



Britholite, monazite, REE carbonates, and calcite: Products of hydrothermal alteration of allanite and apatite in A-type granite from Stupné, Western Carpathians, Slovakia

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ABSTRACT

An uncommon assemblage of primary and secondary accessory REE minerals was identified in a Permian A-type granite clast in polymict conglomerates intercalated in the Cretaceous flysch sequence of the Pieniny Klippen Belt, Western Carpathians, northwest Slovakia. A detailed electron-microprobe study of the granite reveals extensive subsolidus alteration of primary magmatic allanite-(Ce) to ferriallanite-(Ce) and fluorapatite. The Y, Ce-rich fluorapatite was replaced by the dissolution–reprecipitation process to the britholite group mineral members: fluorbritholite-(Y), britholite-(Y), fluorcalciobritholite, and its hydroxyl-dominant analogue (“calciobritholite”). Britholite-(Y) contains up to 5.2 wt.% ThO₂ (0.15 apfu Th); the highest Th content yet reported in naturally occurring Y-dominant britholites. Moreover, the alteration of (ferri)allanite-(Ce) resulted to complex pseudomorphs and overgrowths, including mainly REE carbonate phases: [synchysite-(Ce) to its hydroxyl-dominant analogue “hydroxylsynchysite-(Ce)”, bastnäsite-(Ce)] and calcite, rarely monazite-(Ce), epidote, clinochlore, titanite, TiO₂ phase, and pseudorutile. In some cases, secondary carbonate minerals (mainly synchysite and calcite) replaced a substantial part of former allanite crystals. Moreover, primary magmatic biotite (annite) was partly transformed to acicular stilpnomelane. Textural and compositional data indicate extensive replacement and breakdown of the primary magmatic allanite and apatite by aqueous fluids rich in fluorine and carbon, liberated during a younger post-magmatic, low-temperature hydrothermal-metamorphic overprint of the granite.

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1. Introduction

Allanite and apatite are widespread accessory constituents of many magmatic and metamorphic crustal rocks; particularly granites s. l. and orthogneisses. Their appearance, internal zoning, textural relationships, and compositional or isotopic variations are successfully applied in studying various geological processes in the host rocks, including partial melting, magmatic fractionation, element partitioning and their subsolidus transformation, and hydrothermal alteration. Primary magmatic allanite is a typical accessory mineral of metaluminous and slightly peraluminous granitic rocks, especially of I- and A-type affinity (Bea, 1996; Broska and Petřík, 2008; Broska et al., 2000; Buda and Nagy, 1995; Gieré and Sorensen, 2004; Uher et al., 2009; Vlach and Gualda, 2007; Wood and Ricketts, 2000).

On the other hand, britholite group minerals isostructural to the apatite group are relatively rare in nature, and their occurrences are linked especially to late-magmatic crystallization or subsolidus alteration of

primary minerals in alkali-rich granites, monzonites, (nepheline) syenites, and their pegmatites, carbonatites, and dikes and metamorphic rocks related to them (e.g., Ahijado et al., 2005; Arden and Halden, 1999; Della Ventura et al., 1999; MacDonald et al., 2013; Pekov et al., 2007; Smith et al., 2002; Vilalva et al., 2013).

Primary magmatic rare-element carbonate phases (bastnäsite, synchysite group minerals) appear only in REE-rich peralkaline granitic suites (e.g., Bea, 1996). However, these minerals commonly originated as products of subsolidus to hydrothermal-metamorphic activity where fluorine and carbon-rich fluids were released and secondary REE phases precipitated from the primary magmatic minerals, especially allanite, monazite, xenotime, and apatite (Berger et al., 2008; Buda and Nagy, 1995; Förster, 2001; Hoskin et al., 2000; Johan and Johan, 2005; Littlejohn, 1981; Meintzer and Mitchell, 1988; Ondrejka et al., 2007, 2012; Wood and Ricketts, 2000; and references therein). Secondary subsolidus monazite also originated in some localities as a breakdown product of primary REE phases in gneissic and granitic lithologies (e.g., Bollinger and Janots, 2006; Budzyń et al., 2010; Krenn and Finger, 2007; Uher et al., 2009). The metamorphic transformation of allanite to monazite is complex. For example, allanite is stable in

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interval between ~440 and 580 °C; at lower and even higher temperature, allanite is converted to monazite as has been documented in metapelitic rocks from the European Central Alps (Janots et al., 2008).

In this contribution, we present the low-temperature, post-magmatic alteration, and breakdown phenomena of primary magmatic fluorapatite and allanite-(Ce) to produce an uncommon assemblage of britholite group minerals, including britholite-(Y), fluorbritholite-(Y), fluorcalciobricholite, and its hydroxyl-dominant analogue (“calciobricholite”, not IMA-approved mineral species) as well as secondary monazite-(Ce), REE carbonate minerals of bastnäsite, and synchysite groups and other secondary minerals in Permian A-type granite from Slovakia. Some preliminary results concerning transformation of apatite to britholite were already published (Uher and Ondrejka, 2008), but here we describe the chemical composition of all identified primary and secondary REE-bearing minerals in detail and discuss a possible scenario of their origin.

