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Highly evolved miaskitic syenites deciphering the origin and nature of enriched mantle source of ultrapotassic magmatism in the Variscan orogenic root (Bohemian Massif, Moldanubian Zone)

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Abstract

A detailed study of alkali-rich syenites from the Gföhli unit of the Moldanubian Zone in the Bohemian Massif provides constraints on the exact origin and character of mantle source of ultrapotassic magmatism in the Variscan orogenic root in Central Europe. The syenites are characterized by highly alkaline composition (K2O 11.3–12.7 wt%; K2O/Na2O 6.8–7.5), crust-like isotopic signatures (87Sr/86Sr~0.7116; εNd~335 ≤ –7.8), and significant trace element enrichment (Th, U, Zr, Hf, LILE, LREE). They host an extraordinary amount of zircon (0.5–5 vol%) along with subordinate titanite and apatite, reflecting their miaskitic affinity. Mineral chemistry suggests that syenites formed through fractional crystallization and accumulation from highly reduced,
metaluminous to slightly peraluminous mantle-derived alkaline magmas. Whole-rock geochemistry and Sr-Nd isotopes provide direct evidence that they were produced by partial melting of metasomatic phlogopite-bearing vein network (glimmerites) in the lithospheric mantle, generated by the interaction of (U)HP fluids/melts derived from deeply subducted crustal material (Moldanubian granulites) with wall-rock peridotites. Low-degree partial melting of pure vein component produced unusual geochemical signatures of miaskitic syenites, compared to the composition of common ultrapotassic rocks in the Bohemian Massif, reflecting relatively higher degrees of partial melting of mixed glimmerite-peridotite mantle source.

The emplacement of alkali-rich syenites was almost contemporaneous with the mantle source enrichment and closely followed by initial fast cooling dated by $^{40}$Ar/$^{39}$Ar amphibole-biotite ages ranging between 329.8 ± 1.6 and 331.4 ± 0.7 Ma, corresponding to rapid exhumation of the Variscan orogenic root in Central Europe. The U-Pb apatite age of 305.2 ± 5.3 Ma likely reflects further cooling to lower temperatures. The syenite emplacement was linked to the early impulse of ultrapotassic magmatism associated with the Andean-type subduction of the Saxothuringian domain beneath the Moldanubian block. The close temporal association of K-rich magmatism in the Saxothuringian and Moldanubian Zone is indicated by identical cooling ages of miaskitic syenites and other Saxonian ultrapotassic rocks, as revealed by $^{40}$Ar/$^{39}$Ar dates around 330 Ma.

Keywords: (ultra)potassic magmatism, mantle metasomatism, phlogopite-rich source, low-degree melting, Bohemian Massif

1. Introduction

Mantle-derived potassic to ultrapotassic magmatism, typically related to post-collision extensional settings, represent magmatic proxy to trace lithospheric processes and thus allow to study effects of crustal recycling in subduction zones. The ultrapotassic magmas in orogenic belts are usually characterized by high $\text{K}_2\text{O}$ and MgO contents (Foley, 1992), elevated $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios, enrichment in large ion lithophile elements (LILE) and light rare earth elements (LREE), and continental crust-like isotopic signatures (e.g. Altherr et al., 2004; Conticelli et al., 2009; Zhao et al.,
It is widely accepted that such geochemical and isotopic composition of K-rich magmas is generated by partial melting of lithospheric mantle domains previously modified by modal metasomatism (e.g. Conticelli et al., 2015; Prelević et al., 2012). Metasomatic assemblages of hydrous minerals, commonly forming vein networks entrapped within wall-rock mantle peridotite (Foley et al., 2013), can be reactivated during later melting events, caused by a regional extension (Foley, 1992). Therefore, ultrapotassic magmatic activity typically accompanies high and ultra-high pressure (HP/UHP) metamorphism (Janoušek and Holub, 2007) within deeper levels of subduction zones, as demonstrates occurrences of alkaline K-Mg-rich rocks in many collisional belts, involving Variscan and Alpine Orogen in Europe (e.g. Ersoy and Palmer, 2013; von Raumer et al., 2014).

The internal orogenic domain of the Variscan belt in the Bohemian Massif (Fig. 1a) hosts diverse types of ultrapotassic rocks (Janoušek et al., 2019, 2020; Krmiček et al., 2016; Kubinová et al., 2017) and hence provide a unique insight into geodynamic and magmatic evolution of deeper parts of the Variscan Orogen during subduction-related events. The deep Variscan burial of crustal assemblages is recorded by a close spatial association of HP felsic granulites with garnet-bearing ultrabasic rocks (Kubeš et al., 2022) along with the presence of UHP phases preserved in host granulites (Kotková et al., 2011; Perraki and Faryad, 2014).

This study focuses on mineralogical, geochemical, and isotopic characteristics of alkali-rich miaskitic syenites, combined with conventional geochronological dating, in order to shed light on the petrogenesis and magmatic evolution of the highly evolved member of post-collision K-rich magmatism in the Moldanubian Zone (Bohemian Massif). The syenites geochemically correspond to miaskitic rocks, however, their genesis differs from common miaskitic varieties, since they originated through accumulation of mantle-derived alkali-rich magmas without significant prolonged subsequent differentiation processes at shallow crustal levels (see Marks and Markl, 2017 for review). Importantly, the major element composition and extreme trace element enrichment of the alkali-rich syenites along with their crust-like Sr isotopic signatures identify an exact origin and nature of enriched mantle source for (ultra)potassic magmas in the Bohemian Massif, corresponding to phlogopite-bearing vein network enclosed in the subcontinental lithospheric mantle. Furthermore, our geochemical data indicate that the alkali-rich syenites represent initial melts produced by a low-degree
melting of phlogopite-dominated component, whereas other ultrapotassic members (e.g. durbachites, lamproites, lamprophyres) reflect relatively higher degrees of partial melting of rather mixed peridotite-phlogopite material.

2. Geological settings

The studied intrusion of the alkali-rich syenites is situated southeast of the ultrapotassic Třebíč pluton (Fig. 1b) belonging to the so-called durbachite series of the eastern Moldanubian Zone – the high-grade root of the Variscan Orogen in the Bohemian Massif (Janoušek et al., 2020; Janoušek and Holub, 2007). The internal orogenic domain mostly consists of mélange- to high-grade metamorphic rocks extensively intruded by numerous granitoid plutons (Žák et al., 2014).

The Moldanubian Zone is traditionally subdivided into three principal tectonostratigraphic units differing in lithological assemblages and metamorphic conditions: the Monotonous, Varied and Gföhl units (e.g. Lardeaux et al., 2014). Mid-crustal, amphibolite-facies Monotonous and Varied units, generally termed Drosendorf unit, mainly consist of garnet-sillimanite paragneisses along with subordinate orthogneisses and amphibolites. Neoproterozoic-Early Paleozoic sedimentation ages were determined for the protolith of both mid-crustal complexes (Košler et al., 2014). The lower crustal Gföhl unit is composed of anatectic orthogneisses and migmatites, and amphibolites accompanied by HP granulites (Tajčmanová et al., 2006). The HP felsic granulites usually enclose spinel and/or garnet-bearing peridotites hosting pyroxenite and eclogite layers (Kubeš et al., 2022; Medaris et al., 2005). The magmatic protolith of the Gföhl gneisses shows Cambrian-Devonian ages (Friedl et al., 2004).

The Variscan metamorphic evolution of the Moldanubian Zone was accompanied by extensive plutonic activity taking place in contrasting geodynamic settings, mostly from Late Devonian to Carboniferous (Žák, et al. 2014; references therein). These various igneous stages include: (1) calc-alkaline and high-K calc-alkaline subduction-related suites of the Central Bohemian Plutonic Complex (~373–340 Ma); (2) (ultra)potassic, Mg-rich plutons of the durbachite series, associated with rapid exhumation of the Gföhl unit to mid-crustal assemblages (~340–355 Ma); (3) peraluminous anatectic
S-type and high-K, I-type granitoids (~330–326 Ma) followed by (4) small calc-alkaline intrusions with I-type affinity of the Moldanubian Plutonic Complex (~320–300 Ma).

The vigorous (ultra)potassic magmatism of the Moldanubian Zone, a characteristic feature of the entire European Variscan belt (von Raumer et al., 2014), is documented by widespread occurrence of durbachitic plutons which form two NNE–SSW oriented belts within the Bohemian Massif (see Janoušek and Holub, 2007 for review). Most plutons of the Eastern Durbachite Belt, involving large and smaller satellite bodies on Czech (Třebíč, Jihlava, Drahonín) and Austria territory (Rastenberg, Ybbs), have been previously investigated in detail from a geochemical, geochronological or geophysical approach (e.g. Gerdes et al., 2000; Janoušek et al., 2013, 2020; Kotková et al., 2010; Leichmann et al., 2017). By contrast, the relatively small intrusion of alkali-rich syenites studied here has remarkable geochemical composition and uncertain origin (Leichmann et al., 2004) that has been the focus of only a few petrological/mineralogical studies so far (Kubeš et al., 2021; Leichmann et al., 1998, 2004; Škoda et al., 2009). The syenites have attracted attention especially because of their significantly high radioactivity (U ~390 ppm, Th ~700 ppm; Leichmann et al., 1998) dictated by extreme high field strength elements (HFSE) enrichment (e.g., ZrO\textsubscript{2} up to 2.3 wt%; Leichmann et al., 2004) due to extraordinary amount of zircon (up to 5 vol%; Škoda et al., 2009) and its extensive late hydrothermal alteration (Kubeš et al., 2021).

