Characterization of the metasomatizing agent in the upper mantle beneath the northern Pannonian Basin based on Raman imaging, FIB-SEM and LA-ICP-MS analyses of silicate melt inclusions in spinel peridotite

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Abstract

Silicate melt inclusions (SMI) containing several daughter minerals, residual glass and a CO_2 bubble were analyzed to constrain the composition and evolution of the metasomatic melt present in the upper mantle beneath the Nógrád-Gömör Volcanic Field (NGVF), northern Hungary – southern Slovakia. The SMI were analyzed with a combination of Raman spectroscopy, FIB-SEM and LA-ICP-MS to identify phases and obtain their volume proportions and major- and trace-element geochemistry. Slicing through the entire volume of the inclusions and collecting geochemical information at each slice with FIB-SEM allowed us to model the 3D appearance of the phases within the SMI, and to use this information to calculate bulk major-element compositions.

The partially crystallized SMI are hosted in clinopyroxene in a lherzolite xenolith that shows evidence of a metasomatic event that altered the lherzolites to produce wehrlites. Based on bulk compositions, the SMI trapped the metasomatic melt linked to wehrlite formation in the NGVF. The melt is enriched in Fe and has an OIB-like trace-element pattern, which suggests an intraplate mafic melt similar to the host basalt, but with slightly different chemistry. Pre-entrapment evolution and reaction with the lherzolite wall rock produced an intermediate melt composition. Petrogenetic modeling indicates that the melt was generated as a result of a very small degree of partial melting of a garnet lherzolite source. Following entrapment, a volatile bubble exsolved from the residual melt during ascent to shallow depths as suggested by consistent densities of CO_2 in vapor bubbles. Small crystals, including sulfates and mica, that formed at the boundary of the bubble and the glass indicate that the exsolved fluid originally contained S and H_2O, in addition to CO_2.

Introduction

Primary silicate melt inclusions (SMI) hosted by upper mantle minerals have been commonly used to characterize the melts that infiltrate and react with the mantle phases (e.g., Schiano et al. 1992; 2000; Szabó et al. 1996; 2009; Zajacz et al. 2007; Hidas et al. 2010; Duan et al. 2014). The SMI are considered to represent the original melt composition at the time of entrapment at mantle conditions (Schiano et al. 1992; 2000; Frezzotti 2001). The trapped melt droplet remains isolated, i.e., behaves as a closed system and evolves independently from the host (e.g., Roedder 1984) because of the high elastic modulus of the host minerals that prevents decompression and volumetric changes during and after ascent to the surface (Schiano and Bourdon 1999). However, diffusion into or out of the SMI may still occur to different extents for different elements, depending on the concentrations and diffusion coefficients of the given element in the host mineral. Therefore, in general, the elements most likely to retain their original concentrations in the SMI are those that are least compatible with the host (Qin et al. 1992). Consequently, melt inclusions, if present in great abundance, can be a significant reservoir for incompatible trace elements and volatiles that tend to partition in the melt.

Fluid and silicate melt inclusions are common in peridotite xenoliths of the Carpathian-Pannonian region (CPR) and have been the subject of numerous studies, especially from the Bakony-Balaton Highland (e.g., Török 1995; Szabó et al. 2009; Hidas et al. 2010; Berkesi et al. 2012). The melt inclusions have been interpreted to represent a mafic melt of asthenospheric origin, which obtained an evolved character via interaction with a metasomatized mantle prior to entrapment (Szabó et al. 2009). In the Nógrád-Gömör Volcanic Field (NGVF), two types of SMI have been described. Olivine-hosted SMI in xenoliths from one locality were interpreted to be remnants of a volatile-rich, subduction-related melt which was also responsible for modal metasomatism in the xenoliths (Szabó et al. (1996). These SMI had variable compositions (basaltic to andesitic), which was explained by entrapment at different stages of melt evolution. The other type of SMI hosted in olivine in clinopyroxene-rich cumulate xenoliths represents an evolved version of the alkali basaltic melt underplating the Moho prior to eruption of the host magma (Zajacz et al. (2007).

Previous studies (Liptai et al. 2017; Patkó et al. 2020) classified peridotite xenoliths in the NGVF into two suites based on their modal composition and texture: a dominant 'lherzolitic' suite with no or minimal textural evidence for metasomatism and with both ortho- and clinopyroxenes present as individual grains , and a 'wehrlitic' suite, with clear reaction textures and orthopyroxene absent, except for minor remnant cores within clinopyroxene and olivine. It has been established that the wehrlite suite is the product of interaction between an infiltrating mafic melt and the lherzolite wall rock (Patkó et al. 2020). Recently, primary SMI have been found in clinopyroxene in a xenolith that is part of the lherzolite suite, based on the presence of orthopyroxene. The goal of this study is to characterize the origin, trapping conditions and post-entrapment evolution of these SMI.

Geological setting

The Pannonian Basin in the Carpathian-Pannonian region (CPR) formed during the late Oligocene – early Miocene following the juxtaposition of two microterranes, the Alcapa and Tisza-Dacia (Csontos et al. 1992). During the Neogene, extension driven by subduction rollback on the eastern margin of the CPR (Horváth 1993; Csontos 1995) dominated the tectonics of the region. The extension was accompanied by asthenospheric uplift and resulted in extreme thinning of the lithosphere (Horváth 1993). Following the termination of extension in the late Miocene (~8–7.5 Ma), a large-scale tectonic inversion was initiated by the ongoing push and rotation of the Adria block against the European platform, resulting in a change from extensional to compressional kinematics (Horváth and Cloetingh 1996; Bada et al. 2007).

Beginning in the late Miocene, but mostly during Plio-Pleistocene time, a series of alkali basalt eruptions occurred throughout the CPR, generated via decompressional melting associated with asthenospheric upwelling (Embey-Isztin et al. 1993). The alkali basalts are known to have sampled the upper mantle in at least five locations in the CPR, from west to east: Styrian Basin, Little Hungarian Plain, Bakony-Balaton Highland, Nógrád-Gömör and Perşani Mountains (Fig. 1a).

Based on detailed petrographic observations and geochemical analyses of upper mantle xenoliths, Liptai et al. (2017) defined three major mantle domains beneath the Nógrád-Gömör Volcanic Field (NGVF) (see their Figure 1) referred to as the northern, central, and southern areas. K–Ar ages of the xenolith-hosting basalts are 6.4–4.9 Ma in the northern area, 4.0–2.5 Ma in the central area and ~2.5 Ma in the southern area (Balogh et al. 1981; 1986 and unpublished data). Similar ages were obtained by U/Pb and (U–Th)/He dating for the northern and central areas (7.0 - 5.9 and 3.0 - 1.7 Ma, respectively; Hurai et al. 2013). Smaller lava flows and maars are characteristic of the xenolith-hosting alkali basalts in the northern and southern areas, whereas the central area is dominated by two large lava flows (Babi Hill and Medves Plateau) (e.g., Konecný et al. 1995) (Fig. 1b). The sampling location of the xenolith studied in this paper, Fil'akovo-Kerčik, is interpreted to represent an eroded lava flow (Lexa et al. 2010) and previous studies of xenoliths from this location confirm its association with the upper mantle beneath the Babi Hill and the Medves Plateau (Liptai et al., 2017).

Sample petrography and mineral chemistry

Xenolith NFL1327 containing the SMI studied here is assigned to the 'lherzolitic' suite of the NGVF (Liptai et al. 2017) based on the presence of orthopyroxene as individual grains. The petrography and geochemistry of the xenolith are described by Liptai et al. (2017), and the results are summarized here and in Supplementary Table 1. The xenolith is modally a wehrlite containing 88 vol% olivine, 10 vol% clinopyroxene, 1 vol% orthopyroxene and 1 vol% spinel. The texture of the xenolith is equigranular, and clinopyroxenes appear in clusters (Fig. 2a), whereas olivine-rich areas show the characteristic texture of the wehrlite suite (Patkó et al. 2020). The sample bears microstructural evidence of deformation and subsequent annealing, interpreted to be the result of metasomatizing melts percolating through the sample prior to ascent to the surface (Liptai et al. 2019).

Olivine, orthopyroxene and clinopyroxene have relatively low Mg-numbers (100*Mg/[Mg+Fe] = 85, 88 and 87, respectively) compared to the majority of the lherzolite suite (90–91), which reflects an enrichment in Fe. In addition to Fe, Mn shows high concentrations in olivine (0.25 oxide wt. %) and orthopyroxene (0.25 oxide wt. %) as well, and spinel has an elevated Ti-content (0.41 oxide wt%). Trace element contents of pyroxenes show enrichment in light rare earth elements (LREE) and depletion in Rb, Ba, and Pb. Based on these geochemical characteristics, the xenolith was classified as 'Group IIB' by Liptai et al. (2017). This group represents a transitional type between the lherzolite and a wehrlite suite as the enrichment in Fe, Mn, Ti, and LREE are characteristic of the wehrlites (Patkó et al. 2020), but the textures and the abundance of modal orthopyroxene are more similar to the lherzolite suite. The studied xenolith contains several clinopyroxene grains with primary SMI randomly distributed within each grain (Fig. 2b).

Analytical techniques

Raman spectroscopy

Raman spectroscopy is an ideal tool to interrogate the composition of SMI because it is non-destructive and offers spatial resolution on the order of 1 micron as well as detailed mapping (Bodnar and Frezzotti 2020). Raman analyses included point analyses of constituent phases in the SMI and imaging of three complete silicate melt inclusions (SMI_2, SMI_R, SMI_U). Analyses were conducted at the Research and Instrument Core Facility of the Faculty of Science at Eötvös University, Budapest. The instrument used was a confocal HORIBA Labram HR spectrometer with a Nd:YAG 532 nm wavelength laser excitation and 600 or 1800 grooves/mm optical grating, 50-100 μm confocal hole, 5–80 s acquisition time and a 100x long working distance objective. Laser power was 130 mW at the source and ~50 mW at the sample. Using a 50 μm confocal hole and 1800 grooves/mm grating, the laser spot diameter was measured to be ~1.4 μm and the depth resolution was ~1.7 μm. The spectral resolution using the 1800 grooves/mm optical grating was 0.7 cm^{-1} at 1398.5 cm^{-1} and 0.6 cm^{-1} at 2331 cm^{-1} (defined as the measured full width at half maximum values of two neon atomic emission lines). We note that after peak fitting, a peak position can generally be determined to within ±0.03 cm^{-1} (Lin et al. 2007). Both imaging and analyses of individual phases (where needed) were carried out in the spectral range from 220 to 1900 cm^{-1} initially, and then from 2750 to 4000 cm^{-1} to test for the presence of OH-bonds in hydrous phases. Image mapping at room temperature was conducted using the 600 grooves/mm optical grating, with a step size of 0.5–0.7 μm. Acquired spectra were processed using LabSpec v5. software. For phase identification, the databases of Frezzotti et al. (2012) and the online database of rruff.info (Lafuente et al. 2015) were used.

FIB-SEM

The FIB-SEM technique was applied to four selected silicate melt inclusions (SMI_2, SMI_3, SMI_R and SMI_U), three of which had previously been imaged with Raman spectroscopy. The analyses were conducted in the Research and Instrument Core Facility at Eötvös University, Budapest, with the use of an FEI Quanta 3D dual-beam scanning electron microscope with both secondary- and backscattered-electron detectors. The instrument is also equipped with a silicon drift X-ray energy dispersive (SDD-EDX) detector, which has recently been shown to provide about the same level of precision and accuracy as wavelength dispersive spectrometers (e.g., Ritchie et al. 2012). The accelerating voltage was 10–20 keV, depending on the size of the inclusion and the elements of interest. The beam current was 0.02–4 nA, which permitted the detection of major elements from carbon to barium.

The application of the FIB-SEM technique to fluid inclusions was described in detail by Berkesi et al. (2012), and is summarized in the following steps: (1) a thin (200–300 nm) platinum layer is deposited on the carbon-coated sample surface to mark the location of the inclusion; (2) the sample is then tilted by 52°, so that the milling ion beam is perpendicular to the surface and the electron beam is at a 38° angle; (3) an additional platinum layer of ~1–2 μm is deposited on the pre-selected area as protection from abrasion by the Ga-ion beam (Wirth 2004); (4) trenches are excavated on three sides of the platinum strip using a higher beam current (15–45 nA) to accommodate the waste material produced by the milling (Fig. 3a), (5) slices of equal thickness (400 nm) are milled through the SMI for easier volume reconstruction, exposed phases are analyzed with SEM-EDX, and electron images for each slice are saved (Fig. 3b). Identification of the daughter phases was based on previously obtained Raman spectra, morphology shown on the secondary electron images, brightness on the backscattered electron images, and/or major-element contents inferred from the SEM-EDX spectra. Due to the small size of the daughter minerals (~1–10 μm), the SEM-EDX spectra generally contained mixed signals from the analyzed phase and the adjacent area (host and/or other daughter phases). A spectrum of the host was collected at every slice where daughter phases of the SMI were analyzed, for comparison and better discrimination of the signals. Volume proportions of the constituent phases were determined with Amira^{TM} software developed by Thermo Scientific; the method involves defining the daughter phases on each slice, and then extrapolating the areas to acquire phase volumes between the slices, producing a 3D reconstruction of the entire SMI (Fig. 3c).

