Original paper Origin of apatite-dominated rock penetrating the volcaniclastic fill of the Pleistocene Bažina maar (western Czech Republic)

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The sequence of alkaline basaltic lavas and associated pyroclastic deposits that fill Bažina maar in western Bohemia is transected by a vein of apatite-dominated rock revealed in the S4 borehole. Aside from solid vein fill, apatite also impregnates a significant part of the drilled volcanic sequence. In the main body (depth 60.00–66.60 m), apatite occurs in two texturally distinct types: common cauliflower-type apatite (type 1) is transected by veinlets of coarser (0.2 mm long) apatite crystals (type 2). Both types have grown into open spaces suggesting precipitation from fluids rather than crystallization from melt, which is consistent with generally low trace element contents with slight enrichment in Cs, Sr, U and Pb. Relative to other local Plio-Pleistocene volcanic rocks, apatite vein-fill is shifted in ⁸⁷Sr/⁸⁶Sr towards more radiogenic values (0.7053–0.7054). This suggests that fluids carrying mantle-derived ions mixed with groundwater interacting with granitic country-rock, as also evidenced by the purely crustal character of noble gases trapped in apatite. Unlike the mofettes occurring along the Mariánské Lázně Fault on the eastern margin of the Cheb Basin, the ⁴He/³He ratios from Bažina apatite do not indicate mantle noble gas contribution. According to our model, the originally Sr–P-rich fluids with low ⁸⁷Sr/⁸⁶Sr mixed with Cs–U-enriched groundwater circulating in country-rock granites with radiogenic ⁸⁷Sr/⁸⁶Sr. Therefore, present-day CO₂ outgassing through mofettes related mainly to the Mariánské Lázně Fault (eastern margin of the Cheb Basin) is likely independent of, and unrelated to, volcanism of the Cheb–Domažlice Graben.

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1. Introduction

The Cheb Basin and adjacent uplifted crystalline basement blocks are a region of the Bohemian Massif where volcanic processes persisted until the Pleistocene, and seismic activity continues to the present (e.g., Horálek and Fischer 2008; Ulrych et al. 2013; Fischer et al. 2014). Frequent seismic swarms also recognized by the public raise questions regarding potential geological hazards in this area, and thus elicit scientific attention. A combination of seismic activity, presence of Pleistocene volcanoes, ongoing mantle degassing via mofettes and prevalence of carbonated mineral springs make the area unique not only in the Czech Republic, but also worldwide. Because these phenomena are located in a small area, the region became a target of the interdisciplinary project "Drilling the Eger Rift: Magmatic Fluids Driving the Earthquake Swarms and Deep Biosphere (EGERRift)" under the auspices of the International Continental Scientific Drilling Program (ICDP). The project comprised a set of six shallow (less than 500 m deep) boreholes drilled across the area (Fischer et al. 2022). One of these boreholes (S4) was located within the Pleistocene Bažina maar where it penetrated various volcanic rocks and volcaniclastic deposits cross-cut by enigmatic white-colored rock dominated by apatite (Hrubcová et al. 2023).

In this study, we present data on textures, mineralogy, chemical and isotopic composition of this unusual rock, with the aim of better understanding its origin and role in the Quaternary evolution of western Bohemia. Because (1) igneous apatite-bearing rocks often accompany carbonatite complexes (e.g., Yegorov 1993; Guarino et al. 2017; Mitchell et al. 2020; Savard and Mitchell 2021), and (2) mantle xenoliths hosted by the Miocene Upper Palatinate basanites provide evidence of the carbonatized character of metasomatic agents percolating within the upper mantle beneath the western margin of the Bohemian Massif (Ackerman et al. 2013), a potential presence of carbonatites in the Cheb Basin area may be disentangled. Similar apatite-dominated rocks are not reported from other Cenozoic volcanic regions of the Bohemian Massif, and unraveling the origin of this lithology may shed new light on the Quaternary geological processes in western Bohemia.

2. Geological setting

The Bažina maar belongs to a group of small monogenetic volcanoes in western Bohemia representing the youngest Cenozoic alkaline magmatism of the Bohemian Massif, the easternmost segment of the Variscan orogenic belt in central Europe. The alkaline volcanic rocks erupted mainly along the NE–SW trending Ohře (Eger) Rift, the easternmost branch of the European Cenozoic rift system (Prodehl et al. 1995; Fig. 1a). The Ohře Rift, considered to be a reactivated Variscan suture zone, separates three crustal segments of the Bohemian Massif: the Saxothuringian in the NW from the Moldanubian and Teplá–Barrandian in the SE (Babuška and Plomerová 2001; Mlčoch and Konopásek 2010).

Cenozoic magmatic activity in the Bohemian Massif lasted from the Late Cretaceous until the Middle Pleistocene (Ulrych et al. 2011) and peaked during the Oligocene–Lower Miocene (Ulrych et al. 2002; Holub et al. 2010; Skála et al. 2014; Büchner et al. 2015). Subsequently, after the main volcanic phase, the Ohře Rift (Fig. 1a) was subjected to extension and subsidence along the same NE–SW trending structures during the Miocene (Rajchl et al. 2008), accompanied by a decrease in volcanic activity and its shift to the rift flanks (Rapprich et al. 2007; Ulrych et al. 2016).