3. Sampling and analytical methods

The relatively small intrusion of the alkali-rich syenites (up to 100 m long) from the Gföhl unit of the Moldanubian Zone was systematically sampled in order to cover all differentiated syenite varieties (Fig. 2a–c) (10 samples for each variety), described in Section 4.1. Consequently, the samples were processed to polished thin sections for detailed optical microscopy studies (Fig. 2d, e) and subsequent analytical techniques described below.

Zircon crystals were separated by crushing and sieving of the central syenite variety to a fraction of 64–512 μm and subsequently were concentrated by magnetic and liquid (tetrabromomethane) separation. Secondary electron (SEM) images, showing zircon morphology (Fig.
3a), were taken by a JEOL 6490 LV scanning electron microscope using an accelerating voltage of 15 kV and beam current of 1 nA. Back-scattered electron (BSE) images (Fig. 3b–f) along with major and minor element chemistry of rock-forming and accessory phases (Table 1, 2), were obtained with a Cameca SX 100 electron microprobe (EMP). Operating conditions for individual spot analyses were as follows: wavelength-dispersive mode, an accelerating voltage of 15 kV, a beam current of 10 nA, and a beam size of 2 µm for common accessory minerals (zircon, titanite, ilmenite), 5 µm for silicates (feldspars, amphibole, biotite, chlorite), and 10 µm forapatite. The following natural and synthetic standards were used: sanidine (Si, Al), orthoclase (K), baryte (Ba), albite (Na), wollastonite (Ca), pyrope (Mg), hematite (Fe), titanite (Ti), vanadinite (Cl, V, Pb), zircon (Zr), ThO$_2$ (Th), topaz (F), fluorapatite (P).

Trace elements concentrations of major accessory phases (Table 3) were measured by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). The instrumentation consisted of LSX-213 G2+ laser ablation device and Agilent 7700 ICP-MS analyser with an octopole reaction cell. The laser operates at a wavelength of 213 nm with a pulse duration ≤4 ns. Using helium as a carrier gas with a flow rate of 0.9 l min$^{-1}$. The aerosol was mixed with argon serving as makeup gas with flow rate 1 l min$^{-1}$ and transported to the ICP-MS. The mass spectrometer operated at the forwarded power of 1550 W and Ar gas flow rate of 15 l min$^{-1}$ (outer plasma gas). Ablation spot was from 40 to 50 µm in diameter, regarding the area analyzed. Repetition rate was 10 Hz and fluence 5 J cm$^{-2}$. One spot was analyzed for 60 s. Total integration time was 4.1 s. External calibration was performed using the standard reference materials (SRM) NIST 610 and NIST 612. Quantification was based on the sum of oxides. The total sum of all oxides (estimated from the elemental analysis by LA-ICP-MS) was normalized to 100 wt%. Then the analytes were expressed as elements in ppm. This method is internal standard independent and does not require the precise determination of the reference element by another analytical method at the specific area of the ablation spot. If the sample contains water or another component non-determinable by LA-ICP-MS (e.g. fluorine, hydrogen…), the normalization has to be performed to the sum obtained by subtracting the content of this component from 100 wt% (determined by another method or known from the general mineral formula).
The whole-rock major element composition (Table 4) was determined in the AcmeLabs Vancouver (Bureau Veritas) by ICP-OES after fusion with lithium borate flux. Trace elements, including rare earth elements (REE), were analyzed using ICP-MS with additional lithium tetraborate fusion. In addition, incompatible transition metals (Cr, Ni, V, Sc) were determined by ICP-MS after modified aqua regia digestion. For more analytical details, reproducibility, and detection limits see https://www.acmelab.com. Whole-rock Sr-Nd isotopic analyses were performed at Activation Laboratories Ltd., (ActLabs) Ontario. Sample dissolution in HF:HNO$_3$ and chemical separation procedures for Sr and Nd follow the methodology of Creaser et al. (2004). Isotope analyses were performed using a VG354 5-collector machine in a multi-dynamic data collection mod. Accuracy of the Sr and Nd isotopic composition was monitored using the NIST SRM987 and JNd1-1 isotopic standards. The long-term measured values of these standards were as follows: $^{87}\text{Sr}/^{86}\text{Sr} = 0.710269 \pm 21$ (1σ, n = 50) and $^{143}\text{Nd}/^{144}\text{Nd} = 0.512096 \pm 11$ (1σ, n = 11). For further analytical information see https://www.actlabs.com.

The U-Pb apatite dating (Table 5) along with mineral separation were performed at GeoSep Services (GSS) laboratory, Idaho. Apatite grains were separated from the original sample material using standard procedures combined with specific customized procedures described by Donelick et al. (2005). Laser spot locations were selected using optical microscope Zeiss Axioplan with transmitted light at 2000x magnification, which allowed for the recognition of features below the surface of individual grains. An Agilent 7700x quadrupole ICP-MS equipped with a New Wave Nd-YAG 213 nm laser ablation system was used to acquire the U-Pb isotopic ratios. For all laser analyses, the beam diameter was 20 μm and the frequency was set at 5 Hz, yielding ablation pits 16–18 μm deep. Ultra-high purity He and Ar gas were used to deliver the ablated material into the plasma source. The isotopes measured included $^{43}\text{Ca}$, $^{147}\text{Sm}$, $^{204}\text{Pb}$, $^{206}\text{Pb}$, $^{207}\text{Pb}$, $^{232}\text{Th}$, and $^{238}\text{U}$ (45 scans over 45 sec). Approximately 20 seconds were allowed between each analysis in order to clear the system prior to the next background data collection. Standards used included the Duluth complex FC, McClure Mountain MM, and Durango DR, which encompasses a wide standard age range from 1099 to 31.44 Ma (see Weber et al., 2019 for further analytical information).
$^{40}$Ar/$^{39}$Ar dating experiments were conducted on single biotite and amphibole grains (Table 6) extracted by gently crushing the samples. Loose grains were ultrasonically bathed in deionized water and rinsed until no suspension was released, then dried in a vented oven at 50 °C and inspected under a high-magnification binocular. The single grains were irradiated together for 10 h along with the neutron flux standard sanidine FCs (28.305 ± 0.036 Ma; Renne et al., 2010) in the dedicated Cd-lined CLICIT neutron flux facility at TRIGA-Corvallis (OR, USA). The data were regressed and corrected for instrumental parameters (blank, mass discrimination, SEM dead-time, post irradiation decay, and atmospheric contamination, J-gradient monitoring). Typical blanks (in fA) were $3 \times 10^{-2}$ (m/e = 36), $3 \times 10^{-2}$ (m/e = 37), $7 \times 10^{-3}$ (m/e = 38), $4 \times 10^{-2}$ (m/e = 39), $4 \times 10^{-1}$ (m/e = 40). Individual and pooled age errors are quoted at ± 1σ and include propagation of all instrumental and procedural uncertainties. Plateau ages (PA) are calculated as the inverse-variance weighted mean of contiguous steps featuring a figure of merit (Mean Squared Weighted Deviation, MSWD) falling in the fiducial interval. Total-gas ages (TGA) are calculated by individually summing the Ar isotopes of all fractions and by linearly propagating the associated errors (equivalent to a standard K/Ar age).

4. Results

4.1. Petrography

The petrography of the alkali-rich syenites has been previously described by Leichmann et al. (1998) and Kubeš et al. (2021), and thus only a brief petrographic description of samples used in this study are given here. The investigated syenite intrusion is exposed on the slopes of the Oslava river valley (two outcrops up to 100 m long) situated ca. 4 km northwest of the city Náměšť and Oslavou (Czech Republic), nearby the largest durbachitic body (Třebíč pluton) (Fig. 1b) in the Bohemian Massif (Janoušek et al., 2020). The syenites intrude high-grade crustal assemblages of the Gföhl unit mainly consisting of migmatized gneisses and biotite-bearing migmatites. Both outcrops of alkali-rich syenites are separated from ultrapotassic rocks of the Třebíč pluton by a several hundred meters wide zone of amphibole–biotite gneisses and biotite migmatites. The syenite intrusion consists of three
texturally, mineralogically and petrographically different syenite varieties (Fig. 2a–c), designated in this study as follows: (1) central (2) marginal (3) nodule variety. The classification of individual syenite varieties is based on the combination of both spatial (central–marginal) and textural (nodule) features.

The central variety is built up by fine-grained, orange to red-colored leucocratic rock (Fig. 2a) with a gradual transition to more melanocratic marginal variety. K-feldspar represents the dominant rock-forming mineral (up to 92 vol%) reaching the highest modal amount in central variety. It usually forms subhedral grains of relatively small size (~0.4 cm) compared to K-feldspar from marginal and nodule varieties (up to 1.5 cm). Very fine inclusions containing iron oxide are most likely responsible for its orange to red colour, a typical feature observed within all described syenite varieties (Fig. 2a–c). Subhedral to euhedral amphibole is regularly dispersed in the rock (<5 vol%) and exhibits a relatively high intensity of chloritization, which ordinarily progresses along cleavage plains of amphibole. A characteristic feature of the leucocratic variety is unusually high modal abundances of metamict zircon (~5 vol%) commonly surrounded by abundant microfractures (Fig. 2d). Quartz and plagioclase are typically absent. Tabular grains of biotite are completely replaced by chlorite (<1 vol%). Accessory phases commonly occur as U-thorite, titanite, apatite and ilmenite. Rare relicts of strongly altered thorianite and cheralite were observed exclusively within the central variety (Kubeš et al., 2021).

