc-alkaline series
High-K basaltic andesite
Rhyolite
Dacite
High-K basalt
Andesite
Basaltic andesite
Calc-alkaline series
Basalt
Low-K series
Low-K dacite
Low-K rhyolite
Low-K andesite
Low-K basaltic andesite
Low-K basalt
SiO2 wt%
Al2O3 wt%
TiO2 wt%
Fe2O3 wt%
MnO wt%
CaO wt%
MgO wt%
K2O wt%
Na2O wt%
P2O5 wt%

Figure_07

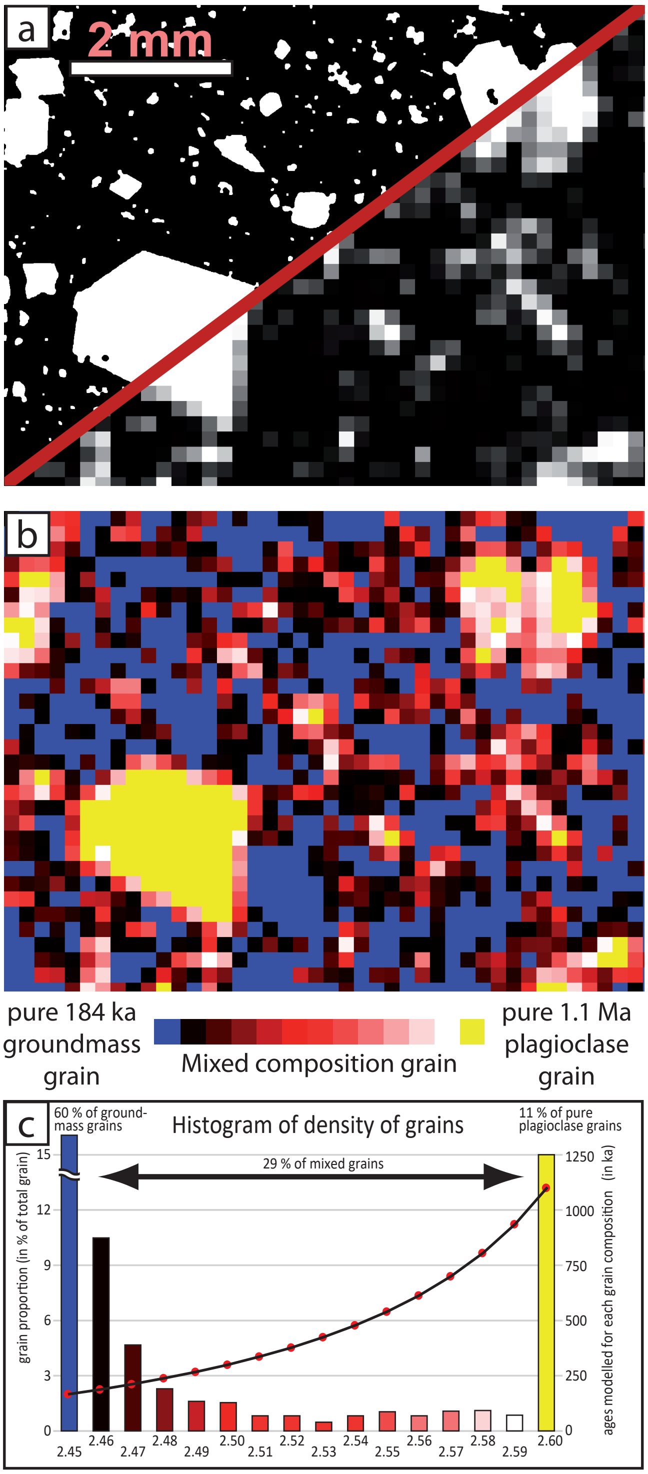
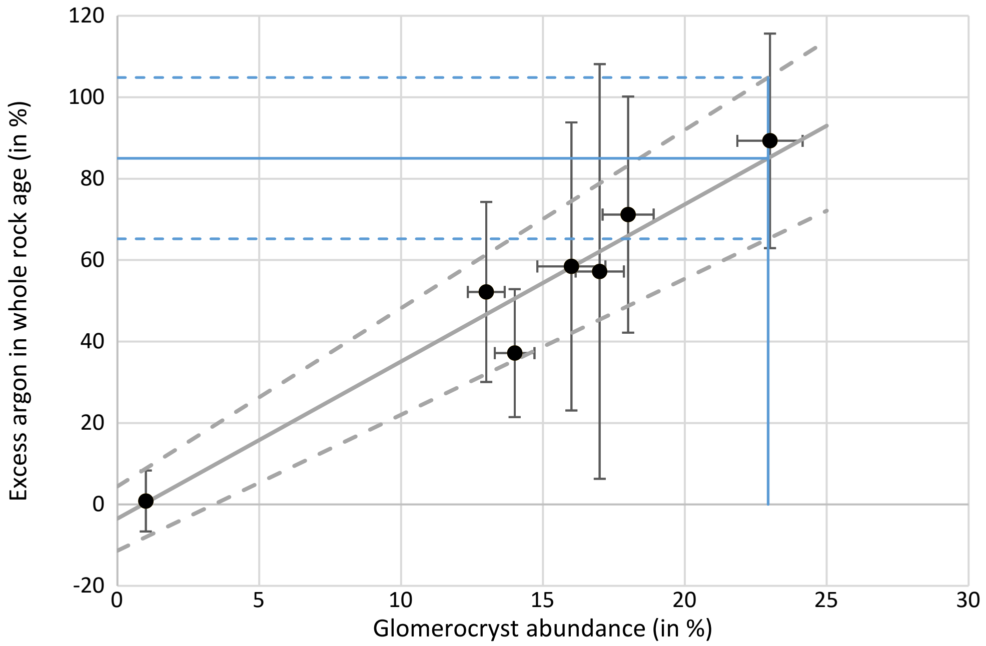
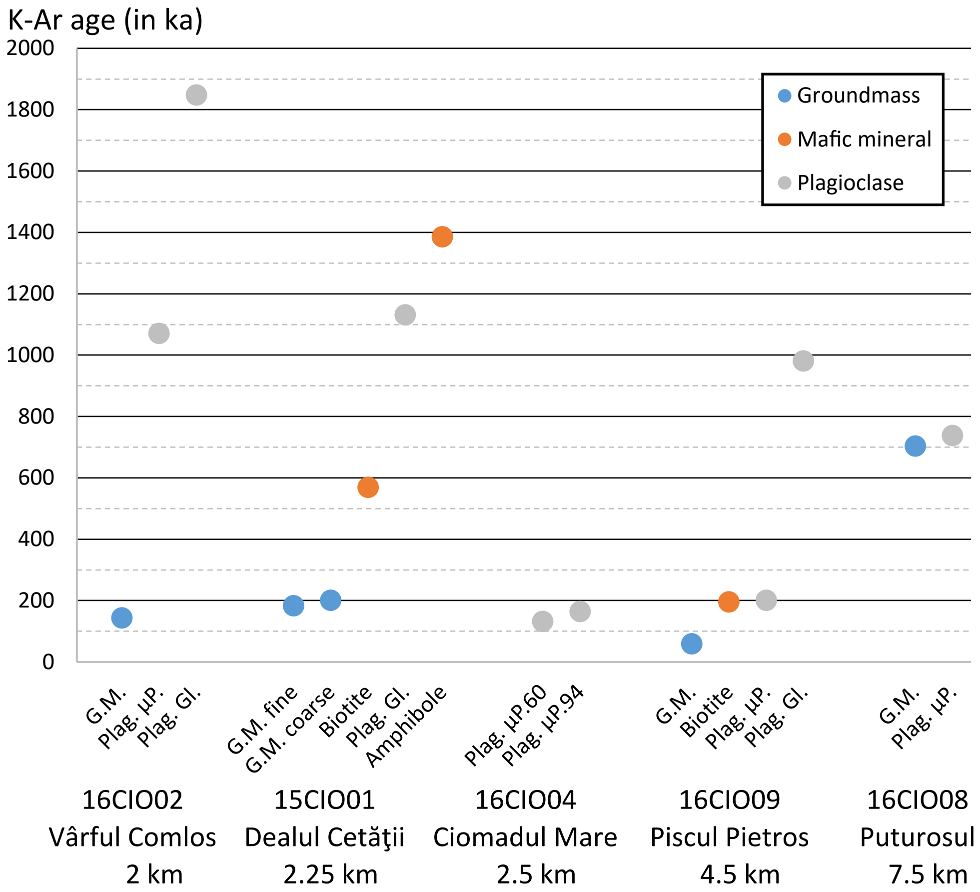