The latest evolution of the Bohemian Massif during the Pliocene and Pleistocene was characterized by a significant re-distribution of tectonic and volcanic activity. The prominent tectonic feature of this period was a system of NW–SE to NNW–SSE trending left-lateral faults,



almost perpendicular to the Ohře Rift, crosscutting the Bohemian Massif into various segments. In the eastern margin of the Bohemian Massif, the Marginal Sudetic Fault was associated with the Early Pleistocene (Gelasian) Bruntál volcanic field (Cajz et al. 2012). In the northern part of the Bohemian Massif, Pliocene reactivation of the Lusatian overthrust was associated with reactivation of the Jičín Volcanic Field (Cajz et al. 2009). Finally, the NNW-SSE transtensional Cheb-Domažlice Graben opened near the western margin of the Bohemian Massif. The Cheb-Domažlice Graben hosts the Cheb Basin

Fig. 1 Sample location: \mathbf{a} – position of the Bažina maar in the Cenozoic tectono-volcanic setting of the Bohemian Massif (CDG – Cheb-Domažlice Graben, MLF – Mariánské Lázně Fault, TF – Tachov Fault); \mathbf{b} – location of the Bažina maar, and the S4 drill-site in western Bohemia; \mathbf{c} – interpreted cross section of the Bažina maar-diatreme volcano with simplified section of the S4 drillcore, and sample positions indicated (after Hrubcová et al. 2023). (Fig. 1a), which initiated in the Eocene, continued during opening of the Ohře Rift and rejuvenated with the activation of the Cheb–Domažlice Graben (Špičáková et al. 2000).

The Cheb-Domažlice Graben is delimited by two fault systems, the Mariánské Lázně Fault zone in the east (Fischer et al. 2012) and the Tachov Fault in the west (Fig. 1a). Both systems differ in the expression of the Pleistocene-Holocene activity. The Mariánské Lázně Fault is associated with massive diffuse degassing of mantle-derived CO₂ through numerous mofettes and springs of mineralized water (e.g., Bräuer et al. 2003, 2008, 2018) and with periodic earthquake swarms (Horálek and Fischer 2008; Fischer et al. 2014), but it lacks signs of post-Miocene volcanic activity. On the other hand, recent seismicity is not pronounced along the Tachov Fault, which is associated with several Pleistocene volcanoes. In addition, geophysical data suggest presence of deep-seated roots with the imprints at the crust-mantle boundary beneath the area including the Cheb Basin (Hrubcová and Geissler 2009; Hrubcová et al. 2005, 2013, 2017).

Scoria cones at Komorní hůrka/Kammerbühl (KH) and Železná hůrka/Eisenbühl (ZH) have been known since the 18th century (e.g., Hradecký 1994; Gottsmann, 1999; Rapprich et al. 2019), while other Pleistocene volcanoes in this area were only discovered in the last two decades. The identification of the Mýtina maar near ZH scoria cone (Mrlina et al. 2009) was followed by the discovery of the Neualbenreuth maar in Germany (Rohrmüller et al. 2018); both maar structures penetrate phyllites of the Dyleň massif. Their Mid-Pleistocene eruption age was determined at 0.29-0.27 Ma (Ar-Ar groundmass: Mrlina et al. 2009; Rohrmüller et al. 2018). Most recently, twin maars Ztracený rybník and Bažina (Fig. 1a) in the northern segment of the Tachov Fault zone were recognized (Hošek et al. 2019; Mrlina et al. 2019), both penetrating granites of the Smrčiny batholith (Fig. 1b).

3. Methods

3.1. Sample collection

Samples of the apatite-rock vein penetrating the volcanic sequence within the Bažina maar fill (Fig. 1c) were obtained from the near-vertical (inclination $<2^{\circ}$) S4 borehole as described in section 1 (Fischer et al. 2022). The S4 borehole penetrated various coherent volcanic rocks and volcaniclastic deposits in the fill of the Bažina maar crater, reached granitic country-rocks at a depth of 170 m, and continued down to 400 m through the massive, nonweathered granites (Hrubcová et al. 2023). The S4 drill core revealed a complex lithology of volcaniclastic rocks

and olivine nephelinite feeding conduit. These rocks were crosscut by apatite-rock veins documented at depths of 60.00–66.60 m (sample S4/61.4) and 72.70–72.80 m (sample S4/72.7), respectively. Nonetheless, apatite impregnation of pyroclastic deposits was observed throughout a significant part of the volcanic sequence.

3.2. X-ray diffraction mineral identification

X-ray diffraction (XRD) analysis was used to obtain the mineralogical composition of the studied samples. Powder mounts were prepared from rock samples via milling in a McCrone mill for 10 minutes, using the back side filling method (PMMA holder). Random powder samples were placed on a zero-background silicon sample holder. Random powders were analyzed using a Bruker D8 Advance diffractometer in the Bragg–Brentano geometry (CuK α radiation, primary and secondary Soller slits 2.5°, Lynxeye XE detector) with automatic divergence slit (ADS, 10 mm). The X-ray diffraction patterns of random powder bulk-rock mounts were recorded in the angular range of 4–80° 2 Θ with a step of 0.015° and a reading time of 0.8 s per step.

