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Allanite from Granitic Rocks of the Moldanubian Batholith (Central European Variscan Belt)

Miloš René

Abstract

Allanite occurs as a relative rare REE mineral in selected granitic rocks of the Moldanubian batholith. This batholith represents one of the largest plutonic bodies in the European Variscan belt. Allanite was found in the Schlieren biotite granites and diorites 1 of the oldest Weinsberg suite, in biotite granodiorites of the youngest Freistadt suite and in dykes of microgranodiorites occurred in the eastern margin of the Klenov pluton. A majority of analyzed allanites are without any magmatic zoning, only allanite grains from the diorites 1 display complicated internal zoning with variable concentrations of Fe, Ca, Th, and REE. Analyzed allanites from the Schlieren granite, diorite 1, and the “margin” variety of the Freistadt granodiorite display ferriallanite-allanite substitution with low $Fe_{ox} = (Fe^{3+}/(Fe^{3+} + Fe^{2+}))$ ratio (0.2–0.5). The analyzed allanites occurring in the microgranodiorites display slightly greater $Fe_{ox} = (Fe^{3+}/(Fe^{3+} + Fe^{2+}))$ ratios (0.45–0.6) and enrichment in Al (up to 2.2 apfu). All analyzed allanites are Mn-poor with its concentrations from 0.01 to 0.04 apfu. The Ce is a predominant rare earth element in all analyzed allanite grains; they are thus identified as allanite-(Ce). The highest concentrations of Ce were found in allanites from diorite 1 (0.31–0.41 apfu).

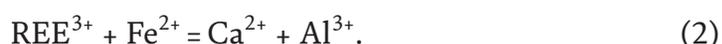
Keywords: allanite, petrology, geochemistry, cerium, bohemian massif, Moldanubian zone

1. Introduction

Allanite ($[Ca, REE]_2[Fe, Al]_3Si_3O_{12}[OH]$) is a common accessory mineral from the epidote group which occurs in intermediate granitic rocks (granodiorites, tonalites, and diorites) and their dyke equivalents (microgranodiorites and microdiorites) (e.g., [1–3]). Although its modal abundance in these rocks is low, allanite is a major residence site for LREE. It is related to epidote by coupled substitution:



and to clinozoisite by



This manuscript concentrates on mineralogy and chemical composition of allanite which occurs as a relatively rare accessory mineral in some intermediate granitic rocks of the Moldanubian batholith of the Bohemian Massif. The Moldanubian batholith represents a large plutonic body in the Bohemian Massif composed of biotite granodiorites, granites, and two-mica granites together with some younger dykes (aplites, pegmatites, felsic granites, and microgranodiorites to microdiorites) [4, 5].

2. Geological setting

The Moldanubian batholith forms one of the plutonic complexes within the Central European Variscan belt, covering 10,000 km² [5] (**Figure 1**). In detail, the Moldanubian batholith is built by multiple plutons, predominantly composed of granitic to granodioritic rocks with either S- or transitional I/S-type character [5–7]. All these granitic rocks can be classified into three main suites. These three suites are represented as (1) coarse-grained, porphyritic I- to I/S-type biotite granites to