2. Regional geology

Paleozoic granitic rocks belong to important and widespread lithologies of pre-Alpine crystalline basement of the Western Carpathians. The main plutonic activity is connected with Variscan orogeny, where orogen-related plutons form the dominant parts of mountains in the Tatric and Veporic superunits. The Variscan granitic rocks (tonalites, granodiorites to granites, and their pegmatites) show calc-alkaline and I- or S-type affinity, and their zircon U-Pb isotope dating reveals Upper Devonian to Carboniferous, ~370 to 340 Ma age interval of solidification (e.g., Broska et al., 2013; Burda et al., 2013; Kohút et al., 2009, and references therein). In contrast to this main stage of Variscan granite formation, small plutons of granites and granite porphyries originated during Permian post-orogenic to anorogenic stage (~280 to 240 Ma; e.g., Poller et al., 2002; Radvanec et al., 2009; Uher and Pushkarev, 1994). This Permian group of the West-Carpathian granites exhibits specialized S- or A-type character, depending mainly on source rocks and tectonic regime (Broska and Uher, 2001; Uher and Broska, 1996). Moreover, the Permian West-Carpathian granites were affected by younger low-temperature hydrothermal overprint during Alpine orogenesis (mainly Jurassic to Cretaceous), where some primary magmatic minerals were transformed into secondary phases (Breiter et al., 2015; Uher et al., 2009).

The investigated rock represents alkali-feldspar biotite granite, which belongs to the Upohlav type of Permian A-type granite group (Uher et al., 1994). The conventional U-Pb isotope zircon dating gave upper intercept age of 274 ± 13 Ma for the Upohlav-type granites (Uher and Pushkarev, 1994). However, these granites are known only as cm-to-m size clasts in conglomerate beds of the Upohlav Formation (Fig. 1), part of the Cretaceous deep-marine flysch sequence of the Pieniny Klippen Belt in the Central Western Carpathians (Marschalko, 1986). We studied a typical cobble size granite clast (~20 cm diameter) in a small abandoned quarry near Stupné village, 8.5 km north of Považská Bystrica town in northwestern Slovakia. The geographic coordinates are N 49°11'39", E 18°26'05". The conglomerates at Stupné are polymict, with 49.8 to 58.3 vol.% limestones and dolomites, 22.5 to 33.0 vol.% volcanic rocks (rhyolites, basalts), 12.8 to 15.9 vol.% clastic sedimentary rocks, 2.1 to 2.4 vol.% granitic rocks, and 1.2 to 2.0 vol.% metamorphic rocks (Marschalko, 1986). Although exact provenance area of the Upohlav granitic clasts remains still ambiguous, they share mineralogical and geochemical analogies with other Permian A-type granite occurrences in the West-Carpathian internal tectonic units (Broska and Uher, 2001; Uher and Broska, 1996; Uher et al., 2009).

3. Analytical methods and formula calculations

Several polished thin sections from the granite clast were investigated in detail by optical study, BSE, and electron microprobe. The heavy mineral fraction of accessory minerals was obtained by crushing the

clast and separation by the Wilfley table, heavy liquid, and the Cook electromagnetic separator at the Earth Science Institute of the Slovak Academy of Sciences in Bratislava.

Accessory minerals were analyzed by the CAMECA SX 100 microprobe at the Department of Electron Microanalysis at the State Geological Institute of Dionýz Štúr (Geological Survey of the Slovak Republic), Bratislava. The minerals were analyzed in wave-length mode with large LLIF, LPET and standard PET and TAP crystals. For the REE-bearing minerals (epidote, apatite, and britholite group minerals, monazite, and REE carbonates), accelerating voltage of 15 kV was preferred to 20 kV to optimize the spatial resolution, less surface damage, and reduced PAP matrix correction factors. Probe current of 20 or 40 nA depended on mineral susceptibility to beam-induced damage. Beam diameter ranged from 1 to 5 µm. For measurements of REE-bearing minerals, the following minerals and synthetic compounds were used as standards: barite (S K α , Ba L α), apatite (P K α), GaAs (As L α), wollastonite (Si K α , Ca K α), TiO₂ (Ti K α), ZrSiO₄ (Zr L α), HfO₂ (Hf L α), ThO₂ (Th M α), UO₂ (U M β), Al₂O₃ (Al K α), ScPO₄ (Sc K α), YPO₄ (Y L α), LaPO₄ (La L α), CePO₄ (Ce L α), PrPO₄ (Pr L β), NdPO₄ (Nd L α), SmPO₄ (Sm L α), EuPO₄ (Eu L β), GdPO₄ (Gd L α), TbPO₄ (Tb L α), DyPO₄ (Dy L β), HoPO₄ (Ho L β), ErPO₄ (Er L β), TmPO₄ (Tm L α), YbPO₄ (Yb L α), LuPO₄ (Lu L β), fayalite (Fe K α), rhodonite (Mn K α), forsterite (Mg K α), SrTiO₃ (Sr L α), PbCO₃ (Pb M α), albite (Na K α), orthoclase (K K α), LiF (F K α), and NaCl (Cl K α).

Numerous mutual interferences are present among spectral lines of measured elements. The spectral lines were chosen with aim to minimize or completely eliminate overlap. In cases when the overlap still exists, the empirical correction factors were applied. Overlaps were resolved for Pb M α -Y L $\gamma_{2,3}$ and Th M $\zeta_{1,2}$, U M β -Th M γ , Th M β and Th N α , U M β -K α , Gd L α -Ce L χ , Gd L α -La L α , L $\chi_{2,3}$, Gd L α -Nd L β_2 , Lu L β -Dy L $\chi_{2,3}$, Ho L χ and Yb L β_2 , Eu L β -Dy L ν , Fe K α and Mn K β , Er L β -Eu L $\chi_{2,3}$, Gd L χ and Lu L ν , Sm L α -Ce L β_2 , Tm L α -Sm L χ , F K α -Ce M $\zeta_{1,3}$, F K α -Mn L β , F K α -Fe L α (Konečný et al., 2004 and later modifications).