LA-ICP-MS

Trace-element concentrations of bulk silicate melt inclusions were determined at the Department of Geosciences, Virginia Tech (Blacksburg, VA, USA), with the use of an Agilent 7500ce quadrupole ICP-MS coupled with an ArF Excimer Laser system. The laser acquisition parameters were: 193 nm wavelength, ~7–10 J/cm^2 energy density, 5 Hz repetition rate and 24–32 μm spot size. The ~ 1.5 cm^3 ablation cell was flushed with He gas at ~ 1.2 L/min; auxiliary Ar gas flow was 1.03 L/min. For each isotope, a 10 ms dwell time was applied. For the external standard, the NIST-612 synthetic glass was used; average Ca concentration, previously obtained by mass-balance calculation for bulk SMI from SEM-EDX analyses, was used for the internal standard. This approach is valid owing to the overall low variability in major-element compositions in the SMI analyzed with FIB-SEM, and we assume that all primary SMI have similar geochemical compositions. Data reduction was carried out using the AMS software of Mutchler et al. (2008). Owing to the small size of the SMI, the laser spot was somewhat larger than the size of the SMI, producing a signal that had a mixed character (host + SMI). To separate the contribution of the host from the signal from the SMI, we followed the calculation procedure described by Halter et al. (2002), as implemented in the software of Mutchler et al. (2008). This calculation uses the concentration of an element that is known for both the inclusion and the host clinopyroxene as an internal standard. The estimation of uncertainty was carried out based on the study of Longerich et al. (1996).

Silicate melt inclusion petrography

The silicate melt inclusions (SMI) usually have isometric or slightly elongated shapes and range from 5 to 20 μm in longest dimension (Fig. 2). They are partially crystallized, and a vapor bubble, glass and several crystals are observable in polarized light (Fig. 4); the crystals are collectively referred to as daughter phases, and are assumed to have crystallized from the trapped melt during cooling (e.g., Frezzotti 2001). Crystal sizes range from a few μm up to 10 μm, whereas the size of the bubble is proportional to the size of the whole inclusion. Two-dimensional Raman imaging in the plane of maximum dimension of the inclusions allowed identification of daughter phases in three selected SMI (SMI_2, SMI_R, SMI_U; Fig. 4). All three SMI contain apatite (Raman bands at 428, 578, 960 and 1070 cm^{-1}) and a volatile-bearing mineral (either amphibole or mica; Raman band at 3675 cm^{-1}). In addition, sulfates including anhydrite (Raman bands at 497, 607, 625, 1109, 1127 and 1159 cm^{-1}) and barite (Raman bands at 460, 627 and 993 cm^{-1}) were found in SMI_2, and clinopyroxene on the SMI wall (hereafter referred to as ‘wall clinopyroxene’), with a spectrum that is slightly different from that of the clinopyroxene host (extra band at 535 cm^{-1}), was identified in SMI_R. Characteristic Raman spectra of the sulfates, the vapor bubble and the wall clinopyroxene are shown in Fig. 4, along with the reference spectrum of the host clinopyroxene. The vapor bubble in all three analyzed SMI contains CO_2, based on the presence of the Fermi diad

(Fermi 1931). The bands of the Fermi diad appear at 1283.5–1387.0, 1284.7–1388.3, and 1284.7–1388.3 cm^{-1} in SMI_2, SMI_R and SMI_U, respectively (Table 1).

FIB-slicing and subsequent SEM-EDX analyses of the melt inclusions confirmed the identification of daughter minerals based on Raman spectroscopy, and revealed additional daughter phases, (sometimes two or more distinct grains of the same phase, as described below) which were too small (i.e., sub-micrometer size) to detect with the petrographic microscope or by Raman spectroscopy. The largest volatile-bearing mineral (up to ~10 μm) in all four analyzed SMI was identified as amphibole based on the SEM-EDX spectra; in SMI_3, two distinct amphibole grains are present. Mica appears in all four SMI as well, and always occurs adjacent to the gas bubble (Fig. 3b). SMI_U contains two distinct ~6–8 μm mica flakes (see BSE images on Fig. 3b). Spinel and apatite are present in all four SMI, the former appearing as an isometric crystal on the border between the glass and clinopyroxene, and the latter is present either as several small (< 1 μm) grains (SMI_U, Fig. 3b) or has an elongated needle shape (e.g., SMI_R; Fig. 5). Sulfide blebs were detected in SMI_R and SMI_U, and tiny (< 1 μm) sulfates (anhydrite ± barite) were observed in SMI_R (Fig. 5), SMI_2 and SMI_3. Note that in SMI_R, both sulfide and sulfate daughter phases are present. The recognition of clinopyroxene that precipitated from the melt onto the inclusion wall was made difficult due to the similarity in composition to the host clinopyroxene; however, irregularities in the shape of the inclusion (e.g., Fig. 5) and SEM spectra yielding slightly different compositions could be used. It is still likely that the modal proportions of clinopyroxene is underestimated and should be considered as a minimum.

Volume proportions acquired with the Amira^{TM} software are shown in Table 2. The modal compositions of the SMI are quite similar to one another. Approximately half of the inclusion volume (43–53 vol. %) is glass. Amphibole and mica show a slightly wider modal range, being present at 22–32 and 0.2–1.2 vol. %, except for SMI_U, where mica is more abundant (9.4 vol. %) than amphibole (7.5 vol. %). Wall clinopyroxene comprises 7–19 vol. % of the inclusions. Spinel, apatite, sulfide, anhydrite and barite (where present) each are usually below 2 vol. %.

Silicate melt inclusion geochemistry

Major element composition

Major-element compositions were acquired from SEM-EDX spectra for the most abundant daughter phases (Table 3, Fig. 5). In the case of volatile-bearing phases, compositions were corrected to sum to a total less than 100 % to account for the volatile content, i.e., 97.5, 96.5 and 95.5 wt. % for amphibole, mica and glass, respectively; taken from average values of daughter minerals of SMI in (Szabó et al. 1996) and from the glass phase in SMI of wehrlite xenoliths from the central NGVF (Patkó et al. 2018). Spinel compositions were corrected by omitting oxides (SiO_2, CaO, Na_2O, K_2O) expected to be present only in surrounding silicate phases and glass. The resulting compositions of the four melt inclusions are similar, as described below.

Clinopyroxene precipitation on the inclusion wall (i.e., wall clinopyroxene) was generally difficult to distinguish from the host, however, several analyses in SMI_2 and SMI_R revealed slightly different major-element compositions. This difference is observable as an increase in FeO (8.5–9.5 wt. %) and Al_2O_3 (5.6–6.1 wt. %) at the expense of MgO (10.4–11.3 wt. %), whereas FeO and Al_2O_3 are lower in the host clinopyroxene, and MgO is higher (5.8–6.4, 4.1–4.9 and 11.9–14.2 wt. %, respectively; Table 3). Amphibole shows little compositional variability among the different SMI and are strikingly enriched in FeO (12.3–14.8 wt. %) and TiO_2 (3.48–6.95 wt. %) compared to amphiboles in most lherzolites of the

NGVF suite (Liptai et al. 2017). In contrast, amphiboles have slightly lower SiO_2, Al_2O_3, MgO and Na_2O contents. Mica grains are usually small, therefore the composition has a larger uncertainty and shows wider variation. However, the enrichment in FeO and the depletion of MgO is very strong, compared to mica (phlogopite) in the melt inclusions from NGVF xenoliths described by Szabó et al. (1996). Spinel is dominantly iron-rich, with a small proportion of chromium and aluminum. In SMI_U, the spinel is richer in aluminum and more depleted in iron (Table 3). Glass is not entirely homogeneous; even on the BSE images of several slices, numerous dark spots, possibly sub-micrometer sized bubbles, are observed. Although the analyses did not identify the nature of these inhomogeneities, they revealed some variability in the Na/K ratio of the glass. In most analyses, the glass appears to be K-rich (K_2O = 2.9–6.0 wt. %), but several areas in SMI_2, SMI_R and SMI_U show Na_2O contents up to 7.2–15.9 wt. % (Table 3). These Na-rich areas also have lower SiO_2-contents (52.0–59.6 wt. %). Similar compositional variability was reported by Szabó et al. (1996) in glass in melt inclusions from the southern part of the NGVF. Furthermore, in SMI_U, the glass also has a slightly elevated iron content (FeO = 2.3–3.4 wt. %).

Bulk major element compositions of the SMI were calculated by mass balance using the compositions of individual phases comprising more than 0.5 vol. % of the inclusion (glass, clinopyroxene, amphibole, ± mica, spinel, apatite; Table 2). The resulting compositions vary within a narrow range among the four SMI. Concentrations of SiO_2 vary between 51.7 and 53.2 wt. %, and FeO contents are between 6.6–8.4 wt. %, which is significantly higher than compositions reported by Szabó et al. (1996) from NGVF inclusions, and closer to the values reported by Zajacz et al. (2007) for melt inclusions trapped in mafic cumulate xenoliths in the NGVF. Apart from the high FeO content, the SMI compositions are in good agreement with those found in wehrlite xenoliths from the NGVF (Patkó et al., 2018).

Trace element composition

Trace element contents of 8 additional SMI in clinopyroxenes from the studied xenolith were acquired by LA-ICP-MS analysis (Table 4). Only the analyses with mass factor (SMI ratio in the mixed ablation signal) ≥ 0.3 were considered. The compositions are similar for all 8 inclusions. Some of the heavy REE (Eu, Tb, Ho, Tm, Lu) yielded high uncertainties due to low concentrations and were therefore omitted from further interpretation. Nevertheless, the SMI produce similar patterns when normalized to primitive mantle composition (McDonough and Sun 1995) (Fig. 6). The SMI are enriched in incompatible elements such as Ba, Nb and Ta (117–530, 19.6–86.7 and 0.92–4.56 ppm, respectively); the concentrations are significantly higher than those in the host clinopyroxene of the xenolith (Supplementary Table 1). Hf and, to a lesser extent, Zr are also depleted. There is a continuous depletion from the light towards the heavy REE, with the former showing concentrations about one order of magnitude higher than the host clinopyroxene (Fig. 6). The most compatible elements (V, Cr, Ni) show the greatest depletion, similar to the pattern of the host clinopyroxene (Liptai et al. 2017).

Discussion

Composition of the metasomatic melt and pre-entrapment evolution

A significant advantage of the FIB-SEM technique compared to homogenization and bulk inclusion analysis is that it can provide high-resolution (sub-micrometer) 3D structural information on the daughter minerals within the inclusion, allowing us to draw conclusions on specific post-entrapment processes. This approach is similar to the recently published method involving X-ray microtomography (Créon et al. 2018) and its high-resolution version (Richard et al. 2018), which is capable of modelling the daughter phases of SMI in 3D. However, a separate analytical procedure needs to be carried out to obtain chemical compositions. With the use of the FIB-SEM-EDX system imaging, structural modelling and major element chemistry can be acquired in one set of measurements, even if the latter may have lower precision than electron microprobe analyses.

As was previously established (Liptai et al. 2017), multiple metasomatic events have affected the upper mantle of the NGVF, and the last event resulted in Fe-, Mn-, Ti- and LREE-enrichment in the minerals (‘Group IIB’). It is suggested that this event can be linked to the formation of the wehrlite series, which has similar geochemical characteristics (Liptai et al. 2017; Patkó et al. 2020). Since that process involved an increase in the proportion of clinopyroxene (Patkó et al. 2020), which also is the host mineral of the SMI in the studied xenolith, the inclusions can be considered to represent the melt that interacted with the peridotite wall rock. This interpretation is further supported by the fact that SMI are distributed throughout the entire grains in which they occur (Fig. 2b), thus eliminating the possibility that the melt fractionated some of the host mineral prior to entrapment (as it was observed by Zajacz et al. 2007 in case of SMIs in olivine). Liptai et al. (2017) concluded that the reacting melt was most likely a mafic melt with an asthenospheric origin, similar to the host basalt, but with a slightly different composition. With the chemical compositions obtained by SEM-EDX, characteristics of this melt can be further refined.