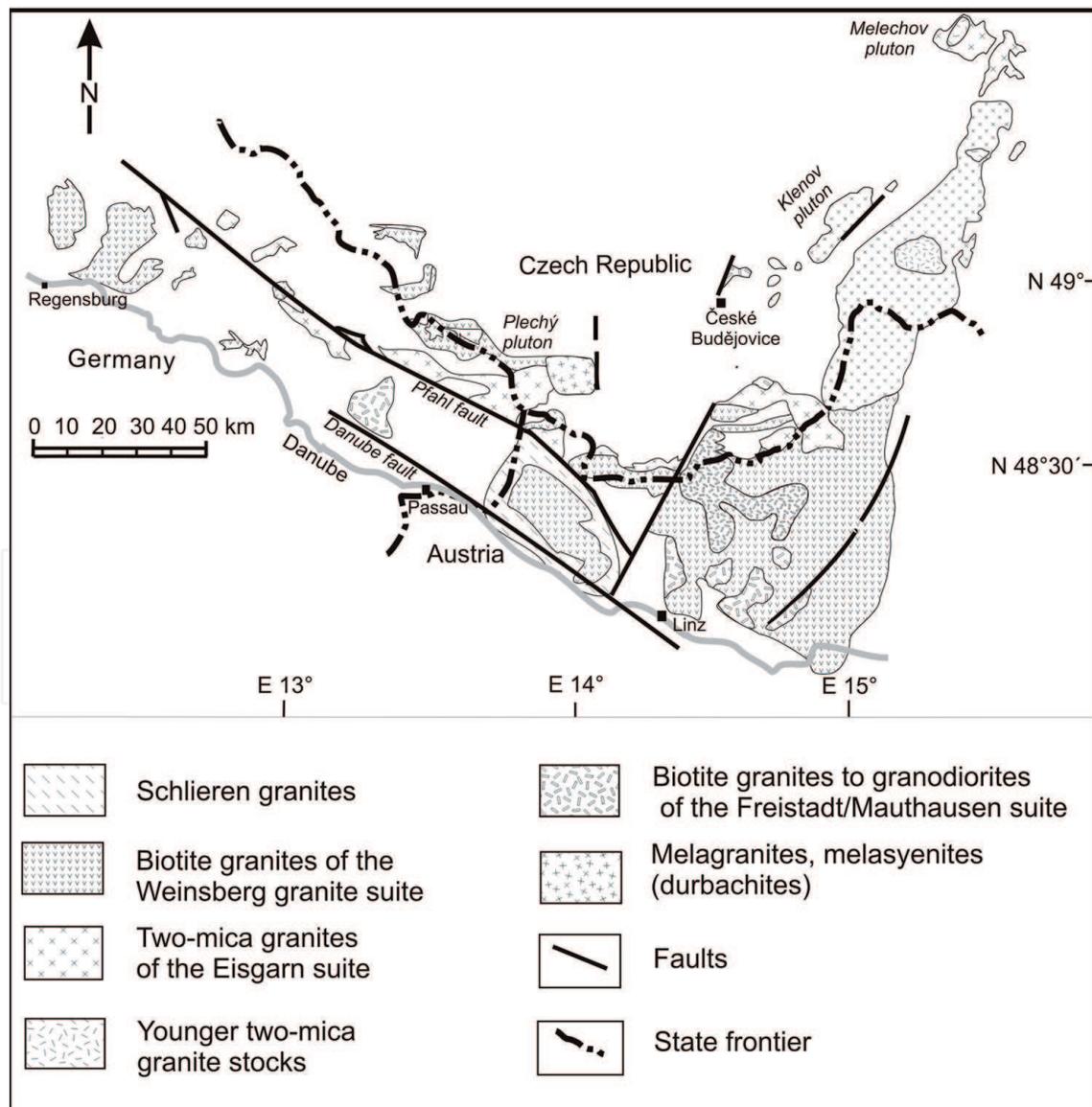


Figure 1. Geological map of the Moldanubian batholith (after [5], modified by the author).

granodiorites of the Weinsberg suite, (2) medium grained, partly porphyritic two-mica S-type granites of the Eisgarn suite, and (3) fine- to medium-grained I/S-type biotite granites to granodiorites of the Freistadt/Mauthausen suite [5, 6, 8].

A significant part of the Weinsberg suite is in situ evolved Schlieren granite, which occurs in the Upper Mühlviertel area (Austria) and attached area of the Bavaria (Germany). Diffuse and irregular contacts, transitional rock varieties, and intrusion of one granite to the other indicate that the Schlieren and Weinsberg granites coexisted as magmas; thus, they are of the same age [9]. However, in the past, the Schlieren granite was originally mapped and described as “coarse grained gneiss” [10]. With intrusion of the Weinsberg granite suite in the Bavarian and Austrian part of the Moldanubian batholith are also connected intrusions of diorite stocks (diorite 1) [11].

Two petrographic varieties were identified in the main body of the Freistadt suite in the Austrian Mühlviertel, the coarse-grained “marginal variety”, and medium-grained “central variety” [12]. Allanite, however, occurs only in granodiorites of the “marginal variety”.

The granitic rocks of the Moldanubian batholith are in some cases intruded by dykes of microdiorites, microgranodiorites, granite and melasyenite porphyries, and stock of highly fractionated two-mica and muscovite granites [11, 13–19].

3. Sampling and methods

Allanite was more commonly found in the Schlieren granite of the Weinsberg suite. As a relatively rare accessory mineral, allanite occurs also in diorites connected with granodiorites of the Weinsberg suite, in granodiorites of the Freistadt/Mauthausen suite and in microgranodiorites occurring on the eastern margin of the Klenov pluton.

