Chapter

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\textsubscript{ox} = (Fe\textsuperscript{3+}/(Fe\textsuperscript{3+} + Fe\textsuperscript{2+})) ratio (0.2–0.5). The analyzed allanites occurring in the microgranodiorites display slightly greater Fe\textsubscript{ox} = (Fe\textsuperscript{3+}/(Fe\textsuperscript{3+} + Fe\textsuperscript{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]_{3}Si_{3}O_{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:

\[
\text{REE}^{3+} + \text{Fe}^{2+} = \text{Ca}^{2+} + \text{Fe}^{3+}
\]
and to clinozoisite by

\[ \text{REE}^{3+} + \text{Fe}^{2+} = \text{Ca}^{2+} + \text{Al}^{3+}. \]  

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 (aplates, 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 km\(^2\) [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].

Figure 1. Geological map of the Moldanubian batholith (after [5], modified by the author).
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 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:
- AlKα—sanidine (TAP), CaKα—fluorapatite (PET), CeLα—CePO4 (PET), DyLα—DyPO4 (LiF), ErLα—ErPO4 (PET), EuLβ—EuPO4 (LIF), FeKα—almandine (LiF), GdLβ—GdPO4 (LiF), HoLβ—HoPO4 (LiF), LaLα—LaPO4 (PET), LuMβ—LuAg (TAP), MgKα—spessartine (LIF), NdLα—NdPO4 (LIF), PrLα—fluorapatite (PET), PbMβ—vanadinite (PET), PmLα—PrPO4 (LIF), SrLα—SrSO4 (TAP), ScKα—ScPO4 (PET), SiKα—sanidine (TAP), SmLβ—SmPO4 (LIF), TbLα—TbPO4 (LIF), ThMβ—CaTh(PO4)2 (PET), TiKα—anatas (PET), TmLα—TmPO4 (LiF), UMβ—metallic U (PET), and YLα—YPO4 (PET). Intra-REE overlaps were partially resolved using Lα and Lβ lines. Empirically determined coincidences were applied after analysis: ThMα on the PbMβ line and ThMα on the UMβ 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 Petrik et al. [21] was used for estimation of the Feox = Fe³⁺/(Fe³⁺ + Fe²⁺) ratio by electron microprobe analyzed allanite.
4. Petrography

The Schlieren granites of the Weinsberg suite are represented by biotite granites consisting of plagioclase (An$_{30-40}$) (32–50 vol.%), K-feldspar (7–37 vol.%), quartz (18–34 vol.%), and biotite (annite, Fe/Fe + Mg = 0.53–0.55, Al$^{4+}$ = 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, Al$^{4+}$ = 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, Al$^{4+}$ = 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$_{25-44}$), K-feldspar, quartz, biotite (annite, Fe/Fe + Mg = 0.60–0.68, Al$^{4+}$ = 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.% SiO$_2$, 10.1–17.8 wt.% CaO, 8.8–15.1 wt.% FeO, and 13.0–24.4 wt.% REE$_3$O$_6$. 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 Fe$^{3+}$(Fe$^{3+}$ + Fe$^{2+}$) 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$_{ox}$ = (Fe$^{3+}$/(Fe$^{3+}$ + Fe$^{2+}$)) 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$_{ox}$ = (Fe$^{3+}$/(Fe$^{3+}$ + Fe$^{2+}$)) ratio without any zoning (Figure 2F). All analyzed allanites are Mn-poor with its concentrations from 0.01 to 0.04 apfu.
Table 1.
Selected representative microprobe analyses of allanite.
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).
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 alanites 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 zoning, as revealed in BSE images: (1) oscillatory zoning [1, 24], (2) normal growth-induced magmatic zoning [2, 22], and (3) complicated internal zoning consisting of a patchwork of domains variable in brightness [21]. In allanite grains from diorite 1, complicated internal zoning was found (Figure 2C and D).

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].
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 $\text{Fe}_{ox} = (\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+}))$ ratio (0.2–0.5). The analyzed allanites occurring in microgranodiorites display partly higher $\text{Fe}_{ox} = (\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+}))$ 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.

Author details

Miloš René
Institute of Rock Structure and Mechanics, Academy of Sciences of the Czech Republic, Prague, Czech Republic

*Address all correspondence to: rene@irmc.cas.cz

IntechOpen

© 2019 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
Allanite from Granitic Rocks of the Moldanubian Batholith (Central European Variscan Belt)
DOI: http://dx.doi.org/10.5772/intechopen.86356

References

[1] Deer WA, Howie RA, Zussman J. Rock-Forming Minerals, vol. 1B Disilicates and Ringsilicates. 2nd ed. Harlow: Longham; 1986. p. 629

[2] Giére R, Sorensen SS. Allanite and other REE-rich epidote-group minerals. Reviews in Mineralogy and Geochemistry. 2004;56:431-493. DOI: 10.2138/gsrmg.56.1.431

[3] Armbruster T, Bonazzi P, Akasaka M, Bermanec V, Chopin C, Giére R, et al. Recommended nomenclature of epidote-group minerals. European Journal of Mineralogy. 2006;18:551-567. DOI: 10.1127/0935-1221/2006/0018-0551

[4] Finger F, Gerdes A, René M, Riegler G. The Saxo-Danubian granite belt: Magmatic response to post-collisional delamination of mantle lithosphere below the south-western sector of the bohemian massif (Variscan orogeny). Geologica Carpathica. 2009;60:205-212