The marginal variety is characterized by medium- to coarse-grained texture, orange colour, lower K-feldspar abundances (7–82 vol%) and relatively high modal amount of amphibole (up to 10 vol%) and biotite (~1.8 vol%) regularly dispersed in the host rock (Fig. 2b). The prevailing K-feldspar usually occurs as subhedral grains with relatively variable sizes (0.6–1.5 cm). The green, pleochroic, sub- to euhedral amphibole grains (Fig. 2e) are locally replaced by secondary chlorite along cleavage plains. In contrast to central variety, zircon amount (0.5 vol%) considerably decreases in marginal variety. Moreover, amount of quartz (~3.5 vol%) and partially chloritized biotite moderately increases in marginal variety relative to central variety. Plagioclase is ordinarily absent or occurs in rare cases as strongly altered relics. Its alteration products are white mica, albite, and scapolite–marialite. Accessory phases usually include titanite, apatite, U-thorite and ilmenite.
The nodule variety was described based on amphibole grains clustering into small nodules (up to 5 cm across) within the medium- to coarse-grained marginal variety (Fig. 2c). Such characteristic feature of nodule variety reflects its high modal amount of amphibole reaching up to 17 vol%. Accordingly, K-feldspar amount is lower (77 vol%) and zircon amount slightly increases (~0.8 vol%) in the nodule variety compared to marginal variety. Plagioclase is mostly absent, whereas quartz (~2.5 vol%) and chloritized biotite (~2 vol%) amount is similar to marginal variety. Accessory phases are titanite, apatite, U-thorite and ilmenite.

4.2. Mineral textures and chemistry (EMP)

4.2.1. Feldspars

The subhedral perthitic K-feldspar (Or86.4–96.7), the most wide-spread rock-forming phase in syenites, exhibits quite uniform chemistry among described varieties (Table 1), with K2O and BaO content varying between 14.2–16.3 wt% and 0.33–0.64 wt%, respectively. Plagioclase is ordinarily absent or rarely occurs as elongated inclusions (<0.3 mm) in the K-feldspar and/or irregular aggregates (0.5 mm) within the K-feldspar rim. Both forms mainly consist of sodic plagioclase (An1.8–7.6) with similar chemistry.

4.2.2. Mafic phases

The sub- to euhedral amphibole dominates from mafic silicates and corresponds to Fe-rich pargasite (Fe/(Fe+Mg) = 0.74–0.91; ^\text{8}(\text{Na+K}) \text{ up to 0.89 apfu}) (Fig. 4a). Amphibole is commonly intergrown with chloritized biotite or gradually replaced by secondary chlorite along its cleavage planes. It has slightly higher total alkali contents (Na+K ~0.77–0.89 apfu) and lower Mg# (0.09–0.17; Mg# = molar Mg/[Mg + FeO]) in marginal and nodule variety compared to central variety (Na+K ~0.61–0.81 apfu; Mg# 0.21–0.26). Note that amphibole in nodule variety and amphibole from direct
contact between central and marginal variety plot in the middle of the fractionation trend shown in Mg# vs. Al diagram (Fig. 4b).

Fresh biotite occurs as tabular grains (<280 µm) enclosed in perthitic K-feldspar and/or closely associated with amphibole. Biotite corresponds to annite (Fe/(Fe+Mg) = 0.82–0.92) with the lowest Mg# values in marginal variety similar to amphibole (Table 1). Biotite is usually replaced by secondary chlorite of chamosite-like composition (Fe/(Fe+Mg) = 0.72–0.83) without significant chemical variations among syenite varieties. Besides, chlorite occurs as extremely fine-grained alteration products of titanite.

4.2.3. Zircon

Zircon usually forms euhedral crystals ranging from 100 to 350 µm in size. They have dominantly well-developed pyramids (101) and prisms (100) (Fig. 3a), less frequently evolved pyramids (121), (211), (301), and prism (110). Early magmatic inclusions in zircon typically consist of U-thorite (Fig. 3b). The vast majority of zircon experienced self-induced structural radiation damage (metamictization), followed by recrystallization (Fig. 3b) and/or fluid-driven hydrothermal alteration (Fig. 3c).

We present only EMP data from unaltered partially recrystallized zircon since the post-magmatic alteration extensively affected zircon chemistry, as exemplified by enhanced contents of non-formula elements (e.g. Ca, Fe, Al, P) and low ZrO₂ content, EMP analytical totals, and BSE intensity (Fig. 3c) (see Kubeš et al., 2021 for details). Pristine zircon (Fig. 3d) has relatively high ZrO₂ (~64–66 wt%) and SiO₂ (~32–33 wt%) contents, and low Th/U ratios (<1.5) with non-formula element contents below EMP detection limits (Table 2). Concentrations of UO₂ (0–1.6 wt%) and ThO₂ (0–1.3 wt%) vary widely on the inter- and intra-grain scale. Zircon from central variety shows slightly decreased HfO₂ content (0.98–1.23 wt%) and thus higher Zr/Hf ratios (~52–67) in contrast to marginal and nodule variety (HfO₂ 1.07–1.96 wt%; Zr/Hf ~32–55).

4.2.4. U-thorite
U-thorite occurs as irregular to rounded relatively small inclusions (<15 µm) enclosed in metamict zircon (Fig. 3b). The chemistry of early magmatic inclusions from only unaltered zircon domains are presented within this section (Table 3). The pristine U-thorite usually exhibit high ThO$_2$ (43.9–56.5 wt%) and UO$_2$ (19.3–30.0 wt%) contents, accompanied by variable ZrO$_2$ concentrations (0.14–4.32 wt%) routinely below 1 wt%, together with high EMP analytical totals (99–101.6 wt%).

4.2.5. Titanite

Titanite in all described syenite varieties exhibits somewhat distinct textural morphologies, mineralogical associations, and zonation patterns. Titanite mainly occurs as sub- to euhedral grains varying from 100 to 700 µm in size, intergrown with amphibole and/or closely associated with ilmenite. It also forms euhedral diamond-shaped crystals (<350 µm) enclosed in K-feldspar, often displaying patchy zonation patterns. In some cases, well-developed subhedral to euhedral crystals have preserved original oscillatory and/or sectorial zonation (Fig. 3e). Similar to zircon, titanite crystals experienced late fluid-driven alteration resulting in partial replacement of titanite by secondary anatase, reflected by high TiO$_2$ content and low EMP analytical totals and BSE intensities of extensively altered titanite domains (see Kubeš et al., 2021 for details). Therefore, chemical composition of pristine titanite is reported in this study (Table 2).

Unaltered titanite has a uniform chemical composition (TiO$_2$ 36–38 wt%, SiO$_2$ 30–31 wt%, CaO ~29 wt%) among individual syenite varieties and distinct textural types. It contains relatively high concentrations of Nb$_2$O$_5$ reaching up to 0.32 wt% (Table 2). Most titanite crystals show somewhat high Ti$^{4+}$/(Al + Fe$^{3+}$) ratios commonly ranging between 8.3–16.2.

4.2.6. Apatite

Apatite is typically present as sub- to euhedral short-prismatic crystals about maximum sizes of 250 µm and/or forms rounded grains reaching up comparable sizes (~200 µm). Apatite is usually
enclosed in perthitic K-feldspar and/or closely associated with amphibole. Apatite displays no visible effects of late alteration in contrast to zircon and titanite. The oscillatory magmatic zoning of apatite grains is commonly preserved (Fig. 3f).

It chemically corresponds to fluorapatite (F ~3.40–3.85 wt%). Concentrations of P₂O₅ and CaO are similar among syenite varieties and vary between 40.7–43 wt% and 55–56 wt%, respectively. Apatite shows uniform and relatively high MnO and SiO₂ contents in described varieties, reaching up to 0.13 wt% and 0.67 wt% (Table 2).

4.2.7. Ilmenite

Ilmenite occurs as irregular grains in the form of small inclusions within amphibole cleavage plains (<10 µm), larger intergrowths with titanite (650–900 µm), and subhedral crystals enclosed in K-feldspar (250–500 µm). Ilmenite has uniform chemical composition (TiO₂ ~52 wt%, FeO ~46 wt%) with Nb₂O₅ content routinely varying between 0.12–0.3 wt% (Table 2).

4.3. Trace elements in minerals (LA-ICP-MS)

4.3.1. Zircon

With respect to the presence of abundant early magmatic U-thorite inclusions in zircon (Fig. 3b), we provide data obtained for inclusion-free grains and/or domains of pristine zircon (Fig. 3d), in line with time-resolved LA-ICP-MS spectra. The partially recrystallized zircon domains with no visible effects of alteration display considerably variable ΣREE, Y, Th, and U contents, within and between syenite varieties, regularly varying from several hundred up to tens of thousands of ppm (Table 3).