The most striking compositional feature is the enrichment of FeO in the daughter minerals (i.e., clinopyroxene, amphibole, mica and spinel; Table 3). Iron appears to be the best geochemical proxy to distinguish wall clinopyroxene from the host clinopyroxene, as the former contains significantly higher Fe contents than the latter (Fig. 7; Table 3). The high FeO concentrations in mica result in annite-like compositions. This is strikingly different from the phlogopites described from SMI found in the southern part of the NGVF by Szabó et al. (1996); however, those inclusions have been interpreted to represent a subduction-related melt, and are only present in olivine in xenoliths from the southern part of the volcanic field. Minor FeO is detectable in the glass of SMI_R and SMI_U (Table 3) as well. Overall, these compositions agree well with the Fe-rich nature of the metasomatizing melt associated with formation of the wehrlite suite (Patkó et al. 2020). However, it should be noted that the accompanying Mn- and Ti-enrichment observed in the rock-forming silicates and spinel (Liptai et al. 2017), respectively, is not reflected in the composition of crystallized phases in the SMI. This may be because Mn is only present in very low amounts and was below detection limit with SEM-EDX, and enrichment of Ti may not be that dominant as it only occurred in spinel, but not in clinopyroxene in the affected xenoliths (Liptai et al. 2017).

Bulk compositions, both for the four SMI analyzed with SEM-EDX and for the eight additional SMI analyzed with LA-ICP-MS, show generally low alkali contents along with a variability in SiO_2 that places them into compositional fields ranging from basaltic andesite and trachyandesite through basalt to picrobasalt and basanite in the TAS diagram (Le Bas et al. 1986) (Fig. 8). Note that compositions of SMI determined by mass balance calculation have much less variability than those obtained by LA-ICP-MS, which show lower SiO_2 and total alkali contents. The greater compositional variability compared to SEM-EDX analyses, and the general consideration that LA-ICP-MS has lower accuracy for major elements, would suggest that a basaltic andesite/trachyandesite – basalt composition is the best estimate for the composition of the trapped melt. This differs somewhat from the composition of the host magma (Fig. 8), which is a basanite with higher total alkali and lower SiO_2 contents and an overall limited variability among the different localities of the Nógrád-Gömör Volcanic Field (Embey-Isztin et al. 1993; Dobosi et al. 1995; Dobosi and Jenner 1999). The difference is also observed when compared to the estimated primitive composition of the host basalt (Zajacz et al. 2007), which plots in the basalt field with lower total alkali- and slightly lower SiO_2-contents (Fig. 8).

The production of basaltic melts with small changes in composition depending on their age throughout the Nógrád-Gömör Volcanic Field has been previously observed by Dobosi et al. (1995). The dominant change observed by these workers was an increase in trace elements (Zr, Nb), and to a lesser extent SiO_2 and total alkali contents. Furthermore, the melt represented by the SMI probably had a different evolution, as it resided in the upper mantle and reacted with the wall rock, instead of undergoing a rapid ascent to the surface like the host magma. Such a reaction is considered to be responsible for forming the wehrlites. Patkó et al. (2020) have established that the metasomatizing melt dissolves orthopyroxene and crystallizes clinopyroxene and olivine, while becoming more intermediate in composition. It is, therefore, suggested that this evolved melt was trapped in the SMI.

Origin of the trapped melt based on trace element composition

Because of the analytical uncertainties resulting from low concentrations, only inclusions with Y/Yb = ~10 (an empirical ratio for mantle environment; McDonough and Sun 1995; Salters and Stracke 2004) were used (SMI_9, SMI_10, SMI_12, SMI_13, SMI_16; Fig. 6; Table 4) during averaging SMI compositions to estimate the composition of the trapped melt. Trace-element patterns of the SMI compared with the compositions of amphiboles with intraplate origin formed during different metasomatic events in the NGVF upper mantle (Group IB and IIB of Liptai et al. (2017) are shown on Fig. 9. Regarding the incompatible trace elements, SMI compositions usually fall between the most enriched amphiboles in Group IB and Group IIB xenoliths. Note that the Group IIB xenolith that contains amphibole is a different sample from the one containing the SMI (Liptai et al. 2017). Although Nb and

Ta are significantly more abundant in the amphibole of the most enriched Group IB xenoliths (Fig. 9a) than in the SMI, their REE+Y patterns show good agreement. However, at equilibrium, amphibole/melt partitioning of these trace elements would not allow these elements to be more enriched in amphibole compared to the melt as the relevant distribution coefficients are less than 1 (Adam and Green 1994; LaTourrette et al. 1995; Dalpé and Baker 2000). This can be explained if the Group IB amphiboles are linked to a different metasomatic event, one with an enrichment of U-Th-Nb-Ta in the reacting melt (Liptai et al. 2017), whereas the SMI represent a different melt that was responsible for the wehrlitic metasomatism.

Trace element patterns of the SMI are generally in good agreement with those of the host basalt (Fig. 9c, d), having an OIB character (Dobosi et al. 1995), but the trapped melt appears slightly less fertile, as depicted by depletion in Ba, Nb (Ta), La, Ce, Hf and Zr (Fig. 9c). The high concentrations of incompatible trace elements in the host basalt may be explained by crystallization of olivine and clinopyroxene (fractionation), thus enriching the remaining melt in incompatible trace elements before eruption (Embey-Isztin et al. 1993; Dobosi et al. 1995; Zajacz et al. 2007). This is supported by the calculated composition of the NGVF basalt before fractionation and crustal assimilation (Zajacz et al. 2007), which shows a better agreement with the analyzed SMI (Fig. 9c). Alternatively, the trapped melt may have followed a different evolution path; i.e., reaction with the peridotite and consuming orthopyroxene while crystallizing clinopyroxene and olivine (Patkó et al. 2020), as mentioned earlier.

To constrain the origin of the trapped melt, the equilibrium melting model of Zajacz et al. (2007) was applied to the studied SMI compositions (Fig. 10). This model is based on calculations of Nb and Y in the partial melts for spinel lherzolite and garnet lherzolite sources with different modal clinopyroxene/garnet ratios. Bulk source compositions were determined using the primitive mantle composition of McDonough and Sun (1995) and mineral-melt partition coefficients from garnet lherzolite melting experiments at pressures between 2.8–3.2 GPa by Salters et al. (2002). Based on the model, Nb is a good indicator for the degree of partial melting, and Y generally indicates the presence of garnet in the source. Furthermore, these elements are in sufficiently high abundances in the SMI to be analyzed with limited uncertainty, and they are considered insensitive to fluid metasomatism in the source. Based on this model (Fig. 10), the melt trapped in the SMI was produced by ~ 2 % melting of a garnet lherzolite, with a clinopyroxene/garnet ratio of ~ 1. The source appears to be slightly more garnet-rich than the calculated parental melt of the Nógrád-Gömör cumulate xenoliths (Zajacz et al. 2007) and the average composition of the host basalt (Fig. 10). However, the latter is already modified due to olivine and clinopyroxene fractionation (Dobosi et al. 1995) and partial crustal assimilation (Zajacz et al. 2007).

In summary, the geochemical characteristics of the melt represented by the SMI point to an OIB-type intraplate melt, with an origin similar to other basaltic magmas present in the region. The observed differences in geochemistry (higher SiO_2 and lower incompatible trace element content compared to the host basalt) can be explained by the combined effects of several possible factors: (1) small differences in the source composition and in the degree of partial melting, (2) fractionation of the host basalt, and (3) evolution of the metasomatic melt via reaction with the peridotite wall-rock prior to entrapment.

Post-entrapment processes

The partially crystallized nature of the SMI in the studied xenolith (Fig. 2c, d) suggests that precipitation of daughter minerals occurred in a slowly cooling environment (Fig. 11a-c). The beginning of crystallization is in many cases a non-equilibrium process. Due to heterogeneous nucleation on the inclusion wall only the host mineral crystallizes initially, even if the melt is saturated with other phases (e.g., Frezzotti et al. 1991). Consequently, clinopyroxene was the first mineral to crystallize on the inclusion wall. Precipitation of volatile-free phases leads to an increase in the concentration of volatile components in the residual melt, and eventually to crystallization of volatile-bearing daughter phases (Frezzotti 2001) such as amphibole, apatite and mica. The presence of glass in the SMI indicates that rapid cooling interrupted the crystallization process, which is interpreted to have occurred during and/or after ascent to the surface.

As a result of crystallization of mostly non-volatile-bearing phases in the SMI the volatile content of the melt increases, as noted above. At the same time, the pressure in the SMI is decreasing as crystallization proceeds owing to the density (molar volume) differences between the crystal phases and the melt. Stated differently, the partial molar volume of, for example, clinopyroxene in the melt is larger than the molar volume of the clinopyroxene phase that is crystallizing from that melt. Because of this, the pressure in the SMI decreases, favoring the exsolution of volatiles from the melt. The density of the CO_2 bubble may be estimated based on the distance between the peaks of the Fermi diad in the Raman spectrum of CO_2 (Rosso and Bodnar 1995). To calculate the density of the CO_2-bubble, the experimentally developed densimeters of Fall et al. (2011) and Wang et al. (2011) were applied, while recognizing that one should ideally use a densimeter developed for the instrument which analyzed the samples in order to minimize errors (Lamadrid et al. 2017). Since the peak shifts are very similar in the three inclusions, the resulting densities (0.38–0.39 and 0.36–0.37 g/cm^3 with the two densimeters; Table 1) are almost identical. We note that the CO_2 bubbles were analyzed at room temperature, and the resulting densities are in the "forbidden region" because they represent densities that are between the density of CO_2 liquid and CO_2 vapor at room temperature (see Table 1 of Wang et al., 2011). However, repeated analyses of the CO_2 bubbles at 40°C yielded the same results within error. We interpret this to indicate that the temperature of the CO_2 in the bubbles was slightly elevated by interaction with the laser, resulting in homogenization of the CO_2 phases during the analysis, thus resulting in correct densities. In addition to the similar densities of all bubbles, their volume proportions in the analyzed SMI are in the same range (7–14 vol. %; Table 2), and the remaining inclusions in the sample have roughly similar-sized bubbles. Both the identical CO_2 densities and the similar volume proportions of the bubbles support the interpretation that the CO_2 was completely dissolved in the trapped melt and that the bubbles were most likely formed via post-entrapment devolatilization during ascent to the surface.

The density of CO_2 in the vapor bubble of SMI can be used to estimate the weight proportion of CO_2 in the trapped melt using mass balance approach. The CO_2 content of the trapped melt, in turn, may be used to estimate a minimum pressure of trapping of the SMI. For the mass balance calculations, volume properties acquired with FIB-SEM analyses were used, along with densities of the daughter minerals or the endmembers closest in composition (diopside, pargasite, annite, hercynite and pyrrhotite for clinopyroxene, amphibole, mica, spinel and sulfide, respectively), CO_2 densities obtained from Raman analysis of the vapor bubbles, and an average glass density of Stolper and Walker (1980). The resulting mass proportion of CO_2 in SMI_2, SMI_3, SMI_R and SMI_U is estimated to be 2.1, 1.9, 1.7 and 1.0 wt.%, respectively. CO_2 concentrations determined in this manner represent minimum values, as some additional CO_2 is contained in the glass phase. Nevertheless, Moore et al. (2015; 2018), Moore and Bodnar (2019), and Wallace et al. (2015) have shown that the majority of the CO_2 is contained in the vapor bubble in silicate melt inclusions, with the vapor bubble containing > 90 % of the total CO_2 in many SMI. We note that the glass is not completely homogeneous in the SMI, which is evidenced by numerous dark spots observable on the BSE image (Fig. 3b, 5). Analyses of these spots did not reveal any compositional difference from the surrounding glass. Given their dark color, the spots may represent tiny gas bubbles that froze in the glass before they could coalesce with the main bubble. The weight proportions of CO_2 determined here are somewhat lower than values reported by Zajacz et al. (2007) for the parental melt of NGVF cumulates (2.20 – 2.55 wt. %), and fall within the range proposed for more oxidized primary OIB magmas (0.2 - 3.0 wt. %; Herzberg and Asimow 2008).