Qualitative processing of the acquired X-ray diffraction data was performed in ZDS-WX (Ondruš 2004) and Diffrac.Eva (Bruker 2015) software, using the PDF-2 database (ICDD 2021). Subsequent semi-quantitative phase analysis was carried out using the Rietveld method (Snyder and Bish 1989) in Topas 5 software (Bruker 2014). Crystal structure models of the phases were obtained from the ICSD database (FIZ 2021). During the Rietveld analysis, scale factors of the phases, their unit-cell parameters and size of the coherently diffracting domains were refined.

The clay fraction (<2 μ m) from sample S4/72.70 was separated by sedimentation in distilled water (Tanner and Jackson 1948). Prior to separation, the samples were sonicated in distilled water for 4 minutes. Clay fractions were saturated with K⁺ using five 24-hour duration saturation cycles with 1M KCl. Excess salt was removed by washing in distilled water to negative reaction with AgNO₃. Oriented preparations were obtained by pipetting the 2.5 ml of sample suspension onto Si-slides. The ethylene-glycol solvation was achieved by exposing Si-slides with clay fraction to ethylene-glycol vapor at 60 °C for 8 hours.

The oriented preparations were analyzed using XRD diffraction in air dry state (ad), after ethylene-glycol solvation (EG), and after K-saturation (ad, EG, heating at 110 °C for 5h, heating at 330 °C for 2 h). The X-ray diffraction patterns of oriented preparations were recorded within a range of $3-50^{\circ} 2\Theta$ with 0.019° steps 2 Θ , and reading time per step of 0.8 s. The X-ray diffraction patterns were modelled with the Sybilla Version 2.2.2 soft-

ware (Chevron ETC proprietary, Aplin et al. 2006). The same software was used for fitting experimental XRD profiles of 001 reflections following a trial-and-error procedure, and the fundamental algorithm was developed by Drits and Sakharov (1976), and Drits and Tchoubar (1990). The program provides a direct comparison between experimental and calculated patterns. Parameter R (Reichweite) denotes the extent of layers ordering in the mixed-layered phases (Jagodzinski 1949). R0 and R1 correspond to the random and ordered stacking of layers, respectively. Parameter N is an average number of coherent scattering domain sizes (CSDs: Drits et al. 1997).

3.3. Petrography and mineral chemistry

Thin sections were studied under a standard petrographic microscope to determine textures and crystallization order of the studied rock samples. Petrographic observations were complemented with back-scattered electron imaging and mineral chemistry analyses on polished cylinders. Quantitative chemical analyses of individual minerals were conducted using a Tescan MIRA 3GMU scanning electron microscope (SEM) at the Czech Geological Survey, Prague, fitted with SDD X-Max 80 mm² EDS detector and AZtecEnergy software (Oxford Instruments).

Point analyses of apatite and smectite, and identification of opaque phases were acquired under the following conditions: accelerating voltage 15 kV, working distance 15 mm, 3 nA probe current, 30 s acquisition time, and electron beam diameter of 30 nm. Mineral standards (SPI) were used for standardization, and pure Co for beam calibration. Structural-chemical formula of apatite was calculated to 5 cations in the position of Ca, and calculation of smectite was based on 11 oxygens.

3.4. Whole-rock trace-element chemistry

For trace element concentration analysis, aliquots of powdered samples were decomposed in a mixture of 27M HF–15M HNO₃ (6:1 v/v) in closed Teflon vials at 130 °C for 72 h. The solutions were then evaporated to incipient dryness and treated three times with small quantities of 15M HNO₃. Thereafter, dried residues were administered with 6M HCl and equilibrated at 80 °C for 24 h. Trace element concentrations in solutions were obtained using an Agilent 7900x ICPMS, housed at the Czech Geological Survey. Reference materials BHVO-2 (Hawaiian basalt, USGS) and JB-2 (arc basalt, GSJ) were prepared together with unknown samples, and their trace element abundances were in agreement with published values (Jochum et al. 2005).

The bulk-rock chemistry data were processed and visualized using GCDkit software (Janoušek et al. 2006).

3.5. Strontium isotope analysis

Strontium was isolated from the matrix via a modified version of conventional Sr.spec (Eichrom, France) column chromatography, described elsewhere (Pin et al. 1994; Míková and Denková 2007). Residual insoluble silicates were not analysed. The Sr fraction was loaded onto previously outgassed Ta single filaments. Strontium isotopic analyses were done using a Triton Plus thermal ionization mass spectrometer (TIMS; Thermo Fisher Scientific, Bremen, Germany) housed at the Czech Geological Survey. TIMS analyses were done in static mode, with simultaneous collection of ⁸⁴Sr, ⁸⁵Rb, ⁸⁶Sr, ⁸⁷Sr, and ⁸⁸Sr, at typical ion beam intensities of 5–7 V on ⁸⁸Sr (100 ratios, each with 8 s integration time). Isotopic ratios were corrected for gain, baseline, isobaric interferences, and instrumental mass fractionation assuming 86Sr/88Sr = 0.1194. External reproducibility was estimated from repeated analyses over a one-year period of the standard NBS-987 (87 Sr/ 86 Sr = 0.710272 ± 19 (2 σ , n = 47)).