Associated silicate and oxide minerals were analyzed using 15 kV accelerating voltage, 20 nA probe current, and 3 to 10 µm beam diameter, with the following standards: orthoclase (Si K α , K K α), TiO₂ (Ti K α), Al₂O₃ (Al K α), chromite or metallic Cr (Cr K α), fayalite (Fe K α), rhodonite (Mn K α), MgO (Mg K α), wollastonite (Ca K α), barite (Ba L α), albite (Na K α), LiF (F K α), and NaCl (Cl K α).

The detection limit slightly vary for each analysis. Averaged detection limits for REE-bearing minerals (at 30 nA) are as follows (concentrations in ppm): S-180, As-870, P-420, Si-420, Ti-450, Th-442, U-665, Al-340, Y-420, La-920, Ce-850, Pr-890, Nd-725, Sm-750, Eu-1010, Tb-995, Dy-1290, Er-1400, Tm-1120, Yb-1010, Lu-2210, Fe-570, Mn-445, Mg-425, Ca-198, Sr-600, Ba-600, Pb-520, Na-450, F-370, and Cl-180. The standard deviations ($\pm 1\sigma$) vary between 0.02 and 0.3 wt. %, in dependence of the specific element concentration and peak measurement time (10 to 90 s).

The formulae of epidote group minerals (allanite, clinozoisite) were normalized on the basis of $\Sigma(A + M + T) = 8$ cations following the procedure of Armbruster et al. (2006), the partition of total iron between Fe²⁺ and Fe³⁺ was calculated from ideal stoichiometry and neutral charge balance, and H₂O content was calculated assuming OH + F + Cl = 1 apfu. Apatite-super group minerals (fluorapatite, britholite group) were calculated based on $\Sigma(M + T) = 8$ cations and OH + F + Cl = 1 apfu (Pasero et al., 2010). Monazite formulae were normalized on 4 oxygen atoms. Formulae of bastnäsite (synchysite and parisite) were calculated on 3 (6 and 9) oxygen atoms and OH + F + Cl = 1 (1 and 2) apfu and $\Sigma B = 1$ (2 and 3) apfu, respectively (where B = S, P, As, C, Si). The formula of chlorite was normalized on the basis of 10 oxygen atoms, OH + F + Cl = 8 apfu, and iron valence calculation. Stilpnomelane was normalized on 28 oxygen atoms, OH + F + Cl = 8 apfu, 2 H₂O molecules, $\Sigma(T + M) = 20$ cations (where T and M = Si, Ti, Al, Fe, Mn, Mg), and iron valence calculation. Titanite and pseudorutile formulae were calculated on the basis of 5 anions (O + F) and 9 oxygen atoms, respectively, including iron valence calculation. All mineral formulae are charge balanced.