a
2 mm
b
pure 184 ka groundmass grain
Mixed composition grain
pure 1.1 Ma plagioclase grain
c
60 % of ground-mass grains
Histogram of density of grains
11 % of pure plagioclase grains
29 % of mixed grains
grain proportion (in % of total grain)
ages modelled for each grain composition (in ka)
0
3
6
9
12
15
0
250
500
750
1000
1250
2.45
2.46
2.47
2.48
2.49
2.50
2.51
2.52
2.53
2.54
2.55
2.56
2.57
2.58
2.59
2.60

Figure_08



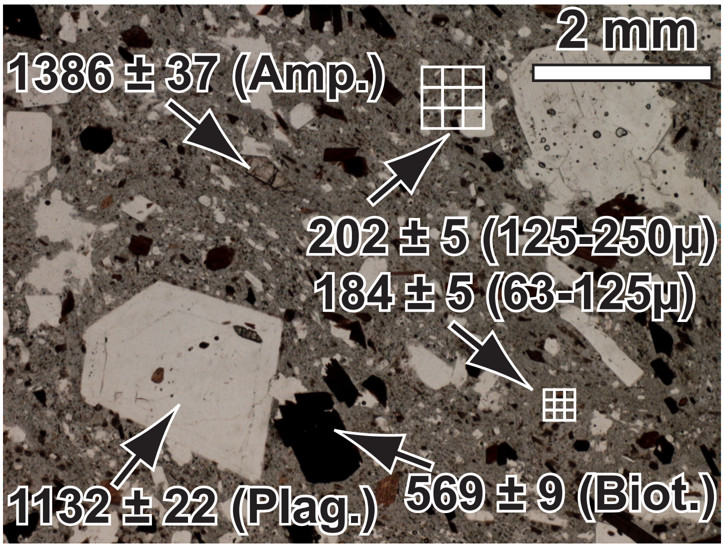
120
100
80
60
40
20
0
-20
0
5
10
15
20
25
30
Excess argon in whole rock age (in %)
Glomerocryst abundance (in %)

Figure_09



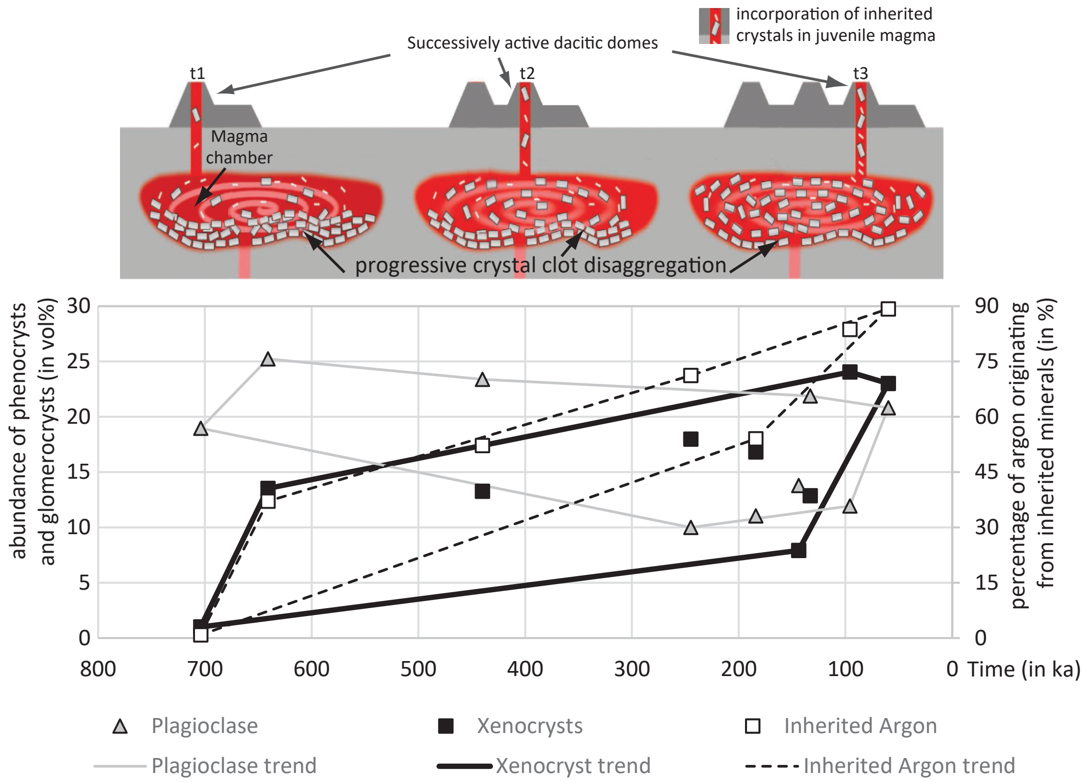
K-Ar age (in ka)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
Groundmass
Mafic mineral
Plagioclase
G.M.
Plag. µP.
Plag. Gl.
G.M. fine
G.M. coarse
Biotite
Plag. Gl.
Amphibole
Plag. µP.60
Plag. µP.94
G.M.
Biotite
Plag. µP.
Plag. Gl.
G.M.
Plag. µP.
16CIO02
Vârful Comlos
2 km
15CIO01
Dealul Cetăţii
2.25 km
16CIO04
Ciomadul Mare
2.5 km
16CIO09
Piscul Pietros
4.5 km
16CIO08
Puturosul
7.5 km