3.6. Noble gas isotope analysis

Two types of apatite were separated from a sample collected at a depth interval of 61.00-61.40 m. The 0.91 g (veinlet texture) and 1.53 g (cauliflower texture) gently crushed aliquots of pure crystal separates (0.5-1 mm) were cleaned in acetone in ultrasonic bath, loaded into stainless-steel holders with a magnetic ball and baked at ca. 80 °C for 24 h in vacuo before the analyses at the Isotope Climatology and Environmental Research Centre, Institute for Nuclear Research (Hungary). Noble gases were released by single-step crushing (150 strokes), purified and separated from the main gases using a cryogenic trap. Helium and Ne abundances were measured by employing HELIX-SFT and VG-5400 noble gas mass spectrometers, respectively. Faraday detector was used for ⁴He, whereas ³He and all Ne isotopes were measured using electron multipliers. Blank levels were ${\sim}5\times10^{{-11}}$ and ${\sim}0.9{-}1\times10^{{-10}}$ ccSTP for He and Ne, respectively (ccSTP: cubic centimeter at standard temperature and pressure, 0 °C and 1 atm). More details on the analytical procedures are described in Papp et al. (2012) and Molnár et al. (2021).

4. Results

4.1. Petrography and mineralogy

Nearly monomineralic apatite rock was documented at several intervals in the S4 drill-core whereby the most prominent occurrence has been located at a depth from 60.0 to 66.6 m (Fig. 2a). Textures vary from massive (Fig. 2b) to fragmental with secondary Mn-oxides infill-



Fig. 2 Nearly monomineralic apatite rocks from the S4 drill-core: $\mathbf{a} - drill-core$ sections 58–67 and 73–76 m with position of apatite rock indicated; $\mathbf{b} - 360^{\circ}$ drill core scan of the apparently massive apatite (62.63–62.91 m); \mathbf{c} – brecciated apatite with dark-grey Mn-oxide crack fill (63.28–63.56 m); \mathbf{d} – brecciated apatite with fragments of olivine nephelinite (75.43–75.66 m); \mathbf{e} – microphotograph of apatite rock from the depth 61.40 m (plane polarized light), Ap1 – aggregates of fine-grained apatite, Ap2 – veinlets of coarser-grained apatite.

ing cracks and cavities between individual apatite chips (Fig. 2c). A more brecciated texture, where apatite chips are mixed with fragments of olivine nephelinite, can occasionally be found (e.g., at depths 75.43–75.66 m: Fig. 2d). The massive domains consist of two texturally different

parts (Fig. 2e). The main mass of the apatite rock (type 1 apatite) consists of aggregates of fine-grained radial sprays (Ap1 in Fig. 2e) crosscut by veinlets of coarser grained apatite (type 2 apatite: Ap2 in Fig. 2e). The distinctively different character of both types of apatite is



Fig. 3 Back-scattered electron images of studied apatite: \mathbf{a} – overall texture of the massive fine-grained apatite (Ap1) crosscut by veinlets of coarser-grained apatite (Ap2), depth 61.40 m; \mathbf{b} – close-up of the "cauliflower" structure of the fine-grained massive apatite (Ap1); \mathbf{c} – close up on the coarser-grained apatite in the veinlets (Ap2); \mathbf{d} – secondary apatite, smectite (Sme) and Mn-oxide fill in the cracks of the olivine nephelinite lava (depth 111.0 m).

particularly apparent using an electron microscope (Fig. 3a). The clustered aggregates of fine-grained radial sprays resemble cauliflower in their structure (Fig. 3b), whereas the veinlets consist of 0.2 mm long apatite needles growing inward from the veinlet walls, frequently leaving open space in the center of the veinlet (Figs 3a, c). Both types are mutually indistinguishable in chemical composition (Tab. 1), and are classified as fluorapatite with negligible admixtures of Mg and Na (both not exceeding 0.02 *apfu*) and part of P possibly substituted with C.

Apart from the macroscopically obvious apatite-rock occurrences, apatite impregnation is dispersed throughout almost the entire volcanic sequence of the Bažina maar. It fills the inter-clast voids in the pyroclastic deposits and, together with laminated smectite and Mn-oxide, fills the cracks in coherent basaltic rocks (Fig. 3d).

Two samples of apatite rocks (S4/61.4 and S4/72.7) represent the main body in the depth 60.0–66.6 m and smaller vein in the depth 72.7 m, respectively. In both samples, well crystallized apatite highly predominates

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over smectite group mineral phases (Fig. 4a). The content of apatite in sample S4/61.4 exceeds 90 wt. %, whereas in sample S4/72.7 it reaches 80 wt. %.

In the clay fraction of S4/72.7, the dominant smectite/chlorite (S/C) mixed-layered mineral (MLM), representing ca. 90 wt. %, with component ratio of approximately 94:6, R0 with N7 was modelled (Fig. 4c). The remaining ca. 10 wt. % consist of illite/smectite/chlorite (I/S/C) MLM with component ratio of 10:81:9, R0, N3. The S component denotes an expandable phase - especially smectite (S2g), I – illite. C layers were modelled with incomplete interlayer, thus the C component expresses non-expandable vermiculite. X-ray diffraction patterns of the K-saturated (K-sat) clay fraction heated to 110 °C and K-sat heated to 330 °C do not differ, thus it can be concluded that the vermiculite layers have hydrated cations in the interlayer, without incomplete Al-hydroxide interlayer (Fig. 4b). The MLMs were modelled as dioctahedral (d_{060} =1.494 Å), with low Fe content in octahedral sheet (0.32 apfu Fe). Small amounts of octahedral Fe (0.2-0.8 apfu Fe, mostly 0.2) were confirmed by