Chondrite-normalized REE patterns (McDonough and Sun, 1995) differ among individual varieties (Fig. 5a). Zircon in central variety typically features heavy rare earth elements (HREE)-enriched patterns (Sm₉/Yb₉ <0.13) with negative Eu anomalies (Euₑ/Smₑ* 0.46–0.71; Euₑ* = √(Gdₑ ×
Zircon in marginal variety has relatively flat REE patterns, slightly enriched in HREE (Sm$_N$/Yb$_N$ 0.36–1.29), with strong negative Eu anomalies (Eu$_N$/Eu$_N^*$ 0.28–0.55), similar to zircon from nodule variety (Sm$_N$/Yb$_N$ 0.17–1.58; Eu$_N$/Eu$_N^*$ 0.35–0.59).

4.3.2. Titanite

Titanite hosts significant amounts of incompatible trace elements such as REE + Y and HFSE, particularly Nb and Ta (Table 3). Titanite is characterized by substantially variable $\Sigma$REE abundances within and between individual varieties, reaching up the highest contents in marginal variety (up to 6477 ppm) in contrast to titanite from central (1748–5097 ppm) and nodule variety (<960 ppm). Yttrium exhibits similar decreases from marginal (30–1864 ppm) through central (37–475 ppm) to nodule variety (46–273 ppm). Niobium and Ta show a relatively uniform distribution in titanite among syenite varieties, varying between 356–1124 ppm and 39–195 ppm, respectively. Other HFSE such as Th, U, and Zr reach up somewhat lower contents ranging from tens to several hundreds of ppm (Table 3), occasionally Zr content rises to thousands of ppm. Titanite usually has low Th/U ratios (0.5–2.9) and Ga concentrations (<23 ppm).

Chondrite-normalized REE patterns of titanite ordinarily feature convex-upward trends (Ce$_N$/Yb$_N$ up to 21.7) with considerably variable Eu anomalies, involving well-marked positive (Eu$_N$/Eu$_N^*$ 1.98–7.01) as well as strong negative Eu anomalies (Eu$_N$/Eu$_N^*$ 0.37–0.74) even within syenite variety itself, as demonstrated by titanite chemistry from marginal variety (Fig. 5b). It should be noted that $\Sigma$REE + Y contents rapidly decreases with the increasing magnitude of positive Eu anomaly (Fig. 5b).

4.3.3. Apatite

Apatite contains rather low HFSE contents compared to zircon and titanite although it commonly reaches up relatively significant amounts of REE and Sr (Table 3). Apatite from central
variety exhibits the highest $\sum$REE (1634–4188 ppm) and Y (630–1560 ppm) contents in contrast to apatite from marginal variety ($\sum$REE 1811–3285 ppm, Y 238–397 ppm) that shows values similar to those from nodule variety ($\sum$REE 1684–3269 ppm, Y 161–496 ppm). Concentrations of Sr are lower in apatite from the central variety (132–196 ppm) compared to apatite in marginal (257–311 ppm) and nodule variety (218–297 ppm).

Chondrite-normalized REE patterns of apatite display slight variations among syenite varieties (Fig. 5c). Apatite from central variety features relatively flat REE patterns ($Ce_N/Yb_N$ 1.8–2.6) caused by enrichment in HREE ($Lu_N$ 279–755). By contrast, apatite in marginal and nodule variety has more pronounced convex-upward REE patterns reflected by higher $Ce_N/Yb_N$ (6.0–20.7) due to lower HREE contents ($Lu_N$ 50–164). Apatite shows deep negative Eu anomalies without any significant variations among described syenite varieties ($Eu_N/Eu_N^*$ 0.25–0.71).

4.4. Whole-rock geochemistry

4.4.1. Major and minor elements

The alkali-rich syenites are generally characterized by significantly high $K_2O$ content (up to 12.7 wt%) and $K_2O/Na_2O$ ratio ($\approx$ 8–7.6) along with moderately high $SiO_2$ (up to 64 wt%) and $Al_2O_3$ (~17 wt%), and low MgO (~47 wt%), CaO (~1.62 wt%), TiO$_2$ (~0.82 wt%), $P_2O_5$ (~0.08 wt%) contents. Syenites have considerably low Mg$#$ (~0.17) and show somewhat variable FeO$_{tot}$ (0.9–5.07 wt%), reaching the highest contents in nodule and marginal variety, similar to MgO, CaO, TiO$_2$, and $P_2O_5$ concentrations (Table 4). Total alkali content (particularly $K_2O$) and $SiO_2$ gradually increases from nodule through marginal to central variety (Fig. 6a). Due to pronounced $K_2O$ enrichment, all syenite varieties fall in the shoshonitic field (Fig. 6b) within the $SiO_2$ vs. $K_2O$ diagram (Peccerillo and Taylor, 1976). The central variety is slightly peraluminous (A/CNK 1.01–1.05; molar $Al_2O_3/[CaO + K_2O + Na_2O]$), whereas marginal and nodule variety display a rather metaluminous character (A/CNK 0.94–0.99; Fig. 6c) (Shand, 1943). By contrast, peralkalinity slightly decreases from marginal and nodule variety (A/NK up to 1.10–1.12; molar $Al_2O_3/[K_2O + Na_2O]$) to central variety (A/NK 1.06–
The K-rich syenites are highly ferriferous and geochemically resemble quartz syenite composition within the multicationic plot B vs. Mg/(Fe + Mg) (Fig. 6d) (Debon and Le Fort, 1988), illustrating a relationship between maficity and Mg# values.

4.4.2. Trace elements

The syenites exhibit various enrichment in total REE contents, with a decreasing trend from central through nodule to marginal variety (∑REE 177–270 ppm, 128–212 ppm, 84–96 ppm, respectively). Chondrite-normalized REE patterns slightly differ among individual varieties (Fig. 7a). Marginal and nodule variety are characterized by convex-upward REE patterns (CeN/YbN 2.85–8.84) with more pronounced negative Eu anomaly typical for nodule variety (EuN/EuN* 0.53–0.87) relative to marginal variety (EuN/EuN* 0.79–0.96). By contrast, central variety displays LREE- and HREE-enriched U-shaped patterns with pronounced MREE depletion (Fig. 7a), featuring weak or no negative Eu anomaly (EuN/EuN* 0.85–1.00).

Primitive mantle-normalized (McDonough and Sun, 1995) extended trace element patterns show strong HFSE (Zr, Th, U, Hf) and LILE (Cs, Rb, Ba, K, Pb) enrichment and significant Nb and Ti depletion along with deep troughs for P (Fig. 7b). All syenite varieties have notably low concentrations of transition metals (Cr 3.1–5.4 ppm, Ni 0.7–1.7, Sc 6–26 ppm). High LILE/HFSE, Th/Ta, Rb/Sr and low K/Rb and Rb/Cs ratios represent a typical signature of syenites.

4.5. Sr-Nd isotopic composition

Strontium and neodymium isotope data were recalculated for the precise (CA-ID-TIMS) U–Pb zircon age of 335.127 ± 0.061 Ma obtained for the Třebíč pluton (Schaltegger et al., 2021), corresponding to contemporaneous emplacement of alkaline (ultra)potassic intrusions in the Gföhl unit (Fig. 1b; see Section 5.5. for details). Whole-rock Sr-Nd isotope geochemistry of central and marginal variety (Fig. 8a; Table 4) of the alkali-rich syenites is characterized by highly radiogenic 87Sr/86Sr335 (~0.7116), similar to those of potassic to ultrapotassic magmas of durbachitic and lamproite series.
within the Moldanubian Zone of the Bohemian Massif (see Janoušek et al., 2019, 2020; Krmíček et al., 2016 for review). Moreover, unradiogenic Nd of syenite samples (εNd335 ≤ −7.8), along with Sr isotopic signatures, strikingly resemble those of mature continental crust (Fig. 8a).

4.6. Geochronology

4.6.1. U-Pb apatite dating

As stated above, apatite has not experienced extensive dissolution during the post-magmatic hydrothermal alteration in contrast to titanite and metamict zircon (Kubeš et al., 2021), and thus represents an ideal phase for dating of (post-)magmatic history of syenites. Overall, twenty-six apatite crystals from marginal variety were analyzed (Table 5). Contents of U and Th in dated apatite grains regularly vary between 4.7–157.3 ppm and 5.7–322.5 ppm, with U/Th values of 0.31–1.07 (median 0.63). Twenty-six spots yield a well-defined isochron date of 305.9 ± 5.3 Ma (MSWD of 2.2; Fig. 9), corresponding to a cooling age of miaskitic syenites.

4.6.2. ⁴⁰Ar/³⁹Ar dating of mafic silicates

The age spectra of amphibole and biotite reveal variable ⁴⁰Ar/³⁹Ar degassing patterns among the samples (Fig. 10a, b). Amphibole 4NL yielded a first, highly discordant, spectrum featuring a prominent hump over the first 80 % of ³⁹Ar released and culminating near 320 Ma at 40 % of cumulative loss (run N319.MS3; Fig. 10a). The trend ends with a final (fusion) step at 329.8 ± 1.6 Ma. The age trend is paralleled by large and progressively declining ³⁶Ar/³⁹Ar ratios early through the gas release, indicating progressive exhaustion of a secondary atmospheric component in the course of the experiment (and most probably associated to degassing of secondary intergrown biotite). A duplicate run on another single crystal produced a much more regular spectrum with a concordant plateau spanning more than 80 % of the total release at 329.4 ± 0.7 Ma (run N320.MS3; Fig. 10a). Biotite 3GN (run N317.MS3; Fig. 10b) shows initially constant apparent ages clustering about a short plateau
segment at 332.1 ± 0.7 Ma (35 % of initial $^{39}\text{Ar}$ released) before evolving into an erratic pattern featuring consecutive deeps (down to 100 Ma) as the extraction proceeds. Conversely, biotite 2AM (run N318.MS3; Fig. 10b) produced a discordant (though less irregular) pattern converging to a short plateau segment at 331.4 ± 0.7 Ma (1σ) in the last 25 % of $^{39}\text{Ar}$ released.