Allanite together with selected rock-forming minerals (plagioclase, biotite) was analyzed in polished thin sections. The back-scattered electron (BSE) images were acquired to study the internal structure of individual allanite grains. Element abundances of Al, Ca, Ce, Dy, Er, Eu, F, Fe, Gd, Ho, La, Lu, Mg, Mn, Na, Nd, P, Pb, Pr, Sc, Si, Sm, Sr, Tb, Th, Ti, Tm, U, Y, and Yb were determined using a CAMECA SX-100 electron microprobe operated in wavelength-dispersive mode. The concentrations of these elements were determined using an accelerating voltage and a beam current of 15 kV and 20 nA, respectively, with a beam diameter of 2–5 μm . The following standards, X-ray lines, and crystals (in parentheses) were used: AlK_{α} —sanidine (TAP), CaK_{α} —fluorapatite (PET), CeL_{α} — CePO_4 (PET), DyL_{α} — DyPO_4 (LiF), ErL_{α} — ErPO_4 (PET), EuL_{β} — EuPO_4 (LIF), FeK_{α} —almandine (LiF), GdL_{β} — GdPO_4 (LiF), HoL_{β} — HoPO_4 (LiF), LaL_{α} — LaPO_4 (PET), LuM_{β} —LuAg (TAP), MgK_{α} —spessartine (LIF), NdL_{β} — NdPO_4 (LIF), PK_{α} —fluorapatite (PET), PbM_{α} —vanadinite (PET), PrL_{α} — PrPO_4 (LIF), SrL_{α} — SrSO_4 (TAP), ScK_{α} — $\text{ScP}_5\text{O}_{14}$ (PET), SiK_{α} —sanidine (TAP), SmL_{β} — SmPO_4 (LIF), TbL_{α} — TbPO_4 (LIF), ThM_{β} — $\text{CaTh}(\text{PO}_4)_2$ (PET), TiK_{α} —anatas (PET), TmL_{α} — TmPO_4 (LiF), UM_{β} —metallic U (PET), and YL_{α} — YPO_4 (PET). Intra-REE overlaps were partially resolved using L_{α} and L_{β} lines. Empirically determined coincidences were applied after analysis: ThM_{α} on the PbM_{α} line and ThM_{γ} on the UM_{β} line. The raw data were converted into concentrations using appropriate PAP-matrix corrections [20]. The detection limits were approximately 400 pm for Y, 180–1700 ppm for REE, and 800–1000 ppm for U and Th. The plot (REE + Y + Th + Mn + Sr) vs. Al proposed by Petrík et al. [21] was used for estimation of the $\text{Fe}_{\text{ox}} = \text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$ ratio by electron microprobe analyzed allanite.

4. Petrography

The Schlieren granites of the Weinsberg suite are represented by biotite granites consisting of plagioclase (An_{20–40}) (32–50 vol.%), K-feldspar (7–37 vol.%), quartz (18–34 vol.%), and biotite (annite, Fe/Fe + Mg = 0.53–0.55, Al⁴⁺ = 2.10–2.13, and Ti = 0.23–0.42 atoms per formula unit (apfu)), (6–32 vol.%). Amphibole was also frequently present (up to 5 vol.%). Accessory minerals are represented by apatite, zircon, ilmenite, magnetite, titanite, and allanite.

The biotite diorites (diorite 1) of the Weinsberg suite consist of plagioclase (An_{37–39}), (50–53 vol.%), biotite (annite, Fe/Fe + Mg = 0.65–0.66, Al⁴⁺ = 2.22–2.93, Ti = 0.37–0.45 apfu), (15–20 vol.%), K-feldspar (8–12 vol.%), amphibole (Mg-hornblende), (3–10 vol.%), and pyroxene (Fe-augite), (1–5 vol.%). Accessory minerals are represented by ilmenite, apatite, zircon, titanite, allanite, and thorite.

The biotite granodiorites of the “marginal variety” of the Freistadt suite consist of plagioclase (An_{25–37}), (32–68 vol.%), quartz (12–32 vol.%), K-feldspar (3–27 vol.%), biotite (annite, Fe/Fe + Mg = 0.44–0.62, Al⁴⁺ = 2.09–2.28, and Ti = 0.30–0.50 apfu), (6–17 vol.%) and muscovite (0–1 vol.%). Accessory minerals are represented by apatite, zircon, ilmenite, titanite, monazite, and allanite.