Ignoring the contributions of other minor volatile components as described below, the minimum depth of trapping of the SMI may be estimated based on the CO_2 abundances of 1.0 to 2.1 wt. % reported above. According to Mysen et al. (1975), the solubility of CO_2 in a tholeiitic melt at 1650°C varies from ~1 wt. % at 0.5 GPa to ~2 wt. % at 1.5 GPa. These workers also showed that the solubility changes little with temperature at temperatures <1500°C at 3 GPa, although data for lower temperatures are not included. Assuming that these results for a tholeiitic melt reasonably approximate the behavior of the SMI studied here suggests that the SMI were trapped at a minimum pressure of 0.5 – 1.5 GPa. These values are in agreement with the depths of 40-50 km and pressures of 1.3 – 1.6 GPa where wehrlitic metasomatism occurred in the NGVF (Patkó et al. 2020). The presence of other volatile-bearing phases in the SMI of this study suggests that the original composition of the volatile bubble did not consist exclusively of CO_2. Crystals growing inside the bubble can be interpreted as having formed during a late crystallization process, following the exsolution of the volatiles from the residual melt (Esposito et al. 2016). Crystals that form in a fluid or melt inclusion not by precipitation directly from the trapped fluid but, rather as a result of interaction between the volatile phase and either the host mineral, glass/melt, or previously-formed daughter minerals are referred to as “step-daughter minerals” (Svensen et al. 1999). In the studied inclusions, anhydrite and barite (where present) are always located on the boundary between the bubble and the glass (Fig. 4, 5). Although they appear to have grown at the expense of the glass, Frezzotti and Touret (2014) suggested that anhydrite can form during the latest stages of ascent. The close association with barite (SMI_2 on Fig. 4) implies a common genesis. Sulphur is a common component in the volatile phase of mantle fluids (e.g., Andersen et al. 1984; Andersen and Neumann 2001; Esposito et al. 2016; Aradi et al. 2019), and it can explain the crystallization of these minerals as the glass contains sufficient amounts of Ca (Table 3) and probably Ba as well.

In addition to sulfates, mica also appears on the boundary between the gas bubble and the glass (BSE images on Fig. 3b and 5), with the exception of SMI_U, where only one of the two mica flakes is in contact with the bubble (Fig. 3b). In all four SMI, mica appears to grow partly inside the bubble. This suggests that mica also formed at a late stage, following the exsolution of the volatile phase. Furthermore, mica may contain a significant amount of OH in its structure. Although this could not be determined by the FIB-SEM analyses, the lack of detected F and Cl in mica may suggest that the only volatile component occupying the OH site is OH, which could have come from H_2O in the bubble. The enriched structural hydroxyl content of clinopyroxenes in xenolith NFL1327 (265 ppm) compared to the average of that in other xenoliths from the same locality (140 ppm) (Patkó et al. 2019) further suggests that the metasomatic agent included water as a component.

Silicate melts transition from the melt (fluid) stage to the glass (solid) over a few tens of degrees, and the higher the cooling rate, the higher the temperature at which this transition will occur (Mysen and Richet 2005). As was shown by Szabó and Bodnar (1996), the NGVF basalts entraining the xenoliths ascended from the depth of entrapment to the surface in a relatively short time (~37.5 hours). This suggests that the cooling rate may only have changed from slow to fast after the eruption. Note that there can be significant differences in the cooling rate in a basaltic lava flow depending not only on time but also on the distance from the contact surface (e.g., Griffiths and Fink 1993). Nevertheless, in the case of the studied xenolith, the time between bubble formation and the solidification of the residual melt was sufficient for sulfate and mica to crystallize (Fig. 11d-f).

Implications

Our study has three major implications. First, it was found that silicate melt inclusions (SMI) hosted in clinopyroxene in the studied NGVF xenolith represent a metasomatic melt that played an important role in the geochemical evolution of the upper mantle of the northern Pannonian Basin. Compositional features of the trapped melt include an enrichment in FeO and a trace-element pattern similar to the host basalt. Based on this, the melt can be linked to the last metasomatic event recorded in the geochemistry of the NGVF upper mantle, which resulted in the formation of wehrlites by alteration of lherzolites. The metasomatizing melt was an OIB-type mafic melt of intraplate origin, with a genesis similar to that of the alkali basalt hosting the xenoliths, i.e., very small degree (~2 %) of partial melting of a garnet lherzolite source.

Second, different post-entrapment processes were identified based on the morphology, composition and arrangements of daughter minerals, residual glass and CO_2-bubble within the SMI. The very similar densities and volume proportions of the CO_2-bubbles in all SMI suggest that the CO_2 exsolved from the residual melt after the entrapment. Following exsolution of the bubble, small mica and sulfate crystals formed on the bubble-melt boundary. This suggests that the volatile phase contained sulfur and possibly H_2O, in addition to CO_2.

Third, our study has shown that a much better understanding of the geochemistry and 3D distribution of phases in SMI is obtained by applying several different complementary analytical methods to interrogate SMI. The FIB-SEM-EDX system is a powerful tool for acquiring precise volume proportions and compositions of daughter phases during a single set of measurements. Analyzing the whole inclusion volume is especially useful if there are several smaller daughter minerals that cannot all be exposed within the same plane for analysis.

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Figure captions

Fig. 1. (a) Locations of alkali basalt occurrences that host ultramafic xenoliths in the Carpathian-Pannonian region. SB – Styrian Basin, LHP – Little Hungarian Plain, BBH – Bakony-Balaton Highland, NG – Nógrád-Gömör, PM – Perşani Mountains. (b) Outcrops of alkali basalt and Miocene andesites (with possible mantle origin; Harangi et al. 2001) in the Nógrád-Gömör Volcanic Field (NGVF) and sampling locality (Fil'akovo-Kerčik) of the studied xenolith.

Fig. 2. (a) Scanned thin section image of the studied xenolith, with well-defined olivine-rich and clinopyroxene-rich areas. (b) Transmitted light, plane-polarized photomicrograph of a clinopyroxene grain hosting silicate melt inclusions (SMI). (c) (d) Photomicrographs showing the SMI selected for analyses presented in this study. The images are merged from a set of photos taken in different focal depths.

Fig. 3. (a) Backscattered electron image of the sample volume containing an SMI, prepared for slicing with the focused ion beam (FIB) following the deposition of the Pt-layer and excavating the surrounding trenches (see text for further details). (b) Photomicrograph of SMI_U (transmitted light, plane polarized); numbered dashed lines and corresponding BSE images indicate different stages of the FIB-slicing. (c) Computed 3D volume of SMI_U indicating daughter phases in different colors (without the clinopyroxene, which is thought to be present all along the inclusion wall).

Fig. 4. Selected Raman spectra of daughter phases and the host clinopyroxene (upper); photomicrographs (transmitted light, plane polarized) and Raman spectroscopic maps of three analyzed SMI (lower). Color code: dark blue – amphibole; light blue – wall clinopyroxene; red – apatite; green – sulfates (anhydrite and barite); yellow – glass; purple – CO_2 bubble; white – host clinopyroxene.

Fig. 5. Backscattered electron (BSE) image of a slice of SMI_R with SEM-EDX spectra of the daughter phases present.

Fig. 6. Primitive mantle (McDonough and Sun 1995) normalized multi-element (a) and rare earth element + yttrium (REE+Y) (b) diagrams of bulk SMI analyzed with LA-ICP-MS.

Fig. 7. Comparison of MgO and FeO concentrations in the rock-forming minerals of the xenoliths and the corresponding minerals in the SMI: (a) wall and host clinopyroxene, both compositions acquired with SEM-EDX; (b) daughter amphibole compared to modal amphibole appearing in the different geochemical groups of the NGVF lherzolite suite (taken from Liptai et al. 2017).

Fig. 8. Composition of glass and bulk SMI acquired with both LA-ICP-MS and mass balance calculations from major element analyses with SEM-EDX, plotted on the total alkali *vs* SiO_2 (TAS) diagram (Le Bas et al. 1986). Compositions of Nógrád-Gömör alkali basalts (Embey-Isztin et al. 1993; Dobosi et al. 1995) and their estimated primitive composition (Zajacz et al. 2007) are plotted, with fields for compositions of SMI found in cumulates (Zajacz et al. 2007) and 'basaltic' SMI in olivine from the southern part of the NGVF (Szabó et al. 1996).

Fig. 9. a, b – Multielement and REE+Y diagrams of the bulk SMI compositions compared to the metasomatic amphiboles of Group IB and IIB xenoliths; c, d – compared to the average host basalt (Dobosi and Jenner 1999) and the calculated primitive composition of the host basalt (Zajacz et al. 2007). Concentrations are normalized to primitive mantle (McDonough and Sun 1995).

Fig. 10. Petrogenetic modelling of the origin of the melt trapped in the SMI (Zajacz et al. 2007). Dashed lines represent modelled compositions of partial melts from spinel and garnet lherzolite, respectively, with primitive mantle composition. Numbers in italics refer to the clinopyroxene/garnet ratio in the source region. Dotted lines represent the degree of partial

melting expressed in percent melting. Average composition of the host basalt (pink diamond) (Dobosi and Jenner 1999) and the calculated parental melt composition for the cumulates (black square) (Zajacz et al. 2007) are plotted for comparison.

Fig. 11. Schematic illustration depicting the evolution history of the metasomatic melt, with different stages in the mantle environment and during/after ascent to the surface. Color code for phases within the SMI: yellow – melt; light blue – wall clinopyroxene; dark blue – amphibole; black – spinel; red – apatite; green – sulfates (anhydrite and barite); orange – mica; purple – volatile bubble; brown – glass.

Table 1. Positions of CO_2 bands and calculated densities (σ indicates reported maximum uncertainties) in thre

Inclusion	Position of CO_2 bands (Fermi diad)		Δ Fermi diad	CO_2 density (g/cm^3)	
	upper band	lower band		Fall et al., 2011 (σ=0.025)	Wang et al., 2011 (σ=0.025)
SMI_2	1283.5	1387.0	103.5	0.348	0.355
SMI_R	1284.7	1388.3	103.6	0.393	0.369
SMI_U	1284.7	1388.3	103.6	0.393	0.364

SMI analyzed with Raman spectroscopy

Table 2. Volumetric proportions (vol%) of recognized phases within the analyzed SMI

	SMI_2	SMI_3	SMI_R	SMI_U
Clinopyroxene	12	7.0	19	19
Amphibole	28	32	22	7.5
Mica	0.5	0.2	1.2	9.4
Glass	43	46	45	53
Apatite	-	0.4	0.5	1.9
Spinel	1.6	0.9	1.0	2.3
Sulfide		-	0.2	0.2
Anhydrite	0.2	0.1	0.1	-
Barite	0.1	0.1	-	-
CO_2 bubble	14	13	12	7.3

Table 3. Major element compositions of the daughter phases and the whole SMI in wt%

	Amphibole					**Mica**			
	SMI_2	SMI_3		SMI_R	SMI_U	SMI_2	SMI_3	SMI_R	SMI_U
		amp1	amp2						
n	4	2	3	7	1	5	3	2	6
SiO_2	39.7 (1.6)	37.9 (3.2)	39.7 (0.2)	38.5 (0.8)	38.5	34.2 (1.6)	41.5 (0.8)	35.9 (3.3)	35.9 (3.0)
TiO_2	3.48 (0.91)	5.23 (1.50)	4.88 (0.61)	3.89 (0.68)	6.95		1.45 (0.22)	3.33 (1.69)	3.93 (1.16)
Al_2O_3	10.6 (0.6)	10.1 (0.4)	10.1 (0.4)	11.4 (0.5)	10.4	11.1 (0.6)	9.04 (1.04)	10.5 (0.4)	14.2 (1.2)
Cr_2O_3				0.76 (0.07)				3.36 (0.74)	
FeO	14.8 (4.6)	14.8 (2.5)	12.3 (0.6)	12.8 (1.1)	12.4	33.8 (3.6)	25.6 (1.4)	29.1 (9.9)	21.1 (2.8)
MgO	11.6 (1.7)	10.8 (1.1)	11.3 (0.7)	11.6 (0.5)	11.0	2.93 (0.51)	3.82 (0.42)	1.73 (0.65)	7.85 (1.12)
CaO	13.6 (0.3)	15.4 (0.2)	15.8 (1.2)	15.3 (0.5)	15.1	5.19 (1.13)	10.3 (1.6)	7.17 (3.37)	2.37 (0.47)
Na_2O	2.25 (0.53)	1.74 (0.11)	2.13 (0.21)	1.75 (0.17)	1.82	1.84 (0.84)	0.93 (0.06)	0.58 (0.16)	2.53 (1.17)
K_2O	1.55 (0.28)	1.59 (0.26)	1.37 (0.27)	1.55 (0.15)	1.40	7.34 (0.93)	3.86 (0.10)	4.81 (1.98)	8.64 (0.60)
Total	97.5	97.5	97.5	97.5	97.5	96.5	96.5	96.5	96.5