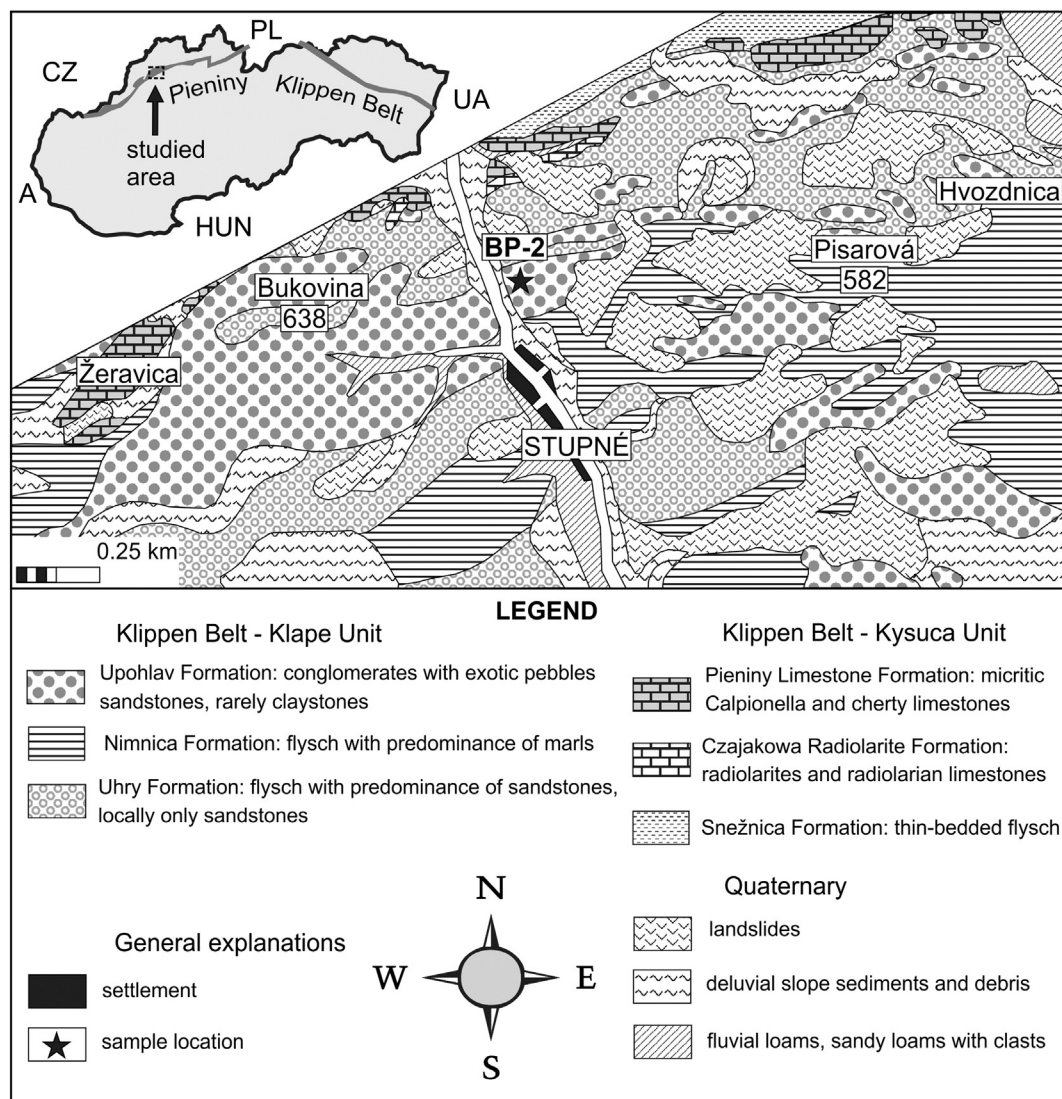


Fig. 1. Schematic geological map of studied area (modified from Mello et al., 2005) with location of the Stupné granite clast in Cretaceous conglomerates of the Upohlav Formation, Slovakia. Abbreviations of adjacent countries: A = Austria, CZ = Czech Republic, PL = Poland, UA = Ukraine, HUN = Hungary.

4. Results

4.1. Sample description

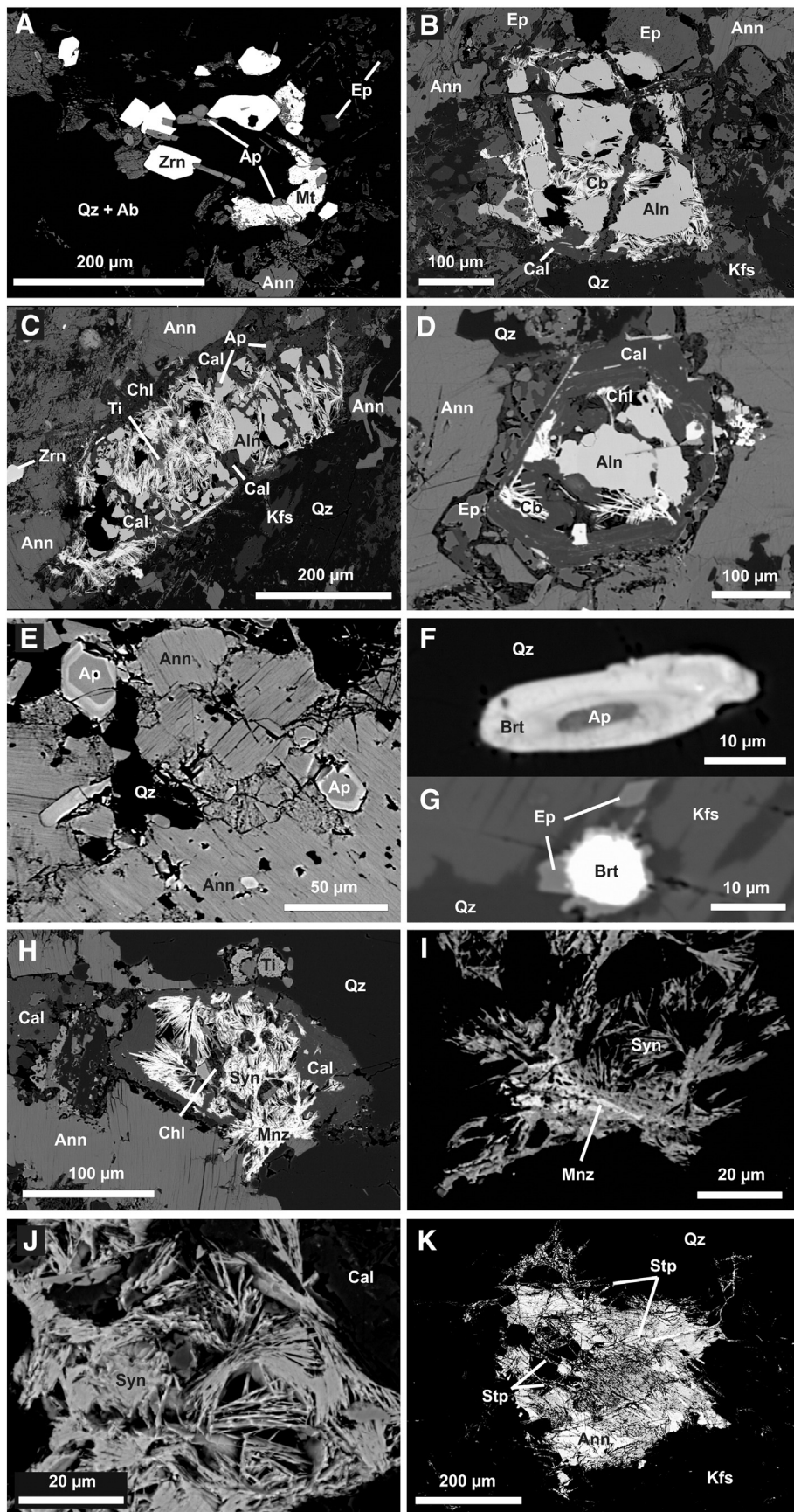
The investigated cobble (BP-2 sample) represents alkali-feldspar biotite granite with medium-grained hypidiomorphic equigranular texture. According to planimetric counting ($n = 3296$ points, 5.3 cm^2 area), rock-forming minerals of the granite comprise (in vol.%) anhedral to subhedral quartz (34.3); perthitic K-feldspar (most likely orthoclase) to hyalophane, $\text{Or}_{82-98}\text{Ab}_{02-18}\text{Cs}_{00-09}\text{An}_{00-01}$ (37.0); and albite plagioclase, $\text{Ab}_{91-98}\text{An}_{01-08}\text{Or}_{00-01}$, with localized K-feldspar exsolution lamellae—antiperthite (23.5), biotite (4.9), and epidote group minerals (0.2). Late anhedral to subhedral interstitial Fe-rich biotite (annite) aggregates exhibit distinct pleochroism, yellowish-green to dark green and greenish-brown color, and annite composition with high $\text{Fe}/(\text{Fe} + \text{Mg})$ atomic ratio (~ 0.95). Fine-crystalline muscovite commonly replaced primary plagioclase. The accessory minerals include primary zircon, fluorapatite, allanite-(Ce), ilmenite, magnetite, and pyrite, together with secondary phases (Fig. 2A). Transparent euhedral zircon crystals have predominantly $\text{P}_4\text{--P}_5$ and D (sub)type morphology according to the zircon typology classification (Pupin, 1980), and this indicates a high-temperature, high-alkaline crystallization environment (Uher and Broska, 1996; Uher and Marschalko, 1993). Moreover, the chemical composition of the