The microgranodiorites from the eastern margin of the Klenov pluton consist of plagioclase (An_{25–54}), K-feldspar, quartz, biotite (annite, Fe/Fe + Mg = 0.60–0.68, Al⁴⁺ = 1.68–2.30, and Ti = 0.13–0.47 apfu), pyroxene (Fe-augite), and amphibole (ferro-actinolite to Mg-hornblende). Accessory minerals are represented by ilmenite, titanite, apatite, rutile, zircon, and rare allanite.

5. Mineralogy and mineral chemistry of allanite

Allanite in these rock types occurs as a rare accessory mineral. It forms in these rocks relatively bigger grains (300–500 μm) and usually occurs on grain boundaries of biotite and plagioclase. Electron microprobe data show that the chemical composition of the epidote-group minerals in analyzed granitic rocks of the Moldanubian batholith varies greatly (**Table 1**). Studied allanites often exhibit irregular alteration, usually along their grain rims without any zoning of unaltered parties. In the BSE images, highly altered allanite parties on their rims are dark (**Figure 2A**). These highly altered parties are enriched in Si, Ti, and Th and depleted in Ca, Fe, Mn, La, and Ce. The altered allanite parties also display lower total analytical sum, which could indicate their hydration. In some other cases, irregular bright parties of BSE in altered allanite grains were found. These bright parties are enriched in Fe and depleted in Si, Ti, Ca, and Th (**Figure 2B**).

Analyzed epidote-group minerals without visible alteration contain 30.9–36.1 wt.% SiO₂, 10.1–17.8 wt.% CaO, 8.8–15.1 wt.% FeO, and 13.0–24.4 wt.% REE₂O₃. The magmatic zoning observed in some analyzed allanite grains (**Figure 2C–E**) seems to be caused by variations in Fe, Ca, Th, and REE contents and Fe³⁺/(Fe³⁺ + Fe²⁺) ratio. Allanites from the Schlieren granites and Freistadt suite are relatively Al-poor (Al = 1.3–1.8 atoms per formula unit, apfu) and display variable Fe_{ox} = (Fe³⁺/(Fe³⁺ + Fe²⁺)) ratio (0.2–0.5). Allanites from the diorite 1 are enriched in Al (1.8–1.9 apfu). Distinctly greater Al enrichment occurs in allanites from microgranodiorites (up to 2.2 apfu). These allanites also display higher Fe_{ox} = (Fe³⁺/(Fe³⁺ + Fe²⁺)) ratio without any zoning (**Figure 2F**). All analyzed allanites are Mn-poor with its concentrations from 0.01 to 0.04 apfu.

Sample	1714-16	1714-19	1724-11	1633-7	1633-12	532-30
Suite	Weinsberg	Weinsberg	Weinsberg	Freistadt	Freistadt	Dykes
Variety wt. %	Schlieren granite	Schlieren granite	Diorite 1	Margin	Margin	Micro- granodiorite
SiO ₂	35.97	34.74	32.01	31.47	31.67	32.36
TiO ₂	1.28	1.29	1.22	1.06	1.20	1.17
Al ₂ O ₃	14.88	14.38	15.78	13.45	14.06	14.69
FeO	8.66	9.33	13.43	15.10	15.20	14.94
MnO	0.43	0.52	0.30	0.41	0.47	0.21
MgO	0.92	1.10	0.91	1.52	1.16	0.24
CaO	11.04	10.89	10.62	10.78	11.34	12.48
La ₂ O ₃	5.15	4.89	6.67	7.40	6.46	5.37
Ce ₂ O ₃	8.89	9.47	12.29	11.48	10.95	8.96
Pr ₂ O ₃	0.61	0.78	1.25	1.09	1.09	0.87
Nd ₂ O ₃	1.91	2.46	3.59	2.85	2.87	2.92
Sm ₂ O ₃	0.07	0.21	0.29	0.08	0.26	0.52
Gd ₂ O ₃	0.00	0.23	0.22	0.16	0.12	0.22
Dy ₂ O ₃	0.00	0.00	0.01	0.17	0.19	0.08
ThO ₂	2.80	2.33	0.20	1.12	1.10	0.10
UO ₂	0.04	0.05	0.01	0.02	0.01	b.d.l.
Total	92.65	92.67	98.80	98.16	98.15	95.13
apfu, O = 12.5						
Si	3.42	3.35	3.04	3.06	3.05	3.12
Ti	0.09	0.09	0.09	0.08	0.09	0.09
Al	1.66	1.63	1.77	1.54	1.60	1.67
Fe ²⁺	0.69	0.75	1.07	1.23	1.23	1.20
Mn	0.04	0.04	0.02	0.03	0.04	0.02
Mg	0.13	0.16	0.13	0.22	0.17	0.03
Ca	1.12	1.13	1.08	1.12	1.17	1.29
La	0.18	0.17	0.23	0.25	0.23	0.19
Ce	0.31	0.33	0.43	0.43	0.39	0.32
Pr	0.02	0.03	0.04	0.04	0.04	0.03
Nd	0.07	0.09	0.12	0.11	0.10	0.10
Sm	0.00	0.01	0.01	0.01	0.01	0.02
Gd	0.00	0.01	0.01	0.00	0.00	0.01
Dy	0.00	0.00	0.00	0.01	0.01	0.00
Th	0.06	0.05	0.00	0.03	0.02	0.00
U	0.00	0.00	0.00	0.00	0.00	0.00