[5] Verner K, René M, Žák J, Janoušek V. A brief introduction in the geology of the Moldanubian batholith. In: Janoušek V, Žák J, editors. Eurogranites 2015: Variscan Plutons of the Bohemian Massif. Post-Conference Field Trip Following the 26th IUGG General Assembly in Prague. Prague: Czech Geological Survey; 2015. pp. 103-109

[6] Gerdes A, Wörner G, Henk A. Post-collisional granite generation and HT/LP metamorphism by radiogenic heating: The Variscan south bohemian batholith. Journal of the Geological Society of London. 2000;157:577-587. DOI: 10.1144/jgs.157.3.577

[7] Breiter K. Geochemical classification of Variscan granitoids in the Moldanubicum (Czech Republic, Austria). Abhandlungen der Geologischen Bundesanstalt. 2010;65:19-25

[8] Vellmer C, Wedepohl KH. Geochemical characterization and origin of granitoids from the south bohemian batholith in Lower Austria. Contributions to Mineralogy and Petrology. 1994;118:13-32. DOI: 10.1007/BF00310608

[9] Finger F, Clemens J. Migmatization and “secondary” granitic magmas: Effects of emplacement and crystallization of “primary” granitoids in southern bohemian massif, Austria. Contributions to Mineralogy and Petrology. 1995;120:311-326. DOI: 10.1007/BF00306510

[10] Fuchs G. Zur Altersgliederung des Moldanubikums Oberösterreichs. Verhandlungen der Geologische Bundesanstalt. 1962:96-117

[11] Fuchs G, Thiele O. Erläuterungen zur Übersichtskarte des Kristallins in westlichen Mühlviertel und im Sauwald, Oberösterreich. Wien: Geologische Bundesanstalt; 1968. p. 96

[12] Klob H. Der Freistädter Granodiorit im österreichischen Moldanubikums. Verhandlungen der Geologische Bundesanstalt. 1971;1:98-142

[13] Němec D. Lamprophyrische und lamproide Ganggesteine in Südteil der Böhmis-Mährischen Anhöhe (ČSSR). Tschermaks Mineralogische Und Petrographische Mitteilungen. 1970;14:235-284. DOI: 10.1007/BF01081341

[14] Vrána S, Bendl J, Buzek F. Pyroxene microgranodiorite dykes from the Ševětín structure, Czech Republic: Mineralogical, chemical and isotopic indication of a possible impact melt origin. Journal of the Czech Geological Society. 1993;38:129-148

[15] Breiter K, Scharbert S. Latest intrusions of the Eisgarn pluton (South
Bohemia—Northern Waldviertel). Jahrbuch der Geologischen Bundesanstalt. 1998;141:25-37

[16] Košler J, Kelley SP, Vrána S. $^{40}\text{Ar}/^{39}\text{Ar}$ hornblende dating of a microgranodiorite dyke: Implications for early Permian extension in the Moldanubian zone of the Bohemian Massif. International Journal of Earth Sciences. 2001;90:379-385. DOI: 10.1007/s00531000154

[17] René M. Ti-rich granodiorite porphyries from the northeastern margin of the Klenov massif (Moldanubian zone of the bohemian massif). Acta Montana Series A. 2003;23:77-85

[18] Harlov DE, Procházka V, Förster HJ, Matějka D. Origin of monazite-xenotime-zircon-fluorapatite assemblages in the peraluminous Melechov granite massif, Czech Republic. Mineralogy and Petrology. 2008;94:9-26. DOI: 10.1007/s0710-008-0003-8

[19] Žáček V, Škoda R, Sulovský P. U-Th-rich zircon, thorite and allanite-(Ce) as main carriers of radioactivity in the highly radioactive ultrapotassic melasyenite porphyry from the Šumava mts, Moldanubian zone, Czech Republic. Journal of Geosciences. 2009;54:343-354. DOI: 10.3190/jgeosci.053

[20] Pouchou JL, Pichoir F. PAP ($\phi-\rho-Z$) procedure for improved quantitative microanalysis. In: Armstrong JT, editor. Microbeam Analysis. San Francisco: San Francisco Press; 1985. pp. 104-106

[21] Petrík I, Broska I, Lipka J, Siman P. Granitoid allanite-(Ce): Substitution relations, redox conditions and REE distributions (on an example of I-type granitoids, Western Carpathians, Slovakia). Geologica Carpathica. 1995;46:79-94

[22] Poitrasson F. In situ investigations of allanite hydrothermal alteration: Examples from calc-alkaline and anorogenic granites of Corsica (Southeast France). Contributions to Mineralogy and Petrology. 2002;142:485-500. DOI: 10.1007/s004100100303

[23] Wood SA, Ricktetts A. Allanite-(Ce) from the Eocene Casto granite, Idaho: Response to hydrothermal alteration. The Canadian Mineralogist. 2000;38:81-100. DOI: 10.2113/gscanmin.38.181

[24] Dahlquist JA. REE fractionation by accessory minerals in epidote-bearing metaluminous granitoids from the sierras Pampeanas, Argentina. Mineralogical Magazine. 2001;65:463-475. DOI: 10.1180/002646101750377506

[25] Beard JS, Sorensen SS, Gieré R. REE zoning in allanite related to changing partition coefficients during crystallization: Implications for REE behaviour in an epidote-bearing tonalite. Mineralogical Magazine. 2006;70:419-435. DOI: 10.1180/0026461067040337