	Clinopyroxene						**Spinel**			
	SMI_2		SMI_3	SMI_R		SMI_U	SMI_2	SMI_3	SMI_R	SMI_U
	wall	host	host	wall	host	host				
n	3	3	6	6	5	2	4	1	6	1
SiO_2	50.2 (2.0)	53.0 (1.1)	49.4 (1.1)	46.0 (1.1)	49.0 (0.9)	49.1 (1)				
TiO_2	1.75 (0.00)	1.09 (0.00)	1.08 (0.55)	1.34 (0.25)	1.15 (0.23)	1.10 (0.02)	1.92 (0.00)	3.74	1.79 (0.09)	
Al_2O_3	5.59 (2.03)	4.78 (0.77)	4.08 (0.39)	6.05 (0.55)	4.23 (0.22)	4.19 (0.42)	7.09 (0.92)	9.54	5.77 (0.83)	43.7
Cr_2O_3			1.36 (0.22)		1.55 (0.20)		11.4 (1.6)	6.33	5.80 (0.72)	3.30
FeO	8.50 (1.31)	2.76 (0.00)	5.81 (0.78)	9.51 (0.72)	6.44 (0.28)	6.18 (0.61)	79.6 (6.1)	80.4	86.6 (3.2)	47.2
MgO	11.3 (2.0)	13.9 (1.0)	12.6 (0.9)	10.4 (0.7)	11.9 (0.3)	11.9 (0.3)				5.81
CaO	22.1 (1.8)	24.0 (1.4)	25.1 (1.5)	25.6 (1.4)	25.5 (0.7)	26.6 (0.5)				
Na_2O	1.66 (0.10)	1.15 (0.17)	0.79 (0.20)	1.03 (0.38)	0.76 (0.32)	0.87 (0.42)				
K_2O				0.49 (0.00)		0.30 (0.00)				
Total	101.10	100.68	100.22	100.42	100.53	100.24	100.01	100.00	99.96	100.00

	Glass							**Whole SMI**			
	SMI_2		SMI_3	SMI_R		SMI_U		SMI_2	SMI_3	SMI_R	SMI_U
	K-rich	Na-rich	K-rich	Krich	Na-rich	Krich	Na-rich				
n	9	1	3	8	4	7	1				
SiO_2	66.5 (1.7)	59.6	65.5 (1.9)	63.6 (1.3)	52 (1.8)	62.4 (1.9)	57.8	53.2	52.9	51.7	52.1
TiO_2								1.53	2.11	1.40	1.26
Al_2O_3	20.3 (0.5)	18.6	18.4 (0.9)	20.3 (1)	17.4 (1.4)	18.9 (1.8)	17.6	14.3	13.7	14.3	15.0
Cr_2O_3								0.27	0.20	0.32	0.11
FeO					1.65 (0.38)	2.34 (0.94)	3.40	8.36	6.57	7.24	7.50
MgO	0.81 (0.27)	0.66	1.61 (0.60)	1.12 (0.24)	0.84 (0.50)	1.56 (0.56)	1.48	6.22	6.38	6.02	5.55
CaO	1.67 (0.48)	1.55	2.81 (1.12)	2.80 (0.83)	2.74 (1.73)	3.12 (0.78)	2.09	9.06	9.95	11.5	10.6
Na_2O	3.40 (2.03)	12.0	2.97 (1.95)	2.10 (1.15)	15.91 (2.39)	1.28 (0.29)	7.23	2.65	2.36	1.71	1.31
K_2O	2.86 (0.71)	3.10	4.21 (1.07)	5.57 (0.80)	4.92 (0.53)	5.95 (1.43)	5.85	1.87	2.68	3.24	4.29
P_2O_5											0.91
F_2O											0.02
Cl_2O											0.04
Total	95.5	95.5	95.5	95.5	95.5	95.5	95.5	97.5	96.9	97.4	98.6

Notes: standard deviation (1σ) values are shown in brackets where the number of analyses (n) exceeds 1.

Table 4. Trace element compositions of SMI analyzed with LA-ICP-MS (ppm)

	SMI_8		SMI_9		SMI_10		SMI_12		SMI_13		SMI_14		SMI_15		SMI_16	
		3σ		3σ		3σ		3σ		3σ		3σ		3σ		3σ
Ba	530	1	193	1	232	1	228	1	194	1	117	1	227	0	311	1
Nb	86.7	1.9	33.4	1.8	41.0	1.7	39.7	1.8	36.1	1.7	19.6	1.3	32.2	1.4	44.1	1.4
Ta	4.56	0.60	1.74	0.79	2.00	0.36	1.87	0.62	1.81	0.89	0.92	0.32	1.78	0.46	1.93	0.69
La	39.1	1.2	15.9	0.6	17.2	0.9	22.8	0.8	18.9	0.8	16.1	0.7	22.4	1.4	19.3	0.9
Ce	83.8	1.5	44.1	0.0	39.3	1.4	55.1	0.7	46.7	0.0	37.8	1.2	49.4	0.8	42.4	1.0
Sr	865	2	338	2	338	2	407	2	405	2	278	2	367	2	364	2
Pr	9.88	0.82	7.20	1.56	5.71	1.88	6.82	1.31	6.09	1.74	4.91	1.98	5.83	1.59	6.29	1.83
Nd	43.0	2.0	29.9	1.8	24.3	2.8	34.1	1.9	29.6	1.4	16.7	2.0	29.0	2.2	24.4	2.7
Hf	2.38	0.96	1.26	1.05	1.68	1.38	1.41	0.86	1.41	0.66	0.51*	2.87	1.64	1.42	1.61	1.06
Zr	152	2	97.3	1.3	64.7	1.7	96.4	1.2	90.9	1.5	61.0	1.3	99.5	1.5	88.5	2.1
Sm	8.27	1.42	3.62	1.63	5.04	1.30	4.03	0.81	6.96	1.05	3.73	1.84	4.07	1.19	4.39	1.71
Eu	2.05	1.28	1.84	0.79	1.32*	1.72	1.58*	1.63	1.74	1.31	0.99*	1.69	1.12*	2.12	1.33*	2.37
Gd	5.49	1.20	4.23	1.88	4.13	1.86	5.93	0.62	5.46	0.92	3.28	2.34	4.44	1.96	3.73	1.54
Tb	0.60*	3.09	0.97*	1.71	0.39*	2.23	0.68*	1.54	0.60*	0.77	0.33*	2.87	0.25*	3.55	0.83*	0.91
Ti	12034	4	8563	3	10722	3	6544	4	7069	4	3043	6	2112	13	9445	3
Dy	4.27	2.45	5.20	1.72	3.99	2.09	3.34	0.00	3.31	0.00	3.14	0.84	3.41	2.30	4.06	2.08
Ho	0.88*	2.04	0.69*	1.57	0.65*	1.18	0.67*	1.67	0.71*	1.05	0.56*	1.48	0.58*	2.73	0.63*	0.85
Y	28.6	4.0	19.2	3.9	15.1	3.0	16.1	3.3	19.0	2.6	11.1	3.2	14.6	4.2	15.5	3.6
Er	2.86	0.74	1.08*	1.98	2.10	1.30	0.96*	1.66	1.67	1.64	0.80*	2.22	0.68*	4.65	2.49	1.13
Tm	0.52*	0.92	0.29*	1.47	0.20*	1.70	0.07*	3.10	0.30*	1.54	0.32*	0.83	0.32*	1.55	0.15*	1.88
Yb	3.87	1.23	2.38	1.01	1.11*	1.40	1.28	0.88	2.06	0.90	b.d.l.	-	0.65*	3.83	1.38*	2.05
Lu	0.45*	1.96	0.28*	2.66	0.19*	3.45	0.23*	3.07	b.d.l.	-	0.18*	2.81	b.d.l.	-	0.23*	3.22
V	127	23	161	16	214	16	200	13	191	14	156	17	98	34	179	16
Cr	b.d.l.	-	2309	55	3032	34	4049	29	3610	26	4856	25	3493	37	3270	31
Ni	134	12	209	8	254	6	297	4	267	6	298	5	260	8	369	5

b.d.l. - below detection limit

* - analyses with high uncertainty

Figure 1

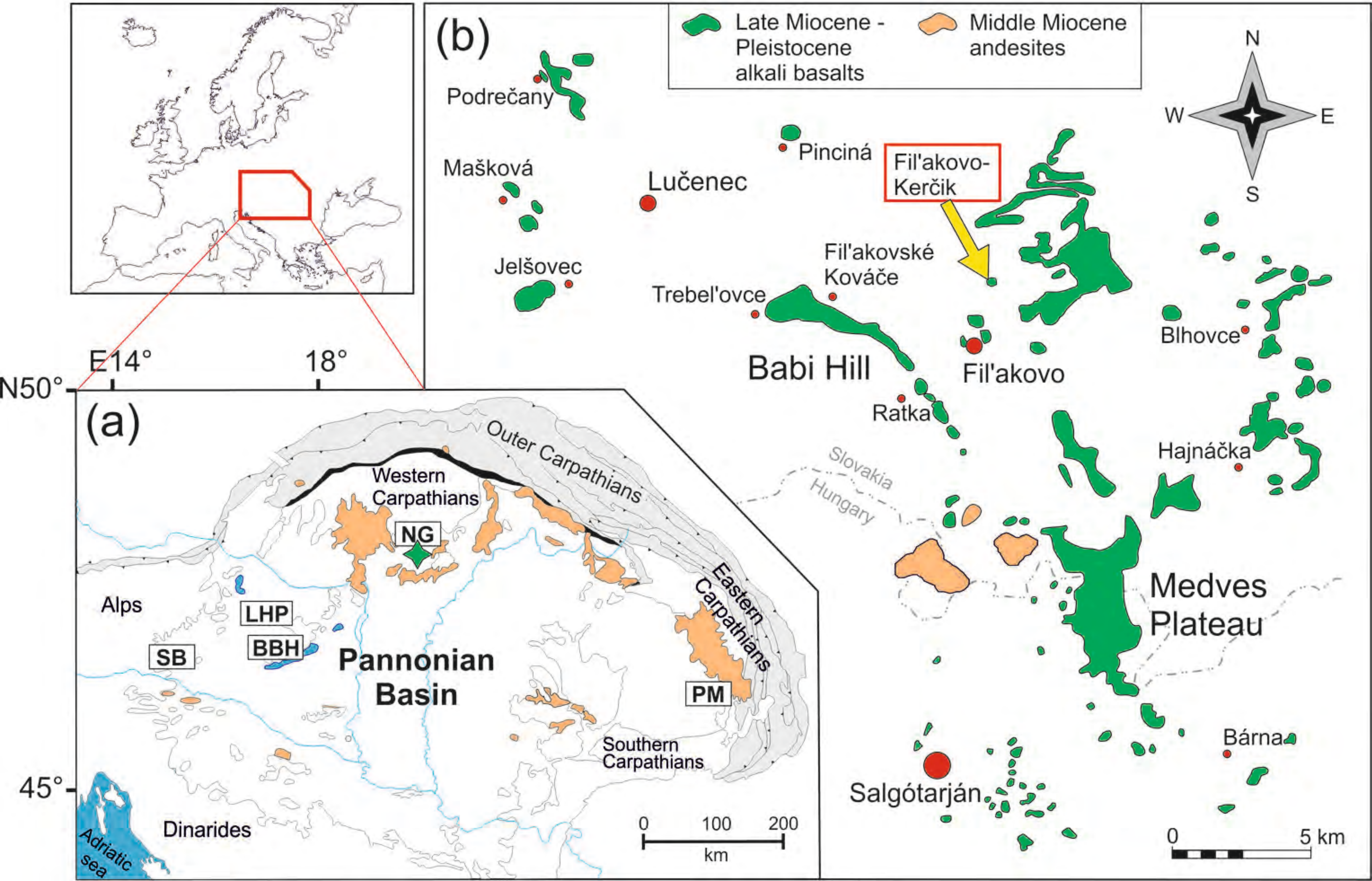

(b)
Late Miocene - Pleistocene alkali basalts
Middle Miocene andesites
N
W
E
S
Podrečany
Pinciná
Mašková
Lučenec
Fil'akovo-Kerčik
Fil'akovské Kováče
Jelšovec
Trebel'ovce
Blhovce
Babi Hill
Fil'akovo
Ratka
Hajnáčka
Slovakia
Hungary
Medves Plateau
Bárna
Salgótarján
0
5 km
E14°
18°
N50°
45°
(a)
Outer Carpathians
Western Carpathians
NG
Eastern Carpathians
Alps
LHP
BBH
SB
Pannonian Basin
PM
Southern Carpathians
Dinarides
Adriatic sea
0
100
200
km