Fig. 4 X-ray diffraction patterns of analyzed apatite samples: a - overall XRD patterns of the S4/61.4 and S4/72.7 samples; **b** – experimental X-ray diffraction pattern of oriented preparation of the clay fraction $(<2 \mu m)$ in air dry state (ad), after ethylene glycol solvation - EG, K-sat = K-saturation, K-sat+110 °C = K-saturation and heating to 110 °C for 5 h, K-sat+330 °C = K-saturation and heating to 330 °C for 2 h, MLMs = mixed layered minerals, Ap = apatite; c - experimental X-ray diffraction pattern of oriented preparation of the clay fraction (<2 µm) after ethylene glycol solvation - EG modelled by Sybilla software, I = illite, S2g = smectite layers with interlayered 2 molecules of ethylene glycol, C = vermiculite with hydrated cations in the interlayer, R0 = Reichweite (Jagodzinski, 1949), Ap = apatite.



	Apatit	e type 1		Apatite type	2
-	ap4	ap5	apl	ap2	ap3
SiO ₂	0.13	0.16	0.14	0.17	0.12
Al ₂ O ₃	0.00	0.00	0.13	0.09	0.08
MgO	0.16	0.14	0.11	0.13	0.07
CaO	53.88	52.44	53.95	54.18	54.11
Na ₂ O	0.10	0.11	0.09	0.09	0.00
P_2O_5	36.8	37.28	38.79	38.75	39.53
F	4.31	4.64	5.15	4.2	4.69
Total	95.39	94.77	98.35	97.61	98.6
Са	4.96	4.96	4.97	4.97	4.99
Mg	0.02	0.02	0.01	0.02	0.01
Na	0.02	0.02	0.02	0.01	0.00
Si	0.01	0.01	0.01	0.01	0.01
Al	0.00	0.00	0.01	0.01	0.01
Р	2.68	2.79	2.82	2.81	2.88
F	1.17	1.30	1.40	1.14	1.28

Tab. 1 Apatite mineral chemistry

P deficiency may reflect irregular surface of microcrystalline apatite and presence of C partly substituting P.

EDS analysis (Tab. 2). Using EDS analysis, the smectite charge is mainly formed by substitution of Mg^{2+} for Al^{3+} in octahedral layer. According to the XRD analyses, smectite is dioctahedral. It is therefore a montmorillonite with mainly Mg^{2+} and less Ca^{2+} in the interlayer. As the both modelled MLM (S2g/C 94:6 and I/S2g/C 10:81:9) are dominated by smectite, the subordinate layers of vermiculite and illite were not considered for EDS data reduction. The detected Cl is probably absorbed to smectite from drilling-liquids.

Tab. 2 Chemical composition of smectite in the apatite vein

	Point	sme1	sme2	sme3	sme4	sme4	sme8	sme10
	SiO ₂	55.06	54.69	55.74	54.71	54.12	56.21	53.46
	Al ₂ O ₃	17.42	17.42	17.52	17.10	16.56	15.92	17.36
	Fe ₂ O ₃	1.91	1.99	1.92	2.88	4.70	7.42	1.90
	MgO	5.39	5.15	5.27	4.87	4.50	4.68	4.58
	CaO	0.78	0.90	0.57	0.70	1.10	1.82	2.10
	Na ₂ O						0.12	
	K ₂ O		0.06			0.07	0.14	
	Cl		0.14	0.13	0.15	0.06		0.11
	Total	80.37	80.14	80.95	80.11	80.63	85.58	79.32
	Si	3.99	3.98	4.01	3.99	3.95	3.91	3.95
tetraedr	Al	0.01	0.02		0.01	0.05	0.09	0.05
	charge	-0.01	-0.02	0.01	-0.01	-0.05	-0.09	-0.05
	Al	1.47	1.48	1.48	1.46	1.37	1.22	1.46
a ata a du	Fe	0.10	0.11	0.10	0.16	0.26	0.39	0.11
octaedr	Mg	0.42	0.42	0.41	0.39	0.37	0.39	0.43
	charge	-0.42	-0.42	-0.41	-0.39	-0.37	-0.39	-0.43
	Mg	0.16	0.14	0.15	0.14	0.12	0.09	0.07
	Ca	0.06	0.07	0.04	0.05	0.09	0.14	0.17
inter-layer	Na	0.00	0.00	0.00	0.00	0.00	0.02	0.00
	Κ	0.00	0.01	0.00	0.00	0.01	0.01	0.00
	charge	0.44	0.43	0.39	0.40	0.42	0.48	0.48



Fig. 5 Trace-element geochemistry of analyzed apatite-rocks: \mathbf{a} – chondrite (Boynton 1984) – normalized REE patterns; \mathbf{b} – ocean-island basalt (OIB: Sun and McDonough 1989) normalized patterns of the extended incompatible trace element contents.