All in all, the different experiments appear to have isolated a common radiogenic component near 330 Ma (Table 6) despite sample-specific irregularities due to secondary alteration to chlorite, both in amphibole and biotite. The near-concordance of the biotite and amphibole data at 330.9 ± 0.39 Ma (pooled mean of four preferred ages noted above) is significant and gives robustness to this estimate with a MSWD score of 2.84 (i.e., just above the fiducial limit of 2.60 at the 95 % confidence interval). The concordance is all the more so compelling given the distinctive retention behavior characterizing these phases (McDougall and Harrison, 1999), clearly pointing to a cooling of the syenite intrusion below ca. 500 °C close to 330 Ma.

5. Discussion

5.1. Mineral assemblages unraveling magmatic evolution of syenites

The alkali-rich syenites host a significant amount of HFSE-bearing phases dominated by zircon along with subordinate titanite and apatite, reflecting their miaskitic affinity. Although the syenites mineralogically and geochemically correspond to miaskitic magmas, they genetically differ from common miaskitic varieties, considering their formation through the accumulation of alkali-rich melts (see below) without subsequent extensive differentiation stage of mafic and/or ultramafic assemblages (e.g. nephelinites, basanites, alkali basaltic rocks) that are typically associated with miaskitic rocks (Marks and Markl, 2017; references therein). The accessory minerals together with major rock-forming phases provide a unique insight into the (post-)magmatic history of the syenites and shed light on their mutual petrogenetic relation with the host rocks.

The miaskitic syenites originated by crystal accumulation mechanism rather than crystallization from residual melt, for the following reasons. Zircon from central variety has lower HfO$_2$ content and
higher Zr/Hf ratio relative to zircon from marginal variety (Table 2), reflecting a degree of magma fractionation (Hoskin and Schaltegger, 2003). Since zircon is generally considered as an early magmatic phase, the extreme ZrO$_2$ saturation of the central variety (ZrO$_2$ up to 2.6 wt%; Table 4) triggered the crystallization of accumulated zircon pockets prior to zircon crystallization in marginal parts of the syenite intrusion. Likewise, higher total alkali content and decreased Mg# of amphibole from marginal variety (Fig. 4a, b; Table 1) demonstrate that amphibole crystallized from more evolved melt. Considering variations in the amphibole chemistry among syenite varieties, best illustrated by the fractionation trend in the Mg# vs. Al diagram (Fig. 4b), nodule variety likely represents a transitional member between central and marginal variety and emphasizes the importance of crystal accumulation. The above-mentioned observations are further supported by different whole-rock trace-element composition of syenite varieties. Significant HREE and HFSE (Zr, Hf, Th, U) enrichment in central variety reflects zircon accumulation (Fig. 7b; Table 1). The nodule variety ordinarily shows intermediate contents of trace elements compared to central and marginal varieties (Fig. 7b), indicating its transitional character. By contrast, the lowest trace element concentrations typical of marginal variety suggest possible AFC-style crustal contamination (see Section 5.2.).

The magmatic origin of zircons is documented by low Th/U ratios (Hoskin and Schaltegger, 2003) and its morphological features (Fig. 3a) resembling those of high-temperature igneous zircons associated with mantle-derived alkali magmas (Škoda et al., 2009). LREE-enriched zircon patterns (Fig. 5a), usually ascribed to occurrences of micro- to submicroscopic inclusions (Zhong et al., 2018; references therein), likely reflect the variable intensity of metamictization and/or recrystallization (see Kubeš et al., 2021 for details), indicating that zircon chemistry cannot be considered as a suitable petrogenetic tracer to decipher the magmatic evolution of the host rocks.

Trace element signatures of titanite correspond to those from igneous rocks worldwide (e.g. Kontonikas-Charos et al., 2019), considering relatively high $\sum$REE and HFSE contents (Table 3) and convex-upward REE patterns (Fig. 5b), mimicking the whole-rock composition (Fig. 7a). Conversely, positive Eu anomalies and variable $\sum$REE + Y contents relate to a late metasomatic overprint of syenites (Kubeš et al., 2021), as suggested by negative Eu anomalies on whole-rock and apatite REE patterns (Fig. 5c, 7a) along with $\sum$REE + Y decrease in titanite depending on the magnitude of
positive Eu anomaly (Fig. 5b). By contrast, relatively high Ti⁴⁺/(Al + Fe³⁺) ratios of pristine titanite (up to 16.2) can indicate a mantle-related magma source (Piuzana et al., 2008). Low Fe₂O₃/Al₂O₃ ratios and Ga contents in unaltered titanite and its preserved negative Eu anomalies (Fig. 5b; Table 3) likely reflect reduction state of the parental magma, since under reducing conditions divalent cations such as Fe²⁺, Ga²⁺, and Eu²⁺ are not favored by titanite, leading to their low contents (Xu et al., 2015). This is in agreement with petrological observations such as the presence of abundant ilmenite and the absence of allanite, whose formation requires high Fe³⁺ proportions in magmas (Sha and Chappell, 1999).

In contrast to other HFSE-bearing phases, igneous fluorapatite shows no visible effects of later alteration and thus represent a suitable petrogenetic tracer. The increase in HREE and Y with decreasing Sr contents in apatite from central to marginal variety (Fig. 5c; Table 3) reflects geochemistry of host magma, particularly increased aluminosity accompanied by higher SiO₂ contents (Fig. 6c; Table 4) (e.g. Chu et al., 2009). Relatively high MnO contents in apatite (Table 2), resembling those from highly fractionated metaluminous to slightly peraluminous granitoids (Belousova et al., 2002), indicate increasing aluminosity and/or reducing conditions (Sha and Chappell, 1999). Taken together, trace element systematics in apatite is highly sensitive to increasing aluminosity and SiO₂ content of the host rocks rather than a degree of magma fractionation, which in turn is reflected by zircon and amphibole chemistry, as discussed above.

5.2. Ultrapotassic affinity versus the role of AFC-style crustal contamination

Although the miaskitic syenites are of cumulate origin, the considerably high K₂O content and K₂O/Na₂O ratio (Table 4), extreme enrichment in HFSE (Th, U, Zr, Hf) and LILE (Cs, Rb, Ba, Pb) (Fig. 7b), and crust-like isotopic signatures (Fig. 8a) indicate their alkaline, ultrapotassic affinity (e.g. Altherr et al., 2004; Conticelli et al., 2015; Foley et al., 1992). High LILE/HFSE, Th/Ta, Rb/Sr as well as low K/Rb and Rb/Cs ratios are generally considered as a characteristic fingerprint of ultrapotassic rocks of the durbachite series (Janoušek and Holub, 2007). Primitive mantle-normalized trace element patterns also suggest a genetic link to ultrapotassic magmatism in the Bohemian Massif (Fig. 7b), as
further indicated by a close spatial association of the alkali-rich syenites with the Třebíč pluton (Fig. 1b). Moreover, the syenites share some geochemical and isotopic features with Group II lamprophyres from Vosges and Schwarzwald (Soder and Romer, 2018), indicating a similar magma source (Section 5.3.).

On the other hand, the highly ferriferous character of the syenites (Fig. 6d), significantly low contents of transition metals (Table 4) and the composition of Fe-rich mafic silicates (Fig. 4) point towards the AFC-style crustal contamination of source magmas of the alkali-rich syenites, as previously proposed for other syenitoids in the Moldanubian Zone (Janoušek et al., 2019). In addition, the presence of quartz and biotite xenocrysts exclusively in marginal and nodule variety indicates assimilation of felsic crustal material during magma ascent (Kubínová et al., 2017). However, the highly unusual major- and trace-element whole-rock fingerprints of miaskitic syenites (extremely high Ba, K, Rb, Th, U, Zr; Fig. 7b; Table 4) cannot be simply ascribed to the hybridization of syenite parental melts by mature crustal material since contents of these elements in the syenites are by far higher than those of crustal continental rocks and sediments (e.g. Rudnick and Fountain, 1995). Thus, unreasonably high proportions of crustal assimilants would be required to generate LILE- and HFSE-rich melts of miaskitic composition (Zhao et al., 2009). Accordingly, the alkali-rich syenites show a different geochemical trend in the A/CNK vs. A/NK diagram (Fig. 6c) compared to strongly contaminated marginal facies of the Třebíč pluton, usually exhibiting notably low K$_2$O, Rb, Ba, Th, and U contents (Janoušek et al., 2020). From this follows that extreme K$_2$O, LILE and HFSE (Th, U, Zr, Hf) enrichment makes the syenites almost entirely insensitive to crustal contamination and provide constraints on the source nature and concurrently its degree of melting (Section 5.4.).