Figure 2

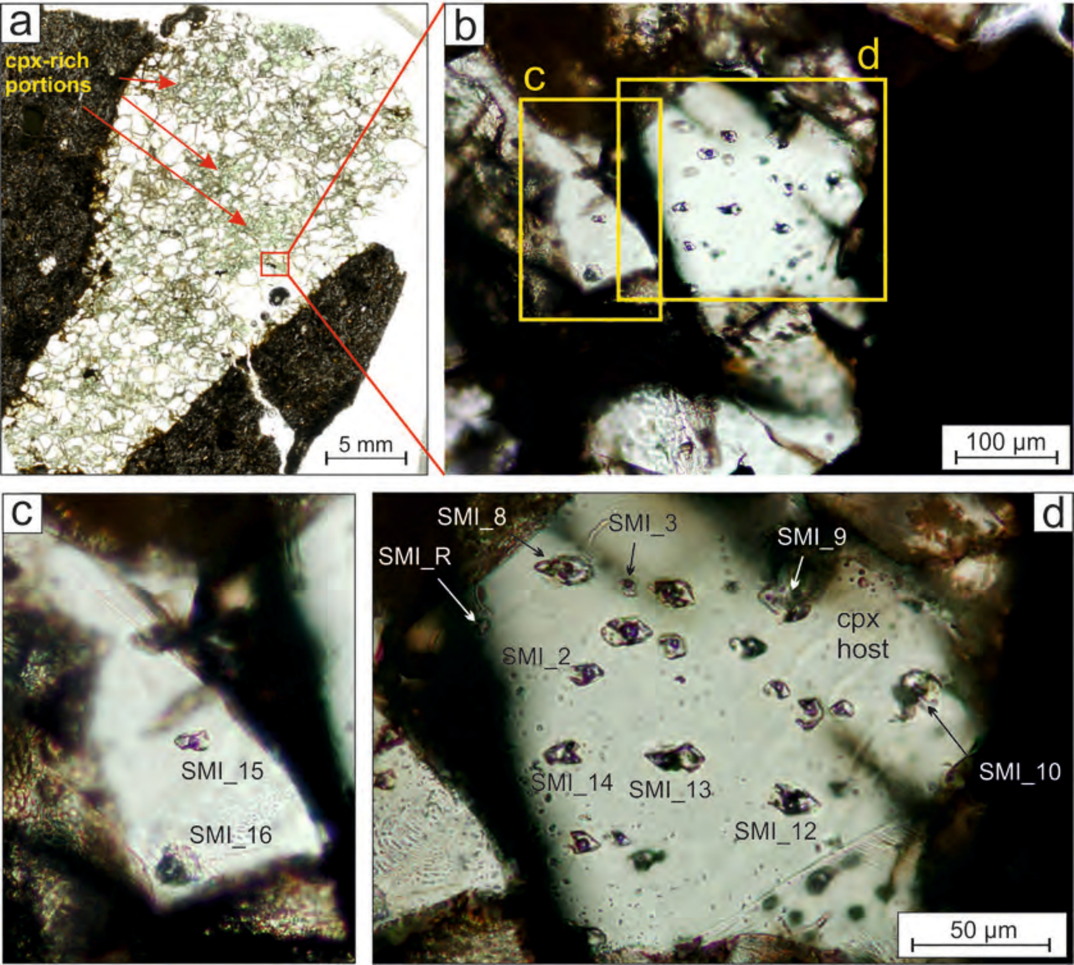

a
cpx-rich portions
5 mm
b
c
d
100 μm
c
SMI_15
SMI_16
d
SMI_8
SMI_3
SMI_9
SMI_R
SMI_2
cpx host
SMI_14
SMI_13
SMI_12
SMI_10
50 μm

Figure 3

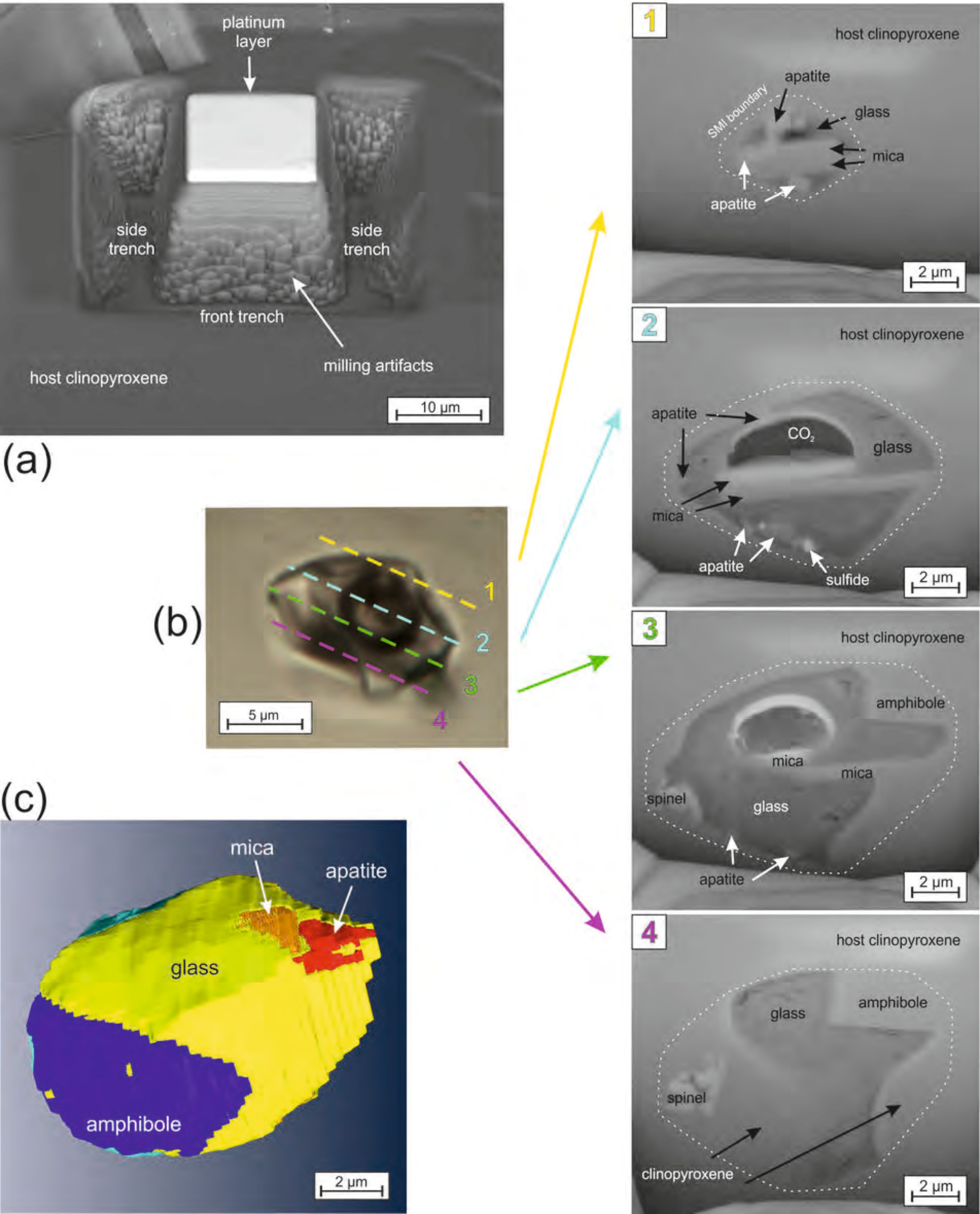

platinum layer
side trench
side trench
front trench
milling artifacts
host clinopyroxene
10 µm
(a)
(b)
1
2
3
4
5 µm
(c)
mica
apatite
glass
amphibole
2 µm
1
host clinopyroxene
apatite
SMI boundary
glass
mica
apatite
2 µm
2
host clinopyroxene
apatite
CO₂
glass
mica
apatite
sulfide
2 µm
3
host clinopyroxene
amphibole
mica
mica
spinel
glass
apatite
2 µm
4
host clinopyroxene
glass
amphibole
spinel
clinopyroxene
2 µm

Figure 4

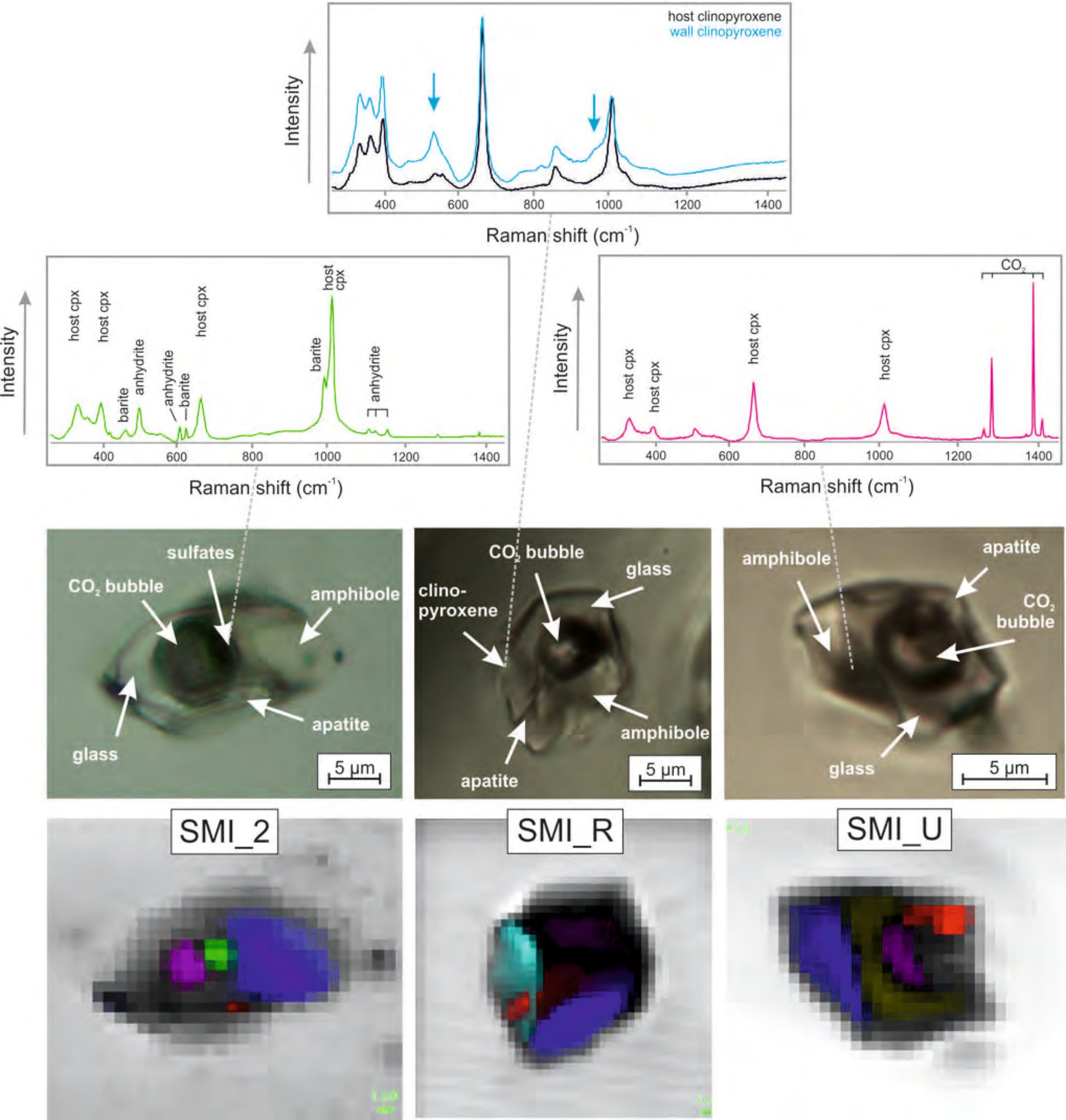

host clinopyroxene
wall clinopyroxene
Intensity
400
600
800
1000
1200
1400
Raman shift (cm^{-1})
Intensity
host cpx
host cpx
barite
anhydrite
anhydrite
barite
host cpx
barite
host cpx
anhydrite
400
600
800
1000
1200
1400
Raman shift (cm^{-1})
Intensity
CO$_2$
host cpx
host cpx
host cpx
host cpx
400
600
800
1000
1200
1400
Raman shift (cm^{-1})
sulfates
CO$_2$ bubble
amphibole
glass
apatite
5 µm
CO$_2$ bubble
glass
clino-pyroxene
amphibole
apatite
5 µm
amphibole
apatite
CO$_2$ bubble
glass
5 µm
SMI_2
SMI_R
SMI_U