b.d.l.—below detection limit and *apfu*—atoms per formula unit.

Table 1.
 Selected representative microprobe analyses of allanite.

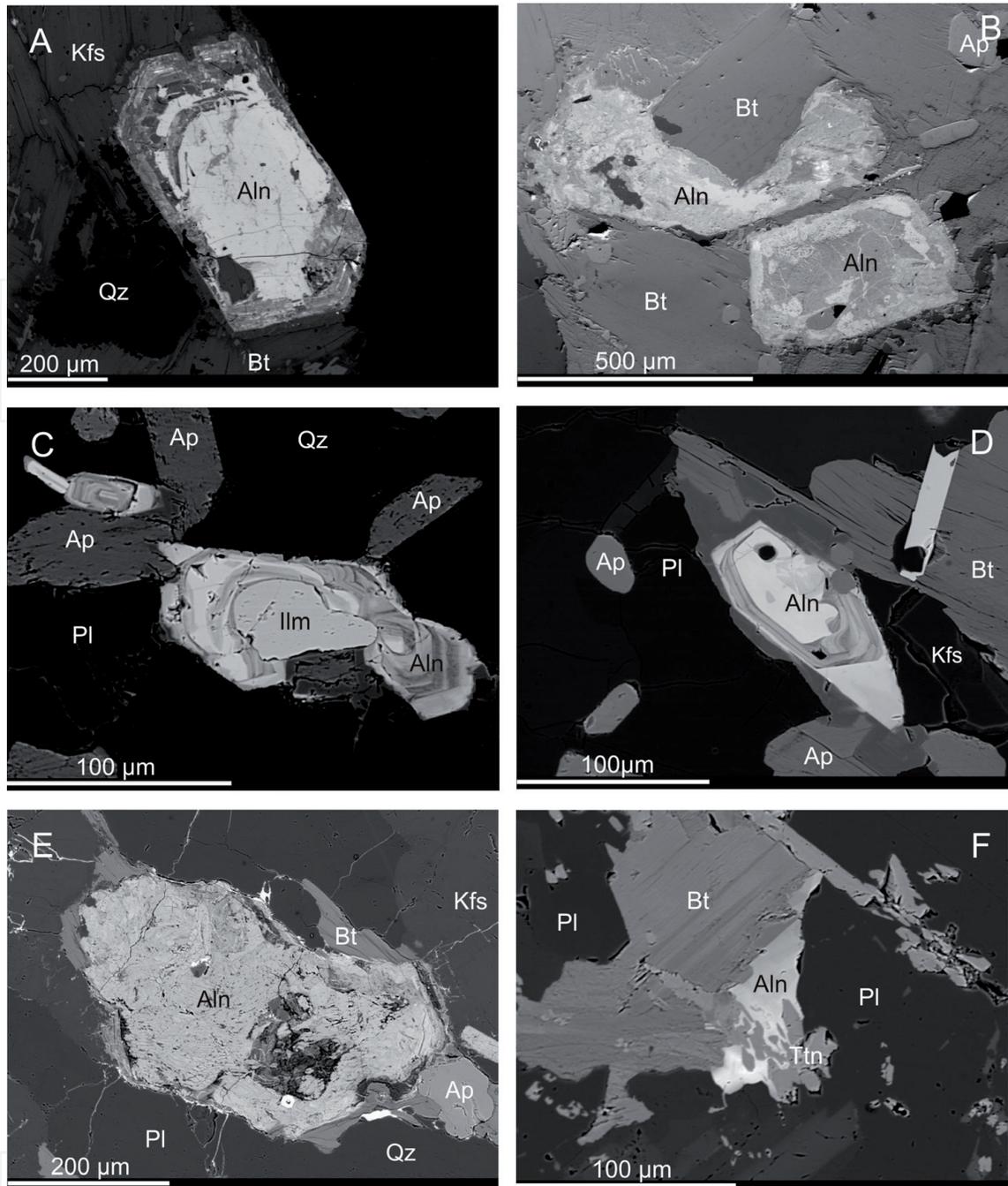


Figure 2. BSE images of allanite, A—partly altered allanite grain from biotite granodiorite of the Freistadt suite, B—highly altered allanite grain from the Schlieren granite, C and D—zoned allanite grains from the diorite 1, E—allanite grain from the Schlieren granite, and F—allanite grain from microgranodiorite. Aln—allanite, Ap—apatite, Bt—biotite, Ilm—ilmenite, Kfs—K-feldspar, Qz—quartz, Pl—plagioclase, and Ttn—titanite.

The majority of analyzed allanites represent substitution between ferriallanite and allanite. Only allanites from the microgranodiorites display substitution between allanite and clinozoisite (**Figure 3**).

All analyzed allanites display variable concentrations of REE with preference of Ce over La. The Ce is predominant in all analyzed allanite grains over other REE studied here; they are thus identified as allanite-(Ce). The highest concentrations of Ce were found in allanites from diorite 1 (0.31–0.41 apfu). The lowest concentrations of Ce display allanites from the youngest microgranodiorite dykes (0.14–0.32 apfu).