4.2. Trace element chemistry

The mineralogical difference between pure apatite and smectite-rich apatite is also reflected in their trace element contents. While the almost pure apatite from 61.4 m depth is characterized by very low REE concentrations ($\Sigma REE = 3.77$ ppm; Tab. 3), REE contents in the sample from 72.7 m depth with significant smectite admixture are higher by nearly two orders of magnitude ($\Sigma REE = 268$ ppm). This observation indicates that the main carrier of REE in this system is smectite whereas pure apatite remains barren in REE. Both samples display smooth REE patterns with apparent enrichment of

Tab. 3 Trace-element concentrations (in ppm) in apatite veins and country-rock granite

Sample	S4/61.4	S4/72.7	S4/366.5 (granite)
P ₂ O ₅ (wt. %)			0.45
Li	2.55	9.92	63.40
Sc	0.27	1.55	2.30
V	333	146	7.32
Cr	3.40	2.98	4.18
Co	4.01	89.90	0.97
Ni	34.9	465	1.35
Cu	9.57	94.0	b.d.l.
Zn	14.80	43.50	57.60
Ga	5.69	12.20	17.60
Rb	6.16	7.47	255
Sr	770	605	41.4
Y	0.22	40.3	10.8
Zr	6.26	4.70	12.4
Nb	3.26	6.55	47.0
Mo	1.67	0.70	0.08
Cd	0.15	0.20	0.66
Sn	0.42	0.53	17.4
Sb	0.24	0.24	0.09
Cs	5.92	5.55	21.7
Ba	84.6	244	170
La	0.95	50.7	5.42
Ce	1.66	101	12.2
Pr	0.19	15.1	1.46
Nd	0.63	59.7	5.50
Sm	0.10	11.0	1.75
Eu	0.03	3.29	0.27
Gd	0.09	10.8	2.14
Tb	0.01	1.33	0.42
Dy	0.05	6.96	2.32
Но	0.01	1.32	0.34
Er	0.02	3.37	0.69
Tm	0.00	0.43	0.08
Yb	0.02	2.61	0.44
Lu	0.01	0.43	0.06
Hf	0.18	0.16	1.58
Та	0.58	1.32	1.62
W	1.17	1.00	1.30
Pb	0.72	1.33	27.0
Th	0.36	0.13	1.79
U	63.4	44.5	8.72

b.d.l. - below detection limit

Tab. 4 Sr isotopic data for Bažina maar apatite rocks and country-rock granite

Sample	Description	⁸⁷ Sr/ ⁸⁶ Sr	2 s.e.
S4/61.4	main apatite rock body	$0.705282 \ \pm$	0.000009
S4/72.7	smaller apatite rich vein	$0.705398 \ \pm$	0.000009
S4/366.5	country-rock granite	$0.793368 \hspace{0.2cm} \pm \hspace{0.2cm}$	0.000011

LREE over HREE (Fig. 5a), having La_N/Yb_N of 29.1 (S4/61.4) and 13.1 (S4/72.7) and suggesting that smectite itself may have weaker enrichment in LREE than apatite.

In the extended incompatible trace element plot, the sample S4/72.7 with significant smectite admixture shows a good correlation with intraplate alkaline rocks (Fig. 5b), having pronounced negative anomalies in Th and Zr, slight depletion in Pb and positive anomalies in Cs and U. The smectite admixture is also reflected in the enrichment of some compatible elements, namely Ni (Tab. 3). The sample S4/61.4 displays similar tendency as in REE, with very low contents of all trace-elements, except for Cs, U, Pb and Sr.

4.3. Isotope systematics of Sr and noble gases

The S4/61.4 and S4/72.7 samples gave mutually wellresolved 87 Sr/ 86 Sr of 0.705282 ± 9 and 0.705398 ± 9 , respectively (Fig. 6). These lie outside of the range of previously analyzed Plio-Pleistocene volcanic rocks of the Bohemian Massif (Ulrych et al. 2013) and trends towards significantly more radiogenic 87Sr/86Sr values of Sr-poor country-rock granite (0.793368 ± 11) , sampled from the S4 drilling at the depth of 366.5 m (Tab. 4).

The noble gas concentrations in the measured apatite separates were generally low, particularly in case of sample S4/72.7 with cauliflower textures (type 1 apatite). Helium-4 concentrations ranged $(1.3-1.8) \times 10^{-7}$ ccSTP/g whereas those of Ne ranged $(1.3-6.5) \times 10^{-10}$ ccSTP/g. Even though a larger number of crystals was crushed in case of the cauliflower-textured apatite (1.53 g), the released amount of noble gases was almost an order of magnitude lower (very close to the instrumental detection limit) than in case of the pure separate. Therefore, it cannot be excluded that the original noble gas budget was affected by secondary processes and results from the cauliflowertextured apatite sample should be treated with caution.