Figure 5

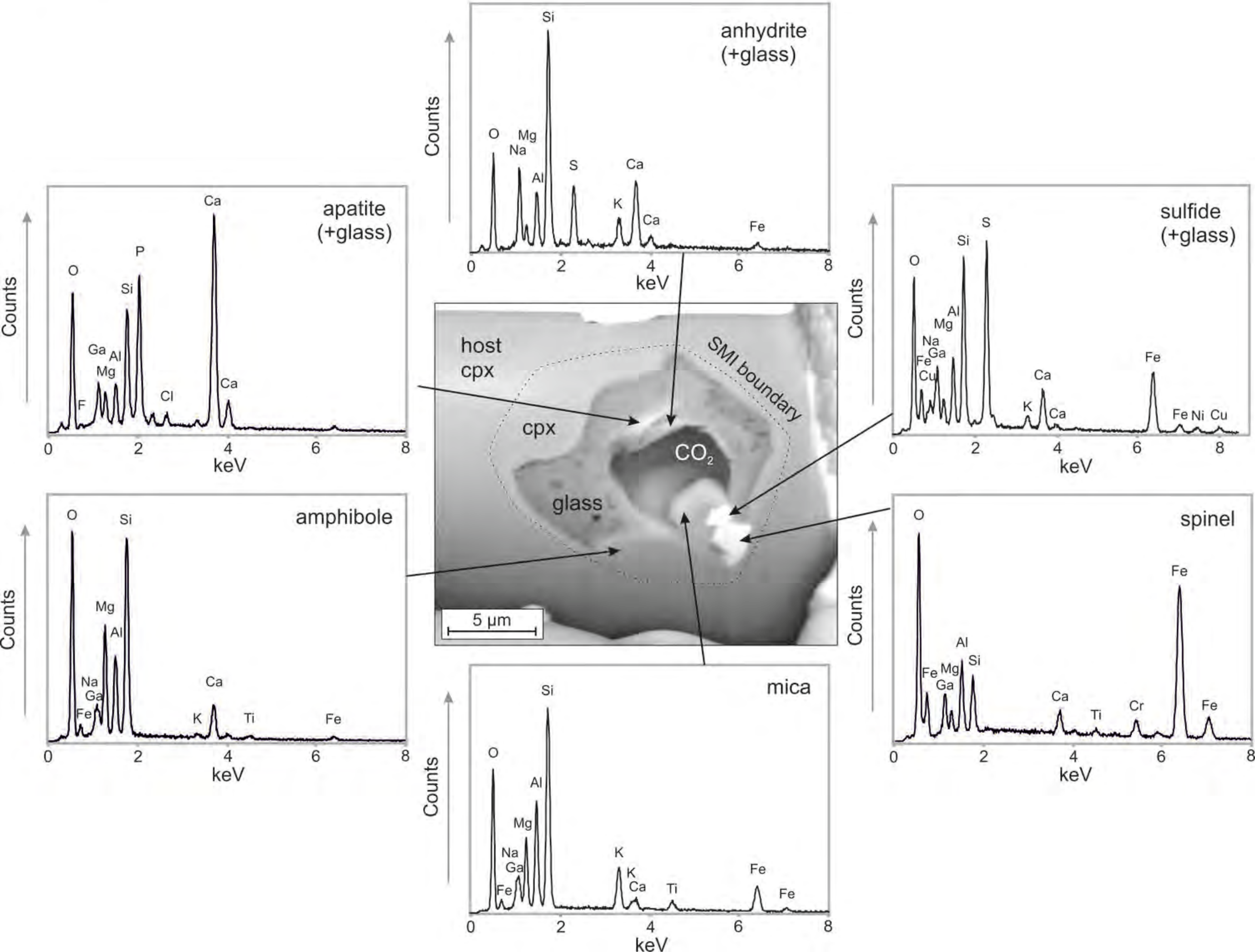
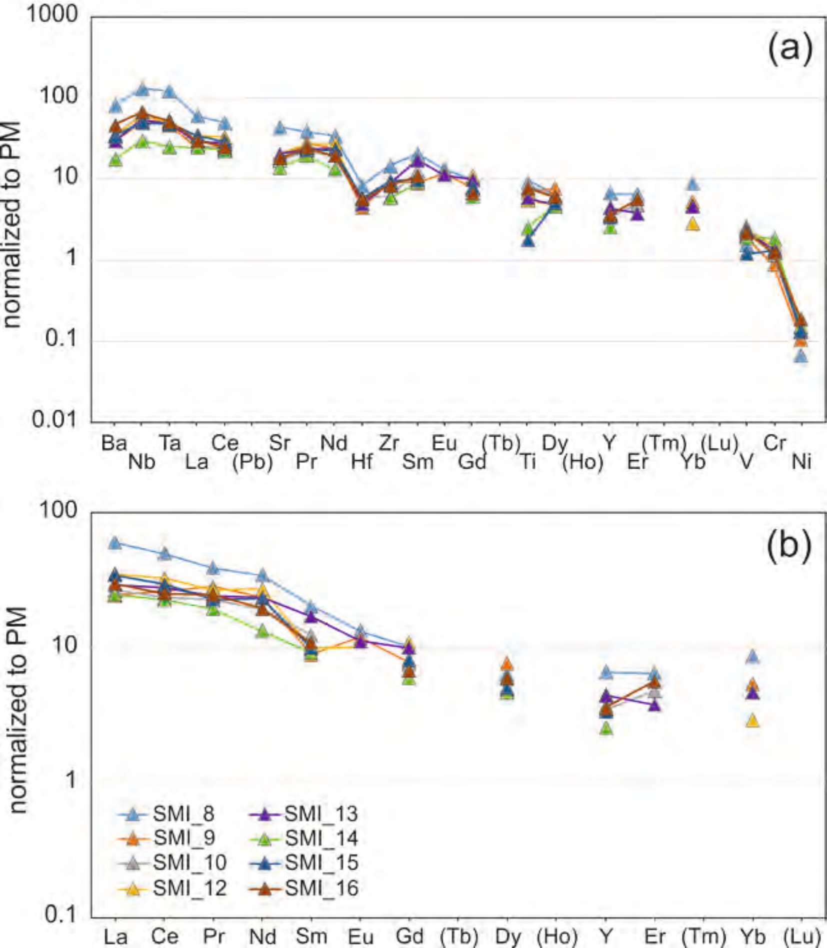
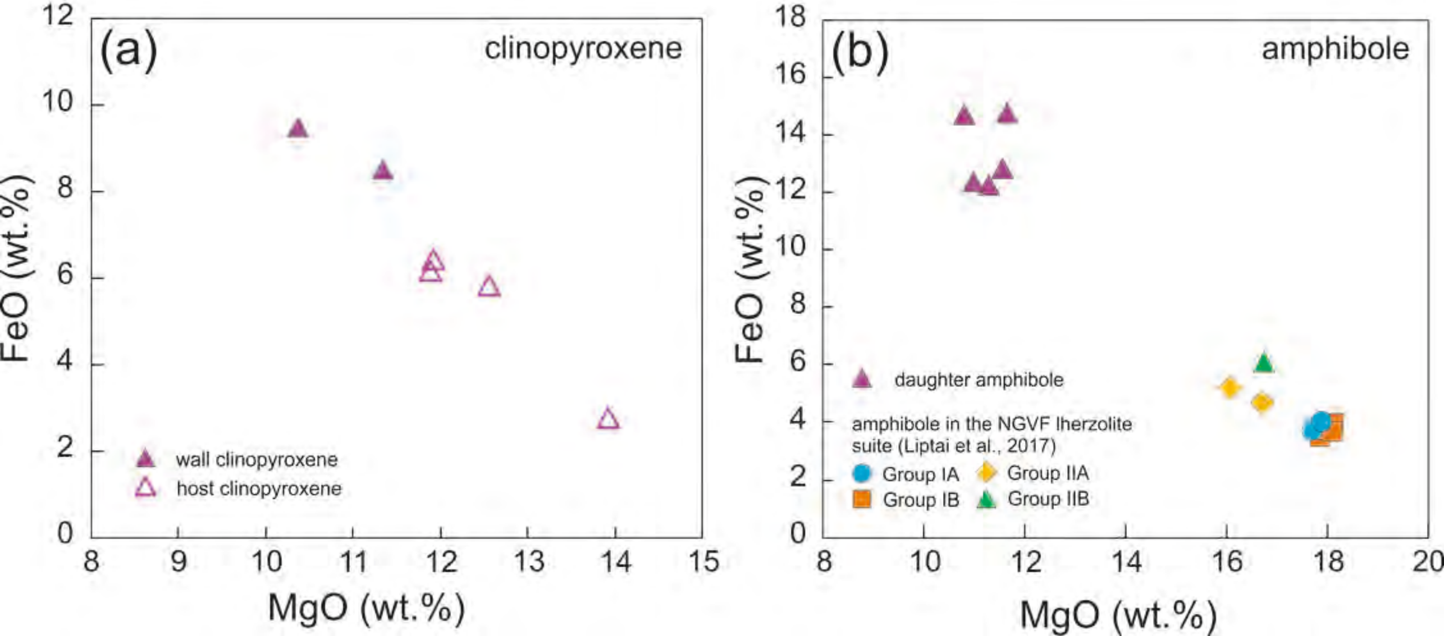

anhydrite
(+glass)
Counts
keV
O
Mg
Na
Al
Si
S
K
Ca
Ca
Fe
0
2
4
6
8
apatite
(+glass)
Counts
keV
O
Ga
Al
Mg
F
Si
P
Cl
Ca
Ca
sulfide
(+glass)
Counts
keV
O
Fe
Cu
Na
Ga
Mg
Al
Si
S
K
Ca
Ca
Fe
Fe
Ni
Cu
amphibole
Counts
keV
O
Na
Ga
Fe
Mg
Al
Si
K
Ca
Ti
Fe
spinel
Counts
keV
O
Fe
Mg
Ga
Al
Si
Ca
Ti
Cr
Fe
Fe
mica
Counts
keV
O
Na
Ga
Fe
Mg
Al
Si
K
K
Ca
Ti
Fe
Fe
host
cpx
SMI boundary
cpx
CO_2
glass
5 µm

Figure 6



(a)
normalized to PM
1000
100
10
1
0.1
0.01
Ba
Nb
Ta
La
Ce
(Pb)
Sr
Pr
Nd
Hf
Zr
Sm
Eu
Gd
(Tb)
Ti
Dy
(Ho)
Y
Er
(Tm)
Yb
(Lu)
V
Cr
Ni
(b)
normalized to PM
100
10
1
0.1
La
Ce
Pr
Nd
Sm
Eu
Gd
(Tb)
Dy
(Ho)
Y
Er
(Tm)
Yb
(Lu)
SMI_8
SMI_9
SMI_10
SMI_12
SMI_13
SMI_14
SMI_15
SMI_16

Figure 7



(a)
clinopyroxene
FeO (wt.%)
MgO (wt.%)
0
2
4
6
8
10
12
8
9
10
11
12
13
14
15
▲ wall clinopyroxene
△ host clinopyroxene
(b)
amphibole
FeO (wt.%)
MgO (wt.%)
0
2
4
6
8
10
12
14
16
18
8
10
12
14
16
18
20
▲ daughter amphibole
amphibole in the NGVF lherzolite suite (Liptai et al., 2017)
● Group IA
◆ Group IIA
■ Group IB
▲ Group IIB