Stupné granite cobble (Uher et al., 1994) reveals post-orogenic, A-type affinity with relatively high Si, K, Zr, Y, and Ga and low Al, Mg, Ca, Sr, P, and V contents, analogous to other similar occurrences of A-type granitic rocks in the Western Carpathians (Broska and Uher, 2001).

4.2. Allanite

Allanite forms scattered euhedral to subhedral shaped crystals, ~ 70 to $\sim 500 \mu\text{m}$ across, associated with biotite (annite), quartz, feldspars, zircon, fluorapatite, and ilmenite. Freshly separated allanite crystals are tabular prismatic, translucent with black color and glassy to pitchy luster. Allanite crystals are commonly partly to fully replaced and overgrown by secondary minerals, mainly REE carbonate phases, calcite, and epidote, and more rarely by monazite, clinocllore, titanite, TiO_2 phase (rutile or anatase or brookite), and pseudorutile (Fig. 2B–D).

Allanite shows a relatively uniform composition with ~ 25 to $27 \text{ wt.}\%$ $(\text{Y} + \text{REE})_2\text{O}_3$ ($0.87\text{--}0.96 \text{ apfu Y} + \text{REE}$) and a predominance of Ce over the other Y + REE; and $\text{Ce}/(\text{Y} + \text{REE})$ atomic ratio attaining around 0.47. The total Al content is relatively low at ($\sim 12 \text{ wt.}\%$ Al_2O_3 ; $\sim 1.4 \text{ apfu Al}$). This content, considered together with the higher content of calculated $^{M1}[\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Al})]$ ratio (0.19 to 0.51), denotes a significant to dominant amount of ferriallanite-(Ce) molecule (ferriallanite to allanite 1 in Table 1; Fig. 3A).



Allanite chemical composition is controlled by a dominant $A2(Y,REE) + M3Fe^{2+} = A2Ca + M3(Fe,Al)^{3+}$ substitution mechanism (Armbruster et al., 2006; Franz and Liebscher, 2004; Gieré and Sorensen, 2004; Petrík et al., 1995), Fig. 3B–C. Moreover, a relatively high titanium content (up to 2.9 wt.% TiO_2 ; ≤ 0.21 apfu Ti) indicates the presence of $M1(Ti^{4+} + Fe^{2+}) = 2M1(Al,Fe^{3+})$ substitution (Fig. 3D) and possibly also $M1Ti^{4+} + O^{2-} = M1(Al,Fe)^{3+} + OH^{-}$ exchange, which control Ti entry into the allanite structure. On the other hand, some allanite analyses determine a distinctly lower Ti content (0.2–0.4 wt.% TiO_2) together with higher Al and slightly lower Fe content and a vacancy in the A2 position (0.03 to 0.15 apfu; allanite 2 in Table 1, Fig. 3A–D). Such allanite represents most likely a younger, recrystallized post-magmatic generation.

Concentrations of other measured elements (P, Th, U, Mn, Mg, Sr, Ba, Pb, F, and Cl) in the studied allanite are below 0.07 apfu.

4.3. Fluorapatite

Primary fluorapatite forms euhedral crystals up to $\sim 100 \mu m$ in size associated with quartz, alkali feldspars, biotite, allanite, zircon, and magnetite (Figs. 2A, E) and is occasionally over-rimmed with britholite group minerals (Fig. 2F). Yttrium and Ce are the most abundant rare-earth elements in fluorapatite. Its crystals normally have regular concentric to oscillatory zoning (Fig. 2E), which reflects variations in Y, REE, Ca, Si, and P concentration during crystal growth. Fluorapatite crystal cores appear dark in BSE and contain elevated Y + REE and Si contents: 1.2 to 3.8 wt.% $(Y + REE)_2O_3$, 0.04 to 0.13 apfu Y + REE, and 0.2 to 1.1 wt.% SiO_2 , 0.02 to 0.10 apfu Si, whereas the rim zones are pale in BSE and relatively enriched in those elements: 4.0 to 6.8 wt.% $(Y + REE)_2O_3$, 0.14 to 0.23 apfu Y + REE, 1.4 to 3.3 wt.% SiO_2 , and 0.12 to 0.28 apfu Si (Table 2). The LREE (La to Eu)/(Y + REE) ratio is 0.5 to 0.6 in both central and rim areas.