Figure_10



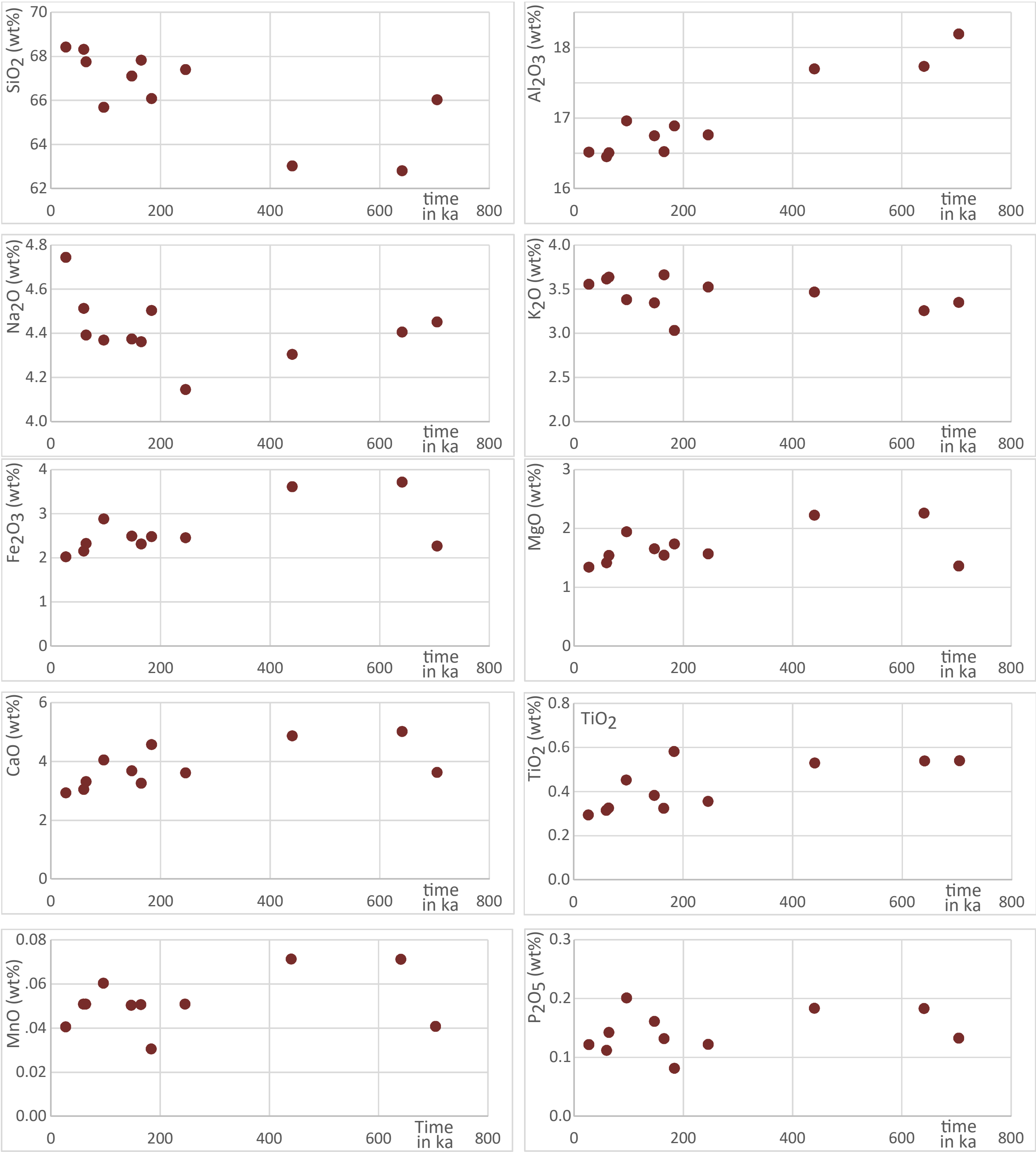
1386 ± 37 (Amp.)
2 mm
202 ± 5 (125-250μ)
184 ± 5 (63-125μ)
1132 ± 22 (Plag.)
569 ± 9 (Biot.)

Figure_11



incorporation of inherited crystals in juvenile magma
Successively active dacitic domes
t1
t2
t3
Magma chamber
progressive crystal clot disaggregation
abundance of phenocrysts and glomerocrysts (in vol%)
percentage of argon originating from inherited minerals (in %)
Time (in ka)
Plagioclase
Xenocrysts
Inherited Argon
Plagioclase trend
Xenocryst trend
Inherited Argon trend

Figure_12



SiO2 (wt%)
Al2O3 (wt%)
Na2O (wt%)
K2O (wt%)
Fe2O3 (wt%)
MgO (wt%)
CaO (wt%)
TiO2 (wt%)
TiO2
MnO (wt%)
P2O5 (wt%)
time in ka
Time in ka