Fig. 6 Sr isotopic ratios of Bažina maar apatite veins in relation to other Plio-Pleistocene volcanic rocks of the Bohemian Massif (after Ulrych et al. 2013) and eruptive features along the Tachov Fault, arranged in a geographic order from NW (top) to SE (bottom).



		mass	³ He	lσ	⁴ He	lσ		$^{20}\mathrm{Ne}$	lσ	$^{21}\mathrm{Ne}$	lσ	²² Ne	lσ	:	:
sample	apatite type	යි	$[ccSTP/g \times 10^{-16}]$	[×10 ⁻¹⁶]	$\begin{bmatrix} ccSTP/g \\ \times 10^{-7} \end{bmatrix}$	×10 ⁻¹²	$\mathbb{R}/\mathbb{R}_{a}$	$\frac{ccSTP/g}{\times 10^{-10}}$	[×10 ⁻¹²]	$\begin{matrix} [ccSTP/g \\ \times 10^{-12} \end{matrix} \end{matrix}$	[× 10 ⁻¹⁴]	$\begin{bmatrix} ccSTP/g \\ \times 10^{-11} \end{bmatrix}$	[× 10 ⁻¹²]	⁴ He/ ²⁰ Ne	²⁰ Ne/ ²² Ne ²¹ Ne/ ²² Ne
9114_p apatite v	reinlet texture	0.91	7.62	1.52	1.75	7.91	0.003 ± 0.0006	6.25	1.12	2.17	5.16	69.9	1.55	279.3 ± 0.5	$9.8\pm0.2\ 0.032\pm0.001$
9114_r apatite cau	ıliflower texture	1.53	1.95	0.84	1.33	7.61	0.001 ± 0.0005	1.12	0.25	b.d.l.		b.d.l.		1179.7±2.6	
b.d.l below dete	ction limit														
ccSTP - cubic cen	timeter at standa	ard tem	perature and	1 pressure,	0°C and 1	atm									
$R - {}^{3}He'^{4}He$ ratio	of the sample														
$R_{a} - (1.382 \pm 0.005)$	$5) \times 10^{-6}$ (Sano et	al. 20	13)												

Both apatite separates contained a very low amount of ³He resulting in R/R_a ratios of 0.001–0.003 R_a (where R is the ³He/⁴He ratio of the sample and R_a is the atmospheric ³He/⁴He \equiv (1.382±0.005)×10⁻⁶; Sano et al. 2013). The ⁴He/²⁰Ne ratios yielded variable values between 279.3 and 1179.7 showing negligible amount of atmospheric contamination. The ²⁰Ne/²²Ne and ²¹Ne/²²Ne ratios are 9.8±0.2 and 0.032±0.001, respectively, in case of the veinlet texture apatite. Combined He–Ne systematics show a clear crustal signature for the fluid inclusion noble gas content of apatite (⁴He, ²¹Ne and ²²Ne ingrowth) with a negligible proportion of atmospheric contamination (<0.1%).

5. Discussion

5.1. Magmatic versus fluid-related origin

The carbonate-rich character of the upper mantle beneath the western margin of the Bohemian Massif has been evidenced from mantle xenoliths hosted by Miocene basanites from the Upper Palatinate (Ackerman et al. 2013) and carbonatites were evidenced elsewhere in the Cenozoic alkaline occurrences of the Bohemian Massif (Rapprich et al. 2017; Mysliveček et al. 2020). Because carbonatites are commonly accompanied by apatitites, i.e. igneous apatite-rocks, worldwide (e.g., Yegorov 1993; Guarino et al. 2017; Mitchell et al. 2020; Savard and Mitchell 2021), the presence of magmatic apatitite in Western Bohemia cannot be excluded. On the other hand, igneous apatiterich rocks are formed by crystallization from melt and are thus characterized by phaneritic texture, filling the entire volume of the rock without any empty voids. This common feature is not borne out by observations from the Bažina maar apatite-rocks, where apatite crystal aggregates are arranged into open space (Fig. 3), suggesting precipitation from fluid. Two lines of evidence prove secondary origin of the apatite investigated here. (i) While global apatitites (e.g., Yegorov 1993; Guarino et al. 2017; Mitchell et al. 2020; Savard and Mitchell 2021) also contain other magmatic phases (e.g., magmatic carbonates, olivine, clinopyroxene, phlogopite, magnetite), Bažina maar apatitite rocks carry solely fluid-precipitated phases (smectite, Mn-oxide). (ii) The igneous apatitites tend to be significantly enriched in some incompatible elements, namely LREE, where apatite in some host alkali rocks often displays extreme enrichments in La_N (1,000 La_N), paralleled by steep LREE/HREE patterns, commonly 2-3 orders of magnitude (e.g., Chu et al. 2009; Zirner et al. 2015). Such a trend is not observed in apatite from the Bažina maar. Only elements mobile in fluids (Cs, U, Sr and to some extent also Li and Pb) clearly depart from generally depleted trends, particularly if pure apatite sample from 61.4 m depth is considered (Fig. 5b).

Tab. 5 Noble gas concentrations and isotope ratios of the measured apatite separates