Similarly, crust-like isotopic signatures of the syenites ($^{87}$Sr/$^{86}$Sr$_{335}$ = 0.7116; $\varepsilon$Nd$_{335}$ $\leq$ 7.8) could not have been produced solely by continental crustal assimilation (Fig. 8b), instead the involvement of a long-term enriched reservoir is necessary to generate such highly radiogenic isotopic composition (Gerdes et al., 2000; Tabaud et al., 2015). Furthermore, as already shown for durbachitic rocks of the Třebíč pluton (Janoušek et al., 2020), likely crustal assimilants are isotopically less evolved ($^{87}$Sr/$^{86}$Sr$_{337}$ $\leq$ 0.7102; $\varepsilon$Nd$_{337}$ > -6.5) than the ultrapotassic primary magma ($^{87}$Sr/$^{86}$Sr$_{337}$ $\geq$ 0.7112; $\varepsilon$Nd$_{337}$ > -7.6). These observations unequivocally preclude the contribution of crustal
contamination as a major mechanism producing the typical crust-like isotopic composition of the syenites, indicating negligible and/or only limited dilution of source isotopic signatures (Fig. 8b).

Trace element modelling confirms that low degree (~1 %) melting of a phlogopite-bearing mantle source (see Section 5.4. for details) would generate appropriate parental melt compositions. We use the batch melting model of Shaw (1970) for the starting composition glimmerite (Förster et al. 2017) and for mineral/melt partition coefficients, we use the values reported in Condamine et al. (2022). The most obvious difference between the modeled melt composition and the studied miaskitic syenites is that the proposed parental melt have higher LREE, Sr and Nb (Fig. 7c). The content of Nb in the melt produced by partial melting of the mantle is strongly affected by the presence of rutile in melting residue (Altherr et al., 2004) which is not incorporated in our model. High contents of these elements reflect LREE and Sr enrichment in the source coupled with small degrees of melting. These differences indicate that the parental melts were during emplacement partially modified by fractionation and assimilation of crustal material (Fig. 7c, 8c, d).

Results from AFC modelling (Bohrson and Spera, 2001) confirm that the assimilation of anatectic melts into fractionated magma can explain the composition of studied rocks (Fig. 7c, 8b–d). The mineral composition requires low degree crystal fractionation (3–5 %) of a parental magma in combination with anatectic melt generated by partial melting of the Moldanubian crust (5GB/9; Buriánek 2008). The depletion in Sr and an insignificant negative Eu anomaly suggest that plagioclase (~60 %) and biotite (~35 %) remained the main crystallizing phase during magma evolution. However, the assumed presence of accessory phases strongly controls the modelled HFSE and REE contents. The crystallization of monazite (1 %; monazite group minerals are typical accessory minerals in durbachites of the Třebič pluton; Buriánek et al. 2022), apatite (0.5 %), and allanite (0.5 %) depleted modelled melt composition mainly in LREE. In addition, variations in the content of accessory phases (e.g. titanite/apatite ratio) can affect REE content in individual samples (Fig. 8d).

5.3. Origin and nature of enriched mantle source
General agreement exists that highly alkaline ultrapotassic magmatism relates to the melting of heterogeneous lithospheric mantle source contaminated by crustal material (e.g. Avanzinelli et al., 2009; Conticelli et al., 2015; Foley, 1992; Jung et al., 2020; Prelević et al., 2012). The significant contribution of mature continental crust to the source region of miaskitic syenites is demonstrated by crust-like isotopic signatures (Fig. 8a), HFSE (Zr, Th, U, Hf) and LILE enrichment (Fig. 7b), and slight negative Eu anomalies (Fig. 7a; Table 4). Depletions in Nb, Ta and Ti suggest the presence of Ti-rich phase in their melting residue (Altherr et al., 2004), a typical feature observed in convergent tectonic settings (e.g. Zhao et al., 2009), signaling that the input of crustal component was probably subduction-related. Peralkaline composition of syenites along with significantly high K$_2$O content and K$_2$O/Na$_2$O ratio (Table 4), exceeding those of lamproite series (Fig. 6b) (Krmíček et al., 2016), suggest a predominance of K-rich phase within their source, most likely phlogopite (Soder and Romer, 2018). LREE-enriched patterns with negative Eu anomalies of marginal and nodule variety, showing no visible effects of crystal accumulation in contrast to central variety (Fig. 7a), possibly indicate partial melting in the presence of residual phlogopite (Kubínová et al., 2017). High Rb/Sr, Ba/Rb, and low Ti/K ratios, admittedly at least partially modified by cumulus processes, may also suggest derivation of syenites from a phlogopite-bearing mantle source (Jung et al., 2020).

Indeed, a key role of phlogopite within the enriched mantle source of ultrapotassic rocks worldwide has been previously demonstrated by many authors (e.g. Conticelli et al., 2015; Prelević et al., 2008; Zhao et al., 2009). However, the exact origin and nature of the mantle source of ultrapotassic magmatism in the Bohemian Massif remain unclear. Basically, two possible alternatives have been proposed by Janoušek et al. (2020): (1) phlogopite-bearing harzburgitic mantle, and/or (2) phlogopite-veined refractory peridotite. With respect to the results of experimental studies (Förster et al., 2019; references therein), the extreme K$_2$O-enrichment of syenites (up to 12.7 wt%) provide direct evidence that highly evolved miaskitic melts were derived from almost pure phlogopite component concentrated within a vein network. Since experimentally produced melts of uniform phlogopite-bearing peridotite exhibit relatively limited K$_2$O enrichment (<4 wt% K$_2$O; Condamine et al., 2016). Instead, partial melting of phlogopite-veined refractory peridotite has successfully generated such extremely K-rich melts (K$_2$O up to 12 wt%; Förster et al., 2017).
Accordingly, K-rich syenites together with durbachitic rocks of the Třebíč pluton (Janoušek et al., 2020) have Sr-Nd isotopic compositions similar to Moldanubian HP granulites and phlogopite-rich veins collectively termed as glimmerites (Fig. 8a) (Becker et al., 1999) that could account for a major source of ultrapotassic magmatism in the Bohemian Massif, as demonstrated above. These glimmerite veins, occurring within ultrabasic massifs in the Moldanubian Zone of Lower Austria, formed through the interaction of wall-rock peridotites with F-rich fluid released during the HP–HT breakdown of phlogopite in the felsic granulites (Becker et al., 1999). The supercritical fluids and/or possibly (U)HP melts derived from subducted felsic metaigneous lithologies (Janoušek et al., 2004), have percolated through overlaying heterogenous subcontinental mantle, which has led to the formation of phlogopite-rich vein network. There is mounting evidence that Moldanubian granulites have truly reached mantle depths, as demonstrated by the spatial association with mantle-derived ultrabasic rocks (Kubeš et al., 2022), preservation of UHP phases in granulites (Kotková et al., 2011; Perraki and Faryad, 2014), and PT estimates of their prograde mineral assemblages (Jedlička et al., 2015). Moreover, HP granulites are spatially and temporally associated with ultrapotassic rocks of the durbachite series and share mutual chemical affinities (Janoušek and Holub, 2007).

A similar petrogenetic scenario was previously proposed for durbachites and Group II lamprophyres from the Vosges and Schwarzwald (Soder and Romer, 2018; Tabaud et al., 2015). The notable geochemical and isotopic similarities between the lamprophyres and the alkali-rich syenites, involving almost identical REE patterns and Sr-Nd isotopic composition resembling those of Moldanubian granulites (Figs. 7a, 8; see Soder and Romer, 2018), indicate comparable mantle source enrichment. However, partial melting of higher proportions of glimmerite component would be required to produce the unusual major and trace element composition of the syenites (Fig. 7c; see Section 5.4.). From this follows that our whole-rock geochemical data demonstrate a derivation of the alkali-rich syenites from a pure vein system consisting of phlogopite-bearing assemblages resembling glimmerites.

5.4. Low-degree partial melting of phlogopite-veined mantle domains
The conspicuous variable enriched composition of miaskitic syenites compared to closely associated ultrapotassic rocks of the Třebíč pluton is suggestive of heterogeneous lithospheric mantle source and particularly a different degree of its partial melting. Assuming that the metasomatic component is concentrated within the vein network, a low degree of partial melting of pure glimmerite material would produce the K-rich melts with extreme trace element enrichment (Fig. 7b, c; Table 4) (Förster et al., 2017, 2019), as demonstrated in case of (ultra)potassic rocks from the Mediterranean region (Conticelli et al., 2009) and Lhasa terrane (Zhao et al., 2009). Taking into account the results of experimental studies investigating melting of mixed peridotite-glimmerite mantle source (Förster et al., 2017), metasomatic assemblages of vein network usually have a lower solidus than surrounding refractory lithospheric mantle. Hence with increasing temperature, during a short thermal pulse likely caused by slab break-off (Janoušek et al., 2020), the phlogopite-veined mantle domains should preferentially partially melt, whereas partial melting of wall-rock peridotite would occur only if the temperature has sufficiently raised. Accordingly, a sufficient heat flux of the invading asthenosphere would trigger partial melting of the phlogopite-bearing metasomatized mantle, producing (ultra)potassic magmas (e.g. Avanzinelli et al., 2009; Becker et al., 1999; Prelević et al., 2008).