The entry of Y and REE into the apatite structure is balanced by two principal heterovalent substitutions: (1) $(Y,REE)^{3+} + Si^{4+} = Ca^{2+} + P^{5+}$ and (2) $Na^+ + (Y,REE)^{3+} = 2Ca^{2+}$ (e.g., Harlov et al., 2003; MacDonald et al., 2013; Pan and Fleet, 2002; Roeder et al., 1987; Rønsbo, 1989). Substitution (1) plays a dominant role in Y,REE-rich fluorapatite from the Stupné granite (Fig. 4A, B). On the contrary, negligible Na concentration (up to 0.1 wt.% Na_2O ; ≤ 0.02 apfu Na) indicate only very restricted role of substitution (2) in the studied fluorapatite.

The chemical composition of the studied fluorapatite is usually expressed by the britholite heterovalent substitution mechanism: $(Y,REE)^{3+} + Si^{4+} = Ca^{2+} + P^{5+}$ (Fig. 4A–B), and its chondrite-normalized REE diagram has a relatively flat pattern without Eu anomaly (Fig. 5). Concentrations of other measured elements (S, As, Ti, Th, U, Sc, Mg, Sr, Pb, Na, and Cl) are generally very low, or below electron-microprobe detection limits.

4.4. Britholite group minerals

Secondary REE-Y-bearing accessory minerals include the following yttrium-rich members of the britholite group (classified in the apatite super-group, Pasero et al., 2010): fluorbritholite-(Y), $Ca_2(Y,REE)_3(SiO_4)_3F$, britholite-(Y) $Ca_2(Y,REE)_3(SiO_4)_3OH$, fluorcalciobriholite $Ca_3(Y,REE)_2(SiO_4)_2(PO_4)F$, and “calciobriholite” $Ca_3(Y,REE)_2(SiO_4)_2(PO_4)OH$, a hydroxyl-dominant analogue of fluorcalciobriholite. The britholite group minerals (BGM) are detected as an outer rim around fluorapatite in quartz (Fig. 2F) or as a

subhedral inclusion ($\sim 10 \mu m$ across) with epidote overgrowths in K-feldspar and quartz (Fig. 2G). BGM chemical compositions are highly variable with different REE/Ca, P/Si and F/OH ratios, reflecting complex isomorphous solid solution in their end-members (Table 2, Fig. 4A). Fluorine-dominant members (atomic F/(F + OH) = 0.51 to ~ 1.0) are the most frequent phases, while hydroxyl-dominant compositions attain lower F/(OH + F) ratio: 0.36 to 0.43 in britholite-(Y), and 0.40 to 0.47 in “calciobriholite”. All BGM compositions have distinct predominance of Y (1.05 to 1.32 apfu) over other REE, where Ce achieves the highest concentrations of 0.24 to 0.45 apfu.

Similarly to Y,REE-rich fluorapatite, the $(Y,REE)^{3+} + Si^{4+} = Ca^{2+} + P^{5+}$ represents dominant heterovalent substitution mechanism (Fig. 4B), whereas $Na^+ + (Y,REE)^{3+} = 2Ca^{2+}$ substitution is insignificant due to low Na content in studied BGM (up to 0.3 wt.% Na_2O ; 0.07 apfu). Moreover, elevated concentrations of U, and especially Th, are characteristic of britholite members in the studied Stupné granite. While thorium concentrations range from 2.5 to 5.2 wt.% ThO_2 (0.07 to 0.15 apfu), uranium reaches only 0.4 to 1.0 wt.% UO_2 (0.01 to 0.03 apfu U), with maximum Th and U concentrations denoting fluorbritholite-(Y) composition. Several possible substitution mechanisms explain the entry of tetravalent Th and U cations into the apatite-britholite structure: (1) $(Th,U)^{4+} + Si^{4+} = (Y,REE)^{3+} + P^{5+}$ (Pekov et al., 2011), (2) $(Th,U)^{4+} + 2Si^{4+} = Ca^{2+} + 2P^{5+}$ (Luo et al., 2011; MacDonald et al., 2013), (3) $(Th,U)^{4+} + B^{3+} = Ca^{2+} + P^{5+}$, or (4) $(Th,U)^{4+} + B^{3+} = (Y,REE)^{3+} + Si^{4+}$ (Oberti et al., 2001). Positive correlation between (Th,U) and Si but negative relationship between (Th,U) and P indicate that mechanism (2) which, together with dominant britholite-type exchange $[(Y,REE)^{3+} + Si^{4+} = Ca^{2+} + P^{5+}]$, forms the complex $(Y,REE)^{3+} + (Th,U)^{4+} + 3Si^{4+} = 2Ca^{2+} + 3P^{5+}$ substitution (Fig. 4E). Britholite Th/U atomic ratio ranges from 4.2 to 7.6, to average 6.2, and the elements maintain positive mutual correlation (Fig. 4F).

Slightly elevated concentrations of Fe and Mn are also typical of investigated BGM with up to 1.6 wt.% FeO and 0.5 wt.% MnO; (Table 2), while S, As, Ti, Al, Sc, Mg, Sr, Pb, Na, and Cl levels are usually very low or below electron microprobe detection limits. The chondrite-normalized REE britholite diagram illustrates relatively flat patterns with distinct negative Eu anomaly, contrasting strongly with their absence in fluorapatite (Fig. 5).