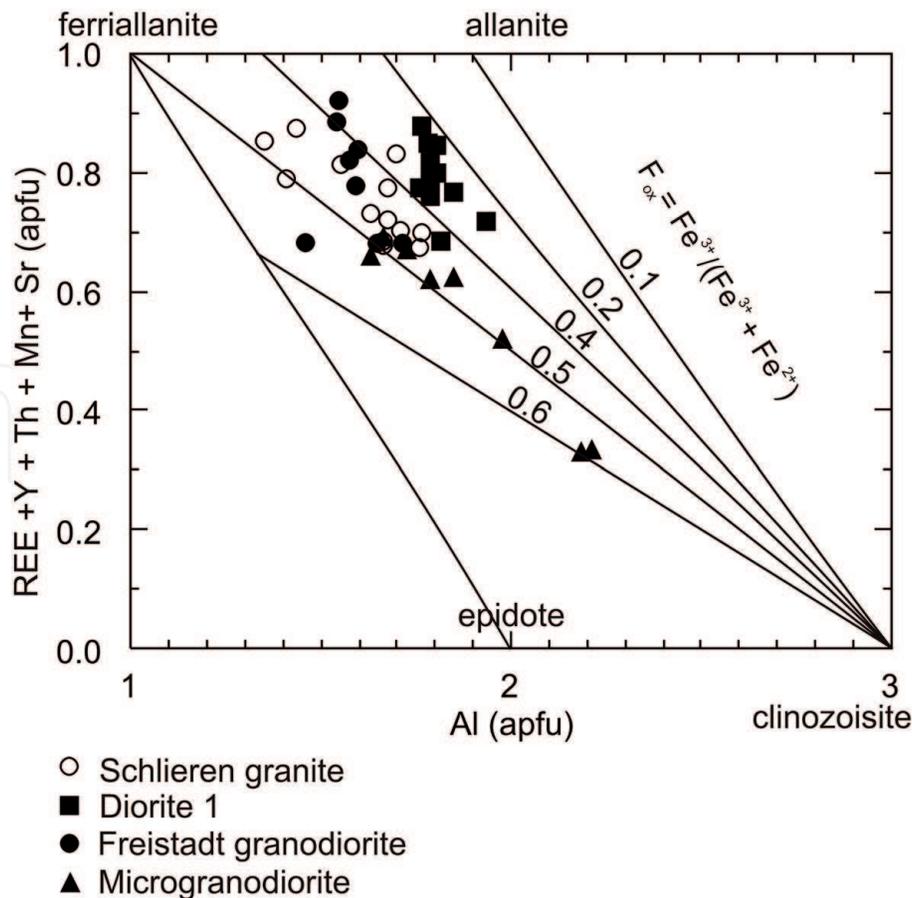


Figure 3. Plot of REE + Y + Th + Mn + Sr: (apfu) vs. Al (apfu) with isolines of the ratio $Fe_{ox} = Fe^{3+}/(Fe^{3+} + Fe^{2+})$ after Petrík et al. [21].

6. Discussion

For allanite, two main substitutions occur, namely the epidote-allanite and the allanite-ferriallanite substitutions [2, 21]. For analyzed allanites from the Weinsberg and Freistadt suites, the allanite-ferriallanite substitution is significant. Similar substitution was found by Petrík et al. [21] in allanites from the I-type granitic rocks of the Sihla tonalite suite in the Western Carpathians. Some highly altered allanite grains which were found in the Schlieren granite (**Figure 2B**) exhibit irregular zonation, which is very similar with the “mushroom-shaped areas” described by Poitrasson [22] from anorogenic granites of Corsica (southeast France). However, in the case of altered allanites from the Schlieren granite, the altered parties are depleted in Si, Ti, Ca, and Th, but enriched in Fe. Some other allanite alteration was found on allanite rims that occurred in the allanite from the Freistadt granodiorite (**Figure 2A**). In this case, the altered allanite rim is enriched in Si, Ti, and Th. Similar enrichment of Th was also found in altered allanites from anorogenic granites of Corsica (southeast France) and in allanites from the Casto granite of Idaho (USA) [22, 23]. Alterations of allanite which were found in allanites from the Schlieren granite and Freistadt granodiorite could be very probably explained by later late- and post-Variscan alteration of the Moldanubian batholith, which was connected with Pb-Zn and U-mineralization, which occurs in this region.

The allanite grains display in some cases three types of zonation, as revealed in BSE images: (1) oscillatory zonation [1, 24], (2) normal growth-induced magmatic zonation [2, 22], and (3) complicated internal zonation consisting of a patchwork of domains variable in brightness [21]. In allanite grains from diorite 1, complicated internal zonation was found (**Figure 2C and D**).