These observations together with our trace element-based partial melting models (Fig. 7c) clearly indicate that the alkali-rich syenites represent an initial product of low-degree melting of metasomatically enriched subcontinental lithospheric mantle beneath the Variscan orogenic root. By contrast, the origin of common members of ultrapotassic magmatism in the Moldanubian Zone of the Bohemian Massif is linked to relatively higher degrees of partial melting of the similar metasomatized source (Janoušek and Holub, 2007; Krmíček et al., 2016; Kubínová et al., 2017), inevitably increasing the contribution of a lithospheric mantle component to the hybrid vein-derived magmas (Janoušek et al., 2020). In this context, extreme HFSE and LILE enrichment along with unusually high K₂O content of miaskitic syenites (Fig. 6b, 7b; Table 4) indicate the dominant contribution of the pure metasomatic component to their parental magmas, with almost negligible input of mixed peridotite-glimmerite source. Since trace element enrichment in partial melting products of the phlogopite-veined depleted mantle are strongly dependent on temperature and therefore on a degree of melting (Fig. 7c); the highest enrichment generally reflects the lowest degree of melting, as was experimentally
demonstrated by Förster et al. (2017). Accordingly, low-degree melting of K-rich mantle domains with non-peridotitic mineral assemblages may produce small-volume partial melts with unique geochemical characteristics (e.g. Foley, 1992), providing a possible explanation for low Mg# of the syenites along with negligible Cr, Ni and V contents (Table 4). Since glimmerites represent unusual mantle rocks with crust-like geochemical and isotopic signatures inherited from their precursors (Moldanubian granulites; Becker et al., 1999), the initial melts (alkali-rich syenites) would be dominated by vein components, whereas later melts (ultrapotassic rocks; Janoušek et al., 2020) will include components from the peridotitic wall rocks.

An analogous vein-plus-wall-rock melting model was applied to lamproitic magmatism in the Western Mediterranean region (Conticelli et al., 2009), where variable geochemical and isotopic composition between lamproites and less evolved calc-alkaline to shoshonitic members were attributed to different degrees of partial melting of lherzolitic mantle along with different proportions of phlogopite and clinopyroxene entering these melts.

5.5. Timing of K-rich magmatism in the Variscan orogenic root

The newly acquired U-Pb apatite age of 305.9 ± 5.3 Ma in the current study (Fig. 9) corresponds to the cooling of the miaskitic syenites instead of their emplacement, considering a higher temperature of crystallization of alkaline ultrapotassic melts (>800 °C; Kotková et al., 2010) relative to the U-Pb closure temperature of apatite (~375–570 °C; Cochrane et al., 2014). Accordingly, the almost contemporaneous emplacement of highly alkaline ultrapotassic rocks in the Moldanubian Zone of the Bohemian Massif is recorded by U-Pb zircon, titanite, and rutile ages in a range of 335–338 Ma obtained for durbachitic plutons (Janoušek et al., 2020; Kotková et al., 2010; Schaltegger et al., 2021), subordinate two-pyroxene syenitoids (Janoušek et al., 2019) and vaugnerite and syenite porphyry from an ultrapotassic dyke swarm (Kubínová et al., 2017). These coeval intrusions reflect the first pulse of ultrapotassic magmatism in the Variscan orogenic belt (Soder and Romer, 2018), near-synchronous and shortly following the exhumation of (U)HP crustal complexes (Janoušek and Holub, 2007).
The initial fast cooling of the alkali-rich syenites recorded by new \(^{40}\)Ar/\(^{39}\)Ar amphibole-biotite dates ranging between 329.8 ± 1.6 and 331.4 ± 0.7 Ma (Fig. 10a, b; Table 6) indicates that exhumation of the internal orogenic domain in the Bohemian Massif must have been a short-lived event, probably driven by buoyancy forces (Medaris et al., 2005), as suggested by relatively narrow time gap between the peak stage of high-grade Variscan metamorphosis (~340 Ma; O'Brien and Rötzler, 2003) and cooling ages of the mantle-derived alkaline syenites. The rapid exhumation of the Variscan orogenic root in Central Europe, accompanying the ultrapotassic magma emplacement (Leichmann et al., 2007), is further supported by: (1) \(^{40}\)Ar/\(^{39}\)Ar dating of units overridden by the Gföhl nappes (Dallmeyer et al., 1992); (2) cooling rates given for mantle-derived rocks (Medaris et al., 2005); (3) presence of granulite clasts in the Culmian foreland basin (Čopjaková et al., 2005).

5.6. Possible geodynamic implications

Our results also shed light on possible geodynamic settings of the emerging subduction channel between Moldanubian and Saxothuringian domains during the Variscan collision (Schulmann et al., 2014; references therein). Whole-rock geochemical and isotope data indicate that miaskitic syenites originated by partial melting of pure glimmerite component veinng mantle wedge (Section 5.3.), derived from Moldanubian granulites (Becker et al., 1999). Assuming that HP granulites represent a deeply buried Saxothuringian felsic metaigneous material (Janoušek et al., 2004), relatively short-lived Andean-type subduction (Late Devonian–Early Carboniferous) appears to be a most likely geodynamic scenario (Schulmann et al., 2009). During subduction of Saxothuringian domain underneath the eastern continental Teplá-Barrandian-Moldanubian block, a local lithospheric mantle could have been extensively affected by melts/fluids derived from the down-going slab material. The mantle enrichment leading to glimmerite veins formation dated at 337 Ma (Becker et al., 1999) was almost contemporaneous with K-rich magmas emplacement (~335 Ma; e.g. Schaltegger et al., 2021). Such widespread mantle refertilization is probably recorded by the presence of K-rich melt inclusions trapped in Saxonian eclogites from Granulitgebirge (Borghini et al., 2020), exhibiting chemical features typical of common durbachitic rocks (Janoušek et al., 2020). Accordingly, occurrences of
genetically related yet widely separated lithospheric mantle fragments in the Moldanubian and Saxothuringian Zone (Schmädicke et al., 2010) may suggest a similar mantle source of ultrapotassic rocks in both major tectonic zones of the Bohemian Massif.

After the formation of phlogopite-rich vein network within the subcontinental lithospheric mantle, a sudden heat pulse was necessary to reactivate these subduction-derived metasomatic assemblages (Janoušek et al., 2020). In our case, buoyancy forces following slab break-off (Medaris et al., 2005) likely triggered low-degree partial melting of glimmerite-veined mantle producing highly alkaline miaskitic and ultrapotassic melts (Foley, 1992; Avanzinelli et al., 2009; Conticelli et al., 2015). The subsequent passage of these melts through continental blocks, accompanied by extensive crustal assimilation (Janoušek et al., 2020), has caused only limited dilution of their initial geochemical and isotopic signatures (Fig. 7c, 8b–d) during magma ascent to shallow crustal levels (ca. 8–15 km; Leichmann et al., 2017). The relatively slow solidification rate of these hot dry magmas and/or possibly their slow ascent through the crust (Kotková et al., 2010) is reflected by the U-Pb cooling age of apatite (Fig. 9) following the initial fast cooling of miaskitic syenites below ca. 500 °C (McDougall and Harrison, 1999) recorded by 40Ar/39Ar dates (Fig. 10a, b). Our 40Ar/39Ar ages are nearly identical to the cooling ages of other ultrapotassic members from the Saxothuringian Zone (e.g. Meissen massif; see Wenzel et al., 1997), highlighting the close temporal yet wide spatial association of mantle-derived K-rich magmatism within the European Variscides.

6. Conclusions

The studied alkali-rich syenites, located in the high-grade Gföhl unit of the Moldanubian Zone, represent a “missing puzzle piece” to decipher the exact origin and nature of enriched mantle source of ultrapotassic magmatism in the Bohemian Massif. The syenites are characterized by having a highly alkaline composition (K₂O ≤12.7 wt%; K₂O/Na₂O ≤7.5), miaskitic affinity, radiogenic Sr and unradiogenic Nd isotopes (87Sr/86Sr ≈0.7116; εNd ≈–7.8), and significant trace element enrichment (e.g. Th, U, Zr, Hf, LILE, LREE). They originated as a result of fractional crystallization and accumulation from highly evolved mantle-derived alkaline magmas. Their extreme major and
trace element geochemistry along with crust-like isotopic signatures bear witness that syenites correspond to products of partial melting of metasomatic phlogopite-rich vein network (glimmerites) in the subcontinental mantle, generated by the percolation of (U)HP fluids/melts released from the deeply subducted continental crust (Moldanubian granulites) during the Variscan collision. Low-degree melting of high proportions of almost pure phlogopite component produced unusual miaskitic melts, compared to common members of ultrapotassic magmatism in the Bohemian Massif (e.g. durbachites, lamprophyres, lamproites), linked to higher degrees of partial melting of mixed glimmerite-peridotite mantle source. The almost contemporaneous emplacement of alkaline magmas with mantle source enrichment was closely followed by initial fast cooling dated by $^{40}\text{Ar}/^{39}\text{Ar}$ amphibole-biotite ages ($\leq 331.4$ Ma), indicating rapid exhumation of the high-grade root of the Variscan Orogen, whereas U-Pb apatite age of $305.9$ Ma rather reflects subsequent cooling to relatively lower temperatures. The initial cooling ages of syenites, recorded by $^{40}\text{Ar}/^{39}\text{Ar}$ plateau ages clustering at $330$ Ma, strikingly resemble those of Saxothuringian K-rich intrusions, reflecting simultaneous ultrapotassic activity in both major tectonic zones of the Bohemian Massif. The short-lived Andean-type subduction of the Saxothuringian domain beneath the continental Moldanubian block is the most likely petrogenetic model of coeval K-rich magmatism in these widely geographically separated tectonic zones.