4.5. Monazite-(Ce)

Rare monazite-(Ce) forms 5 to 20 μm large anhedral or platy crystals and aggregates associated with REE carbonate (synchysite), calcite, and TiO_2 phase (Fig. 2H–I). The monazite shows a relatively high Th and Ca content: 6 to 13.5 wt.% ThO_2 (0.06 to 0.13 apfu Th) and 4 to 8 wt.% CaO (0.17 to 0.37 apfu Ca). Although this indicates the dominant cheralite (formerly brabantite) substitution (e.g., Bea, 1996; Ondrejka et al., 2007): $Ca^{2+} + Th^{4+} = 2(REE,Y)^{3+}$ (Table 3, Fig. 6), the Ca^{2+} content together with slightly elevated concentrations of Sr^{2+} (~ 1 wt. % SrO , 0.03 apfu Sr), and Ba^{2+} (~ 0.6 wt.% BaO , 0.01 apfu Ba) highlight their apparent surplus over $Th^{4+} + U^{4+}$. Moreover, the monazite compositions show low analytical totals around 95 to 96 wt.% and significant deviation from ideal stoichiometry; the A site cation total is 1.15 to 1.33 apfu, while B site cations attain only 0.88 to 0.98 apfu (Table 3). These features affirm partial hydration of monazite and/or the presence of sub-microscopic rhabdophane or synchysite intergrowths.

Fig. 2. BSE images of rock-forming and primary vs. secondary accessory minerals of the Stupné granite. (A) Assemblage of primary magmatic zircon (Zrn), fluorapatite (Ap) and magnetite (Mt) in quartz (Qz), albite (Ab), annite (Ann), and secondary epidote (Ep). (B–D) Primary magmatic allanite-(Ce) to ferriallanite-(Ce) crystals (Aln) in association with quartz (Qz), K-feldspar (Kfs), annite (Ann), zircon (Zrn), fluorapatite (Ap), partly replaced by assemblage of secondary minerals: REE carbonates (Cb), calcite (Cal), epidote (Ep), clinochlore (Chl), and TiO_2 phase (Ti). (E) Primary magmatic fluorapatite crystals with distinct regular REE-enriched overgrowths in association with annite (Ann) and quartz (Qz). (F) Fluorapatite (Ap) replaced by britholite-group minerals (Brt) in quartz (Qz). (G) Britholite-group mineral (Brt) with overgrowths of epidote (Ep) in quartz (Qz) and K-feldspar (Kfs). (H–J) Aggregates of thin platy crystals of REE carbonate minerals, mainly synchysite-(Ce) to “hydroxylsynchysite-(Ce)” (Syn) in association with monazite-(Ce) (Mnz), calcite (Cal), clinochlore (Chl), and TiO_2 phase (Ti) form complete replacements after primary allanite-(Ce) to ferriallanite-(Ce). (K) Thin lamellar crystals of stilpnomelane (Stp) replacing primary magmatic annite (Ann) in association with quartz (Qz) and K-feldspar (Kfs). See also text for explanation.

Table 1

Representative compositions and structural formulae of allanite-(Ce), ferriallanite-(Ce) and epidote from the Stupné granite (wt.%), bd—below detection limit.

Mineral	Ferriallanite	Allanite 1	Allanite 2	Epidote	Mineral	Ferriallanite	Allanite 1	Allanite 2	Epidote
SiO ₂	30.54	30.53	31.94	37.05	Si	2.975	2.995	3.000	2.978
TiO ₂	2.64	2.81	0.21	0.03	Al T	0.025	0.005	0.000	0.022
ThO ₂	0.52	0.52	bd	bd	Sum T	3.000	3.000	3.000	3.000
UO ₂	bd	0.03	bd	bd	Ti	0.193	0.207	0.015	0.002
Al ₂ O ₃	11.87	11.97	14.52	21.71	Al M1	0.337	0.379	0.607	0.976
Y ₂ O ₃	0.12	0.20	0.30	0.10	Fe ³⁺ M1	0.349	0.287	0.343	0.000
La ₂ O ₃	7.02	6.35	3.45	0.02	Fe ²⁺ M1	0.074	0.130	0.000	0.000
Ce ₂ O ₃	12.33	11.96	11.16	0.08	Mg	0.044	0.000	0.000	0.000
Pr ₂ O ₃	2.08	1.24	1.59	0.05	Sum M1	0.998	1.003	0.965	0.978
Nd ₂ O ₃	3.86	4.09	5.76	bd	Al M2	1.000	1.000	1.000	1.000
Sm ₂ O ₃	bd	0.08	0.63	bd	Sum M2	1.000	1.000	1.000	1.000
Eu ₂ O ₃	0.28	0.46	0.52	bd	Al M3	0.000	0.000	0.000	0.059
Gd ₂ O ₃	0.20	0.27	0.45	0.04	Fe ³⁺	0.000	0.000	0.021	0.925
Tb ₂ O ₃	0.07	0.03	0.14	0.11	Fe ²⁺	0.979	0.979	0.905	0.000
Dy ₂ O ₃	0.13	0.15	0.12	0.11	Mn	0.021	0.021	0.074	0.015
Ho ₂ O ₃	bd	bd	0.09	bd	Sum M3	1.000	1.000	1.000	1.000
Er ₂ O ₃	bd	0.18	0.13	bd	Ca A1	0.990	0.988	0.994	1.000
Tm ₂ O ₃	0.12	0.13	0.12	0.11	Na	0.010	0.012	0.006	0.000
Yb ₂ O ₃	0.08	0.12	0.03	0.03	Sum A1	1.000	1.000	1.000	1.000
Lu ₂ O ₃	0.03	0.13	bd	0.07	Th	0.011	0.012	0.000	0.000
Fe ₂ O ₃ calc.	4.76	3.89	5.14	15.30	U	0.000	0.001	0.000	0.000
FeO	12.94	13.51	11.53	0.00	Y	0.006	0.010	0.015	0.004
MnO	0.26	0.26	0.93	0.22	La	0.252	0.230	0.120	0.001
MgO	0.31	bd	bd	bd	Ce	0.439	0.430	0.384	0.002
CaO	10.00	10.10	10.37	23.16	Pr	0.074	0.044	0.055	0.001
SrO	bd	bd	bd	0.07	Nd	0.134	0.143	0.193	0.000
BaO	bd	bd	0.06	bd	Sm	0.000	0.003	0.020	0.000
PbO	bd	bd	bd	0.03	Eu	0.009	0.015	0.017	0.000
Na ₂ O	0.05	0.06	0.03	bd	Gd	0.006	0.009	0.014	0.001
H ₂ O calc.	1.54	1.53	1.57	1.86	Tb	0.002	0.001	0.004	0.003
Total	101.73	100.58	100.79	100.15	Dy	0.004	0.005	0.004	0.003
					Ho	0.000	0.000	0.003	0.000
					Er	0.000	0.006	0.004	0.000
					Tm	0.003	0.004	0.003	0.003
					Yb	0.002	0.004	0.001	0.001
					Lu	0.001	0.004	0.000	0.002
					Ca A2	0.053	0.073	0.049	0.995
					Sr	0.000	0.000	0.000	0.003
					Ba	0.000	0.000	0.002	0.000
					Pb	0.000	0.000	0.000	0.001
					Sum A2	1.000	0.992	0.885	1.019
					OH	1.000	1.000	1.000	1.000