The allanite-clinozoisite substitution that is significant for allanite from microgranodiorites occurring in the eastern margin of the Klenov pluton was also found in allanites from epidote-bearing tonalites in the Bell Island pluton, Canada [25].

7. Conclusions

Allanite occurs in some intermediate to basic igneous rocks of the Moldanubian batholith. It was found in the oldest Schlieren granites and diorite 1 of the Weinsberg suite, in the youngest granodiorites of the Freistadt/Masuthausen suite, and in selected dykes composed of microgranodiorites in the eastern margin of the Klenov pluton. Analyzed allanites from the Schlieren granite, diorite 1, and the “margin” variety of the Freistadt granodiorite display ferriallanite-allanite substitution and a low $Fe_{ox} = (Fe^{3+}/(Fe^{3+} + Fe^{2+}))$ ratio (0.2–0.5). The analyzed allanites occurring in microgranodiorites display partly higher $Fe_{ox} = (Fe^{3+}/(Fe^{3+} + Fe^{2+}))$ ratio (0.45–0.6) and enrichment in Al (up to 2.2 apfu).

The allanites from the Schlieren granite and Freistadt granodiorite display in some cases variable alteration which is coupled with different behaviors of Si, Fe, Ti, and Th. This alteration is very probably connected with late- and/or post-Variscan hydrothermal alteration of these granitic rocks.

Acknowledgements

This study was carried out thanks to the support of the long-term conceptual development research organization RVO 67985891 and the project of the Ministry of Education, Youth and Sports (ME10083). I am also grateful to P. Gadas and R. Škoda from the Institute of Masaryk University for technical assistance by electron microprobe analyses of selected minerals (allanite, plagioclase, biotite, amphibole, and pyroxene). I am also grateful to Michael Aide for numerous comments and recommendations that helped to improve this paper.

Conflict of interest

The author declares no conflict of interest.

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