Acknowledgements

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Figure captions

**Fig. 1 (a)** Location of the Bohemian Massif and occurrences of the Variscan basement within the regional frame of western-central Europe **(b)** Simplified geological map of the eastern Moldanubian Zone hosting widespread ultrapotassic intrusions. Modified on the basis of the Czech Geological Survey on-line maps application (https://www.geology.cz)

**Fig. 2** Representative hand specimens of major syenite varieties: **(a)** central **(b)** marginal **(c)** nodule. Microphotographs of common mineral assemblages in alkali-rich syenites: **(d)** significant amount of metamict zircon typically surrounded by abundant microfractures (central variety; plane-polarized light) **(e)** subhedral amphibole enclosed in perthitic K-feldspar (marginal variety; plane-polarized light). Abbreviations: Kfs = K-feldspar, Zrn = zircon, Amp = amphibole

**Fig. 3 (a)** Characteristic zircon morphology from alkali-rich syenites (central variety; SEM image) **(b)** Strongly metamict zircon showing dissolution-reprecipitation textures particularly within its crystal interiors, containing early magmatic U-thorite inclusions (central variety; BSE image) **(c)** Partially altered zircon typically displaying low BSE intensity (nodule variety; BSE image) **(d)** Inclusion-free zircon exhibiting only limited effects of alteration (marginal variety; BSE image) **(e)** Subhedral titanite with sector zoning within the core and oscillatory zonation in rims (marginal variety; BSE image) **(f)** Euhedral apatite showing weak oscillatory zoning in the crystal core (marginal variety; BSE image). Abbreviations: Zrn = zircon, U-Thr = U-thorite, Bt = biotite, Kfs = K-feldspar, Chl = chlorite, Ttn = titanite, Amp = amphibole, Ap = apatite

**Fig. 4 (a)** Binary plot ⁰(Al + 2Ti) vs. ⁰(Na + K) and **(b)** Mg# [Mg/(Mg + Fe)] vs. ⁴Al diagram showing compositional variations in amphiboles from individual syenite varieties compared to amphibole chemistry from the ultrapotassic Třebíč pluton (Janoušek et al., 2020). Amphiboles from direct contact between central and marginal variety are marked in the Mg# vs. ⁴Al plot (see Section 5.1. for details)

**Fig. 5 (a–c)** Chondrite-normalized (McDonough and Sun, 1995) REE patterns of accessory phases
Fig. 6 Classification diagrams for syenite varieties (a) Binary plot SiO$_2$ vs. Na$_2$O + K$_2$O (Middlemost, 1994) (b) SiO$_2$ vs. K$_2$O (Pecceillo and Taylor, 1976) (c) A/CNK vs. A/NK (Shand, 1943) (d) Multicationic plot B vs. Mg# (Debon and Le Fort, 1988). The whole-rock composition of ultrapotassic rocks of the Třebič pluton (TP) and its marginal facies (Janoušek et al., 2020) along with lamproites (Krmíček et al., 2016) from the Bohemian Massif is illustrated for comparison.

Fig. 7 (a) Chondrite-normalized REE patterns and (b) primitive-mantle-normalized multielement spider plot for syenite varieties, standardized values are from McDonough and Sun (1995). Grey compositional fields for ultrapotassic rocks of the Třebič pluton based on data from Janoušek et al. (2020). (c) Results of trace element-based partial melting models. Grey-blue and hatched fields show the composition glimmerite and melt generated by glimmerite melting experiments at 10 kbar and 1125 °C respectively (Förster et al., 2017). Red lines show melt compositions modelled by 0.1 and 5 % (red numbers denote the amount of melt in %) batch melting of a phlogopite-bearing mantle source (composition as that proposed by Förster et al., 2017). Source was 0.45 olivine, 0.30 clinopyroxene, 0.20 phlogopite, and 0.15 orthopyroxene, with melting proportions of 0.30 olivine, 0.20 clinopyroxene, 0.40 phlogopite, and 0.10 orthopyroxene. Mineral/melt distribution coefficients used in the modelling are from Condamine et al. (2022). Green line showing results of the best-fit AFC model. This model requires a total of 3 % (green number denotes the amount of melt in %) fractional crystallization in combination with assimilation (assimilation rate/fractionation rate is 0.8) of leucogranitic melts generated by partial melting of the Moldanubian crust (sample III; Buriánek 2008). The fractionating mineral assemblage from melt generated by 1 % batch melting of a phlogopite-bearing mantle source was modeled as Pl (60 %) + Bt (35 %) + Mnz (1 %) + Ap (0.5 %) + Aln (0.5 %), and mineral/melt distribution coefficients are taken from Stepanov et al. (2012), Padilla et al. (2016), Were et al. (2021).

Fig. 8 (a) Binary plot $^{87}$Sr/$^{86}$Sr$_{335}$ vs. $\varepsilon$Nd$_{335}$ illustrating the isotopic composition of the miaskitic syenites relative to other mantle and crustal lithologies from the Moldanubian Zone together with hybrid rocks of glimmerite veins and the durbachitic Třebič pluton (TP), adapted after Janoušek et al. (2020). (b) Zoomed part binary plot of $^{87}$Sr/$^{86}$Sr$_{335}$ vs. $\varepsilon$Nd$_{335}$ showing the possible mixing hyperbola.
between the crustal contaminant and enriched mantle source for durbachtic analyses from the Třebíč Pluton according to Janoušek et al. (2020). (c) Binary Ba vs. Rb and (d) Ce vs. Rb/Sr (logarithmic scale) diagrams show result batch melting modelling of a phlogopite-bearing mantle source (red vector correspond to 30 % melting mantle source) and assimilation and fractional crystallization (AFC) modelling (green vector correspond to 5 % fractionation). Details of modelling are the same as reported in Fig. 7c, and the number denotes the amount of melt in %. Grey-blue and hatched fields show the composition glimmerite and melt generated by glimmerite melting experiments at 10 kbar and 1125 °C respectively (Förster et al. 2017). PM = primitive-mantle composition values are from McDonough and Sun (1995)

**Fig. 9** Tera-Wasserburg concordia diagram with results of zircon dating; grey band represents the U decay constant uncertainty. MSWD = mean square of weighted deviations

**Fig. 10** Results of $^{40}\text{Ar}/^{39}\text{Ar}$ dating for (a) amphibole and (b) biotite from miaskitic syenites. PA = plateau ages, MSWD = mean square of weighted deviations
Isochron age = 305.96 ± 5.38 Ma (n=26)

$^{207}\text{Pb}^{206}\text{Pb}$ initial = 0.796 ± 0.025

MSWD = 2.2
(a) 

\[ \Delta^{39}\text{Ar}_{\text{am}}/^{39}\text{Ar}_{K} \]

Amphibole 4NL

\[ \text{PA (Ma)} = 329.4 \pm 0.7 \text{ (1}\sigma\text{)} \\
(33/74; \text{MSWD} = 1.83) \]

\[ 329.8 \pm 1.3 \text{ (1}\sigma\text{)} \]

(b) 

\[ \Delta^{39}\text{Ar}_{\text{am}}/^{39}\text{Ar}_{K} \]

Biotite 2AM

\[ \text{PA (Ma)} = 332.1 \pm 0.7 \text{ (1}\sigma\text{)} \\
(18/62; \text{MSWD} = 1.73) \]

\[ \text{PA (Ma)} = 331.4 \pm 0.7 \text{ (1}\sigma\text{)} \\
(28/98; \text{MSWD} = 1.71) \]
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**Cation proportions (apfu)**

- Si: 2.996
- Ti: 0.124
- Al: 1.001
- Fe: 0.000
- Ca: 0.003
- Ba: 0.010
- K: 0.958
- Na: 0.035
- Mg: 0.111
- F: 0.000
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Note: Direct contact between central and marginal variety (see text for details). b.d.l.: below detection limits.
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Sr-Nd isotope data recalculated for the U-Pb zircon age of 335 Ma determined for the ultrapotassic Třebíč pluton (Schaltegger et al., 2021; see Section 4.5. for details)

LOI: loss on ignition; b.d.l.: below detection limits; empty entries: not determined; FeO₉₆ represents total iron oxide content.
Table 5 Results of U-Pb geochronological dating of apatite

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<th>Grain</th>
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<th>$^{206}$Pb/$^{238}$U</th>
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<th>$^{207}$Pb/$^{235}$U</th>
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<th>$^{208}$Pb/$^{238}$U</th>
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</tbody>
</table>

J: irradiation factor from co-irradiated flux monitor FC sanidine (28.305 ± 0.036 Ma; Renne et al. 2010)

%40 Ar*: % of radiogenic argon

TGA: total gas age

PA: plateau age integrated over selected, contiguous steps

MSWD: mean squared weighted deviation of plateau steps about the corresponding PA

n/N: number of steps included in PA over total number of steps
☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:
Melting of phlogopite-veined mantle produced alkali-rich syenites (K$_2$O 11.3–12.7 wt%) 

HFSE enrichment (e.g. ZrO$_2$ 0.06–2.60 wt%) caused by low-degree partial melting 

Rapid exhumation of the Variscan orogenic root recorded by $^{40}$Ar/$^{39}$Ar ages (~330 Ma)