5.2. Source and nature of the fluids

The fluid origin of the apatite veins opens a question about the nature of fluids from which apatite precipitated. Strontium isotopic ratios of other volcanic centres (Komorní hůrka, and Železná hůrka-Mýtina) along the Tachov Fault lineament form a cluster of ⁸⁷Sr/⁸⁶Sr around 0.7035, and thus may be minimally contaminated and, therefore, be representative of the local mantle source of primitive melts, whereas the likely altered Mýtina volcanic bomb is an outlier with 87 Sr/ 86 Sr > 0.704. The Bažina Maar apatite veins are displaced towards more radiogenic ⁸⁷Sr/⁸⁶Sr values than either of these ranges, and lie between the un-radiogenic mantle-like values represented by the other analysed Plio-Pleistocene volcanic rocks from eruptive centres along the Tachov Fault lineament (Ulrych et al. 2013) and significantly more radiogenic Sr isotopic ratios of the country-rock granites (Fig. 6; Tab. 4). This implies that cations employed in apatite crystallisation were of a mixed isotopic character. The main source of cations (Ca+Sr) had mantle-like ⁸⁷Sr/⁸⁶Sr signature and elevated Sr contents comparable to other Cenozoic volcanic centres in the Bohemian Massif. It likely mixed with local groundwater, which would have leached Sr from older granites present in the area, thereby acquired a significantly more radiogenic (87Sr/86Sr = 0.79337) character. Due to much lower Sr concentrations the groundwater endmember leverage (Tab. 3) on the ⁸⁷Sr/⁸⁶Sr of the mixture is somewhat muted. Weathering of the mafic alkaline volcaniclastic rocks may liberate Ca²⁺ with Sr admixture carrying mantle-like signature inherited by secondary mineral precipitates, as documented on sedimentary limestones at the foothills of the Doupovské hory volcanic complex (Rapprich et al. 2023). In the case of the Doupovské hory, the source of Ca and Sr was represented by a large extent of weathering of mafic volcaniclastic rocks under subtropical conditions. The volume of the volcanic rocks in the Bažina maar is lower by several orders of magnitude, which is rather unlikely to represent the sufficient source of elements required for building the massive apatite veins together with apatite impregnations in the volcanic rocks. In addition, alteration of the small volume of volcanic rocks may not explain the source of required amounts of P, also unlikely to be derived from P-poor country-rock granite (Tab. 3). For these reasons, transport of elements employed in the apatite precipitation by fluids from a dry (not degassing) mantle-derived source underneath the Bažina maar appears to be a plausible scenario.

Mixing of fluids carrying signature of mantle-derived rocks with groundwater circulating in country-rock granites would also explain the elevated contents of Cs and U (Fig. 5b). The important role of crustal fluids in formation of the apatite veins is also supported by noble gas data, showing a purely crustal origin of fluid inclusions encapsulated in apatite crystals. The combined He–Ne isotope



Fig. 7 Model of the apatite precipitation within the Bažina maar.

data supports the hypothesis of fluid circulation through regional granite, from which they also gathered crustalderived noble gases rather than simple infiltration of the rain-water directly from the maar lake, because in such a case the noble gases would carry atmospheric signature. The absence of any mantle signature in noble gas isotope systematics also suggests that volcanic and post-volcanic hydrothermal activity at Bažina was not associated with outpourings of mantle-derived gases, which are otherwise known from the eastern margin of the Cheb Basin (e.g., Bräuer et al. 2003, 2008, 2018).

The entire model of fluid provenance and mixing is schematically displayed in Fig. 7. The fluid from which the apatite precipitated was rather neutral or slightly alkaline because aluminian phosphates (e.g., crandallite) crystallize at pH < 6.5, instead of common phosphates (Dill 2001). Similar conditions may also be derived from the structure of smectite, in which no layers with incomplete Al-hydroxy interlayer (HI) were identified. Incomplete HI interlayer is formed in the pH interval of ca. 4.6-5.8 (Rich 1968; Georgiadis et al. 2020), thus pH at which the MLM identified in samples from this study formed was higher than ca. 5.8.

5.3. Pleistocene activity of the Cheb–Domažlice Graben

The mantle-like signature in various isotopic systems (He, C, CO_2) of the gases from mofettes distributed along the Mariánské Lázně Fault (e.g., Bräuer et al. 2003; Fig. 1b) virtually connects these emanations with

Pleistocene primitive mantle-derived alkaline rocks (olivine nephelinites and olivine melilitites) in Western Bohemia. As previously mentioned, unlike most of the mofettes, all the Pleistocene volcanoes are distributed along the Tachov Fault, representing the western margin of the Cheb-Domažlice Graben (e.g., Hradecký 1994; Mrlina et al. 2009, 2019; Rohrmüller et al. 2018; Hošek et a. 2019; Hrubcová et al. 2023; Fig. 1b), where mantlederived gas emanations are not as frequent as along the Mariánské Lázně Fault. In such a case, these mofettes would represent degassing process associated with volcanism or its termination, and evidence of mantle-derived gases should be documented in closely post-magmatic hydrothermal precipitates. The isotope systematics of noble gases from the apatite veins genetically connected with the Bažina maar, display purely crustal component without any mantle-derived flux (Tab. 5). We may therefore conclude, that as is the case today, mofettes in the geological past occurred separately from the Pleistocene volcanoes of the Cheb-Domažlice Graben and these two manifestations do not have to be directly connected with each other.

6. Conclusions

- Petrological data show that apatite veins that crosscut the Bažina maar fill volcanic sequence precipitated from fluids.
- Apatite composition suggests mixed provenance of the cations and fluids, from which apatite precipitated. The fluids carrying mantle-derived ions with low ⁸⁷Sr/⁸⁶Sr mixed with Cs–U-enriched groundwater circulating in country-rock granites with radiogenic ⁸⁷Sr/⁸⁶Sr.
- The noble gas data obtained from the apatite vein suggest that the precipitation of apatite was not associated with release of mantle-derived gases, compared to those observed in recent mofettes. The modern degassing related to the Mariánské Lázně Fault (eastern margin of the Cheb Basin) cannot be simply linked to post-volcanic manifestations.

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