Figure 8

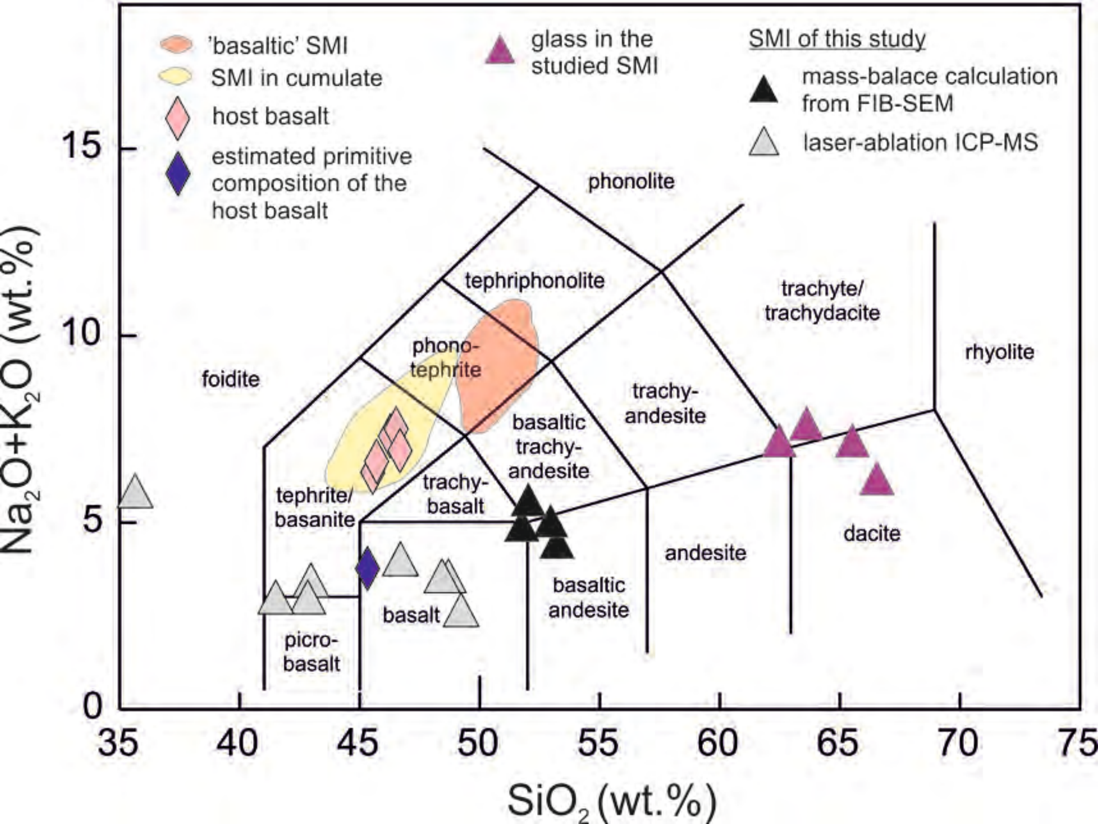

'basaltic' SMI
SMI in cumulate
host basalt
estimated primitive composition of the host basalt
glass in the studied SMI
SMI of this study
mass-balace calculation from FIB-SEM
laser-ablation ICP-MS
phonolite
tephriphonolite
phono-tephrite
foidite
trachyte/ trachydacite
rhyolite
trachy-andesite
basaltic trachy-andesite
trachy-basalt
tephrite/ basanite
andesite
dacite
basaltic andesite
basalt
picro-basalt
15
10
5
0
35
40
45
50
55
60
65
70
75
Na2O+K2O (wt.%)
SiO2 (wt.%)

Figure 9

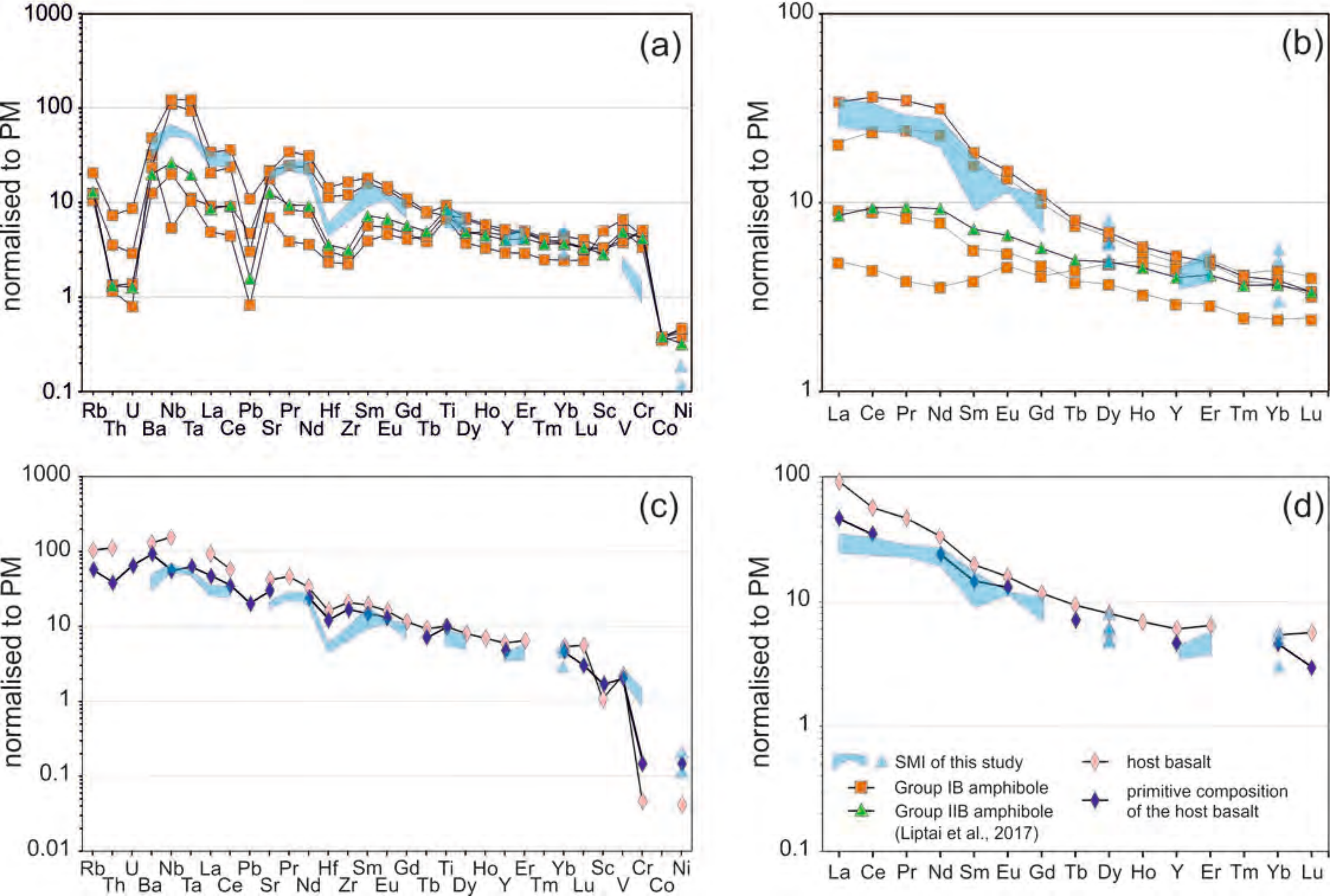
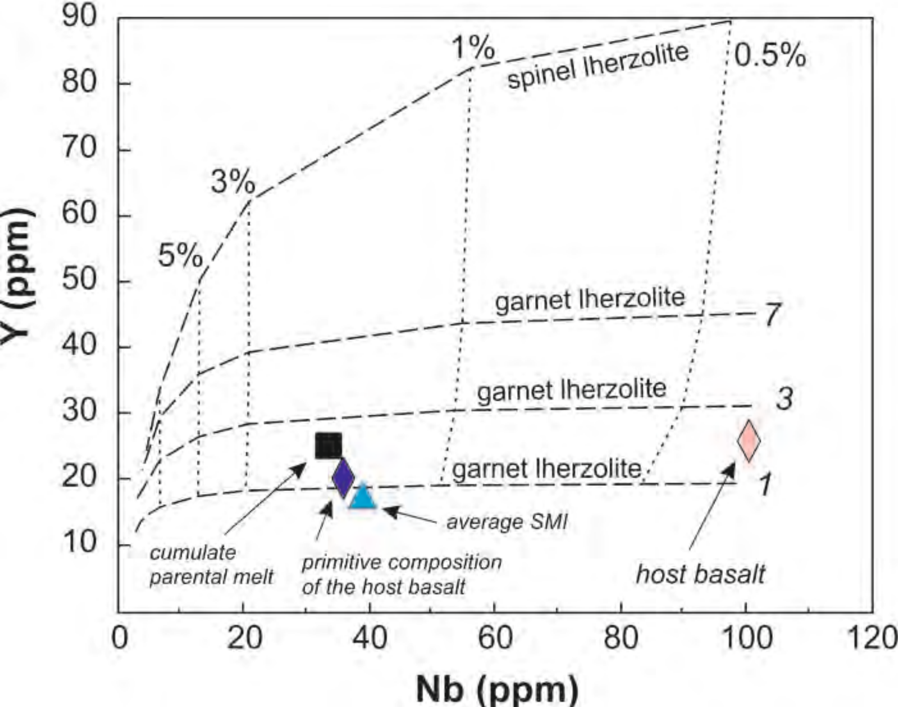
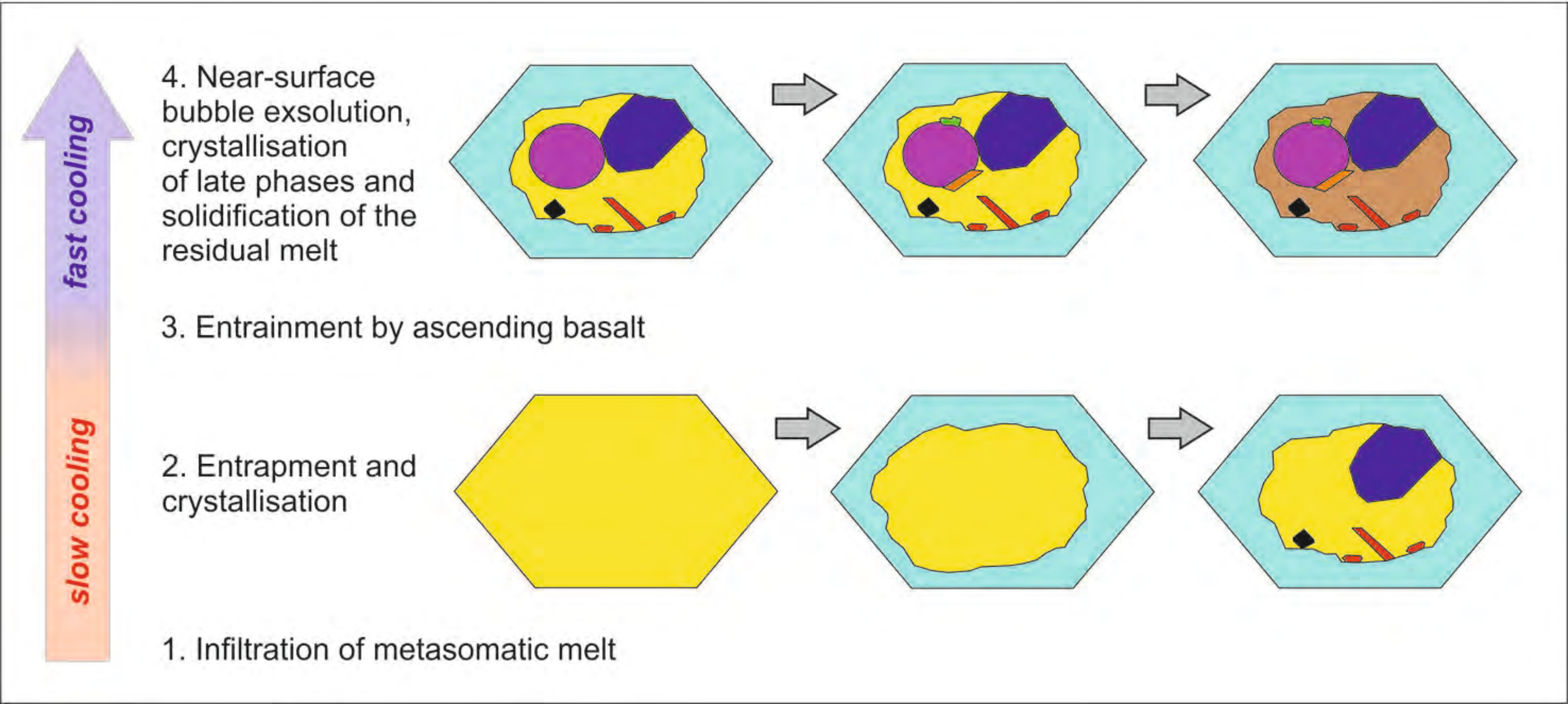

(a)
(b)
(c)
(d)
normalised to PM
1000
100
10
1
0.1
0.01
Rb Th U Ba Nb Ta La Ce Pb Sr Pr Nd Hf Zr Sm Eu Gd Tb Ti Dy Ho Y Er Tm Yb Lu Sc V Cr Co Ni
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Y Er Tm Yb Lu
SMI of this study
Group IB amphibole
Group IIB amphibole
(Liptai et al., 2017)
host basalt
primitive composition
of the host basalt

Figure 10



90
80
70
60
50
40
30
20
10
Y (ppm)
0
20
40
60
80
100
120
Nb (ppm)
1%
spinel lherzolite
0.5%
3%
5%
garnet lherzolite
7
garnet lherzolite
3
garnet lherzolite
1
average SMI
cumulate
parental melt
primitive composition
of the host basalt
host basalt

Figure 11


fast cooling
slow cooling
4. Near-surface bubble exsolution, crystallisation of late phases and solidification of the residual melt
3. Entrainment by ascending basalt
2. Entrapment and crystallisation
1. Infiltration of metasomatic melt