Contents of P, F and Cl are below detection limits.

4.6. REE carbonate minerals

The REE carbonate minerals comprise the synchysite and bastnäsite group members. Scarce bastnäsite-(Ce) occurs as tiny anhedral inclusions up to 20 µm across in dominant synchysite group minerals. The synchysites form radial or irregular aggregates of thin tabular crystals up to ~50 µm long in cavities and cracks of altered allanite crystals (Fig. 2J), in association with secondary calcite, epidote, and chlorite, but also with monazite and Ti-bearing phases in some places (Fig. 2B–D, H–J). In some cases, the secondary carbonate minerals (mainly synchysite and calcite) replaced a substantial part of former allanite crystals (Fig. 2D). Rarely, synchysite-(Ce) associates with a secondary monazite, calcite, clinocllore, and TiO₂ phase, replacing the primary fluorapatite or annite (Fig. 2H). A tiny (~0.5 µm across) euhedral inclusion of uranium-bearing thorianite [(Th,U)O₂] was detected in synchysite.

The calculated stoichiometry for bastnäsite-(Ce) closely approximates the (REE,Y)(CO₃)(F,OH) formula, with very low Ca/(Ca + REE + Y) and high F/(F + OH) ratios of 0.01 to 0.03 and 0.66 to 0.71, respectively. Its compositions show unambiguous dominance of light REE (LREE; La to Nd) over other REE, with Ce > La > Nd > Pr abundances, and 0.43 to 0.46 apfu Ce, while calcium reaches only around 0.9 wt.% CaO (0.03 apfu Ca) (Table 4, Fig. 7A).

Synchysite-(Ce) [CaCe(CO₃)₂(F,OH)] reveals a significantly higher Ca/(Ca + REE + Y) ratio (0.36 to 0.55) in comparison to bastnäsite-(Ce). Again, LREE predominates here, with Ce³⁺ the dominant REE

cation (18 to 23 wt.% Ce₂O₃; 0.34 to 0.45 apfu Ce), while Ca attains 15 to 18 wt.% CaO (0.8 to ~1 apfu Ca). The F/(F + OH) ratio shows very variable values (0.31 to 0.78) and presence of both hydroxyl- and fluorine-dominant members: “hydroxylsynchysite-(Ce)” and synchysite-(Ce). Although one composition approaches parisite-(Ce), [Ca(Ce,La)₂(CO₃)₃(F,OH)₂] stoichiometry (Table 4), this may simply be a synchysite and bastnäsite mixture. While bastnäsite Th concentrations attain 0.5 to 1.4 wt.% ThO₂ (0.004 to 0.01 apfu Th), the synchysite Th contents vary between 0.4 and 4.5 wt.% ThO₂ (0.005 to 0.052 apfu Th). Synchysite analyses show moderately to slightly elevated Fe, Al, and Si concentrations: up to 4.7 wt.% FeO (≤0.19 apfu Fe), up to 0.6 wt.% Al₂O₃ (≤0.03 apfu Al) and up to 1.4 wt.% SiO₂ (≤0.07 apfu Si). These values negatively correlate with REE + Y and calculated Cor (CO₃)²⁻, thus indicating possible (Fe,Al)³⁺ + Si⁴⁺ = (REE,Y)³⁺ + C⁴⁺ substitution (Fig. 7B).

The chondrite-normalized REE diagram of bastnäsite and synchysite group minerals displays clear dominance of LREE, mainly La to Nd, over their heavy Gd to Lu counterparts (Fig. 8).

4.7. Associated secondary minerals

Calcite forms massive pseudomorphs after primary allanite, and in some cases, it contributes important volume to former allanite crystals, mainly their outer parts (Fig. 2B–D). Calcite commonly associates with radial aggregates of synchysite (Fig. 2B–D, H). However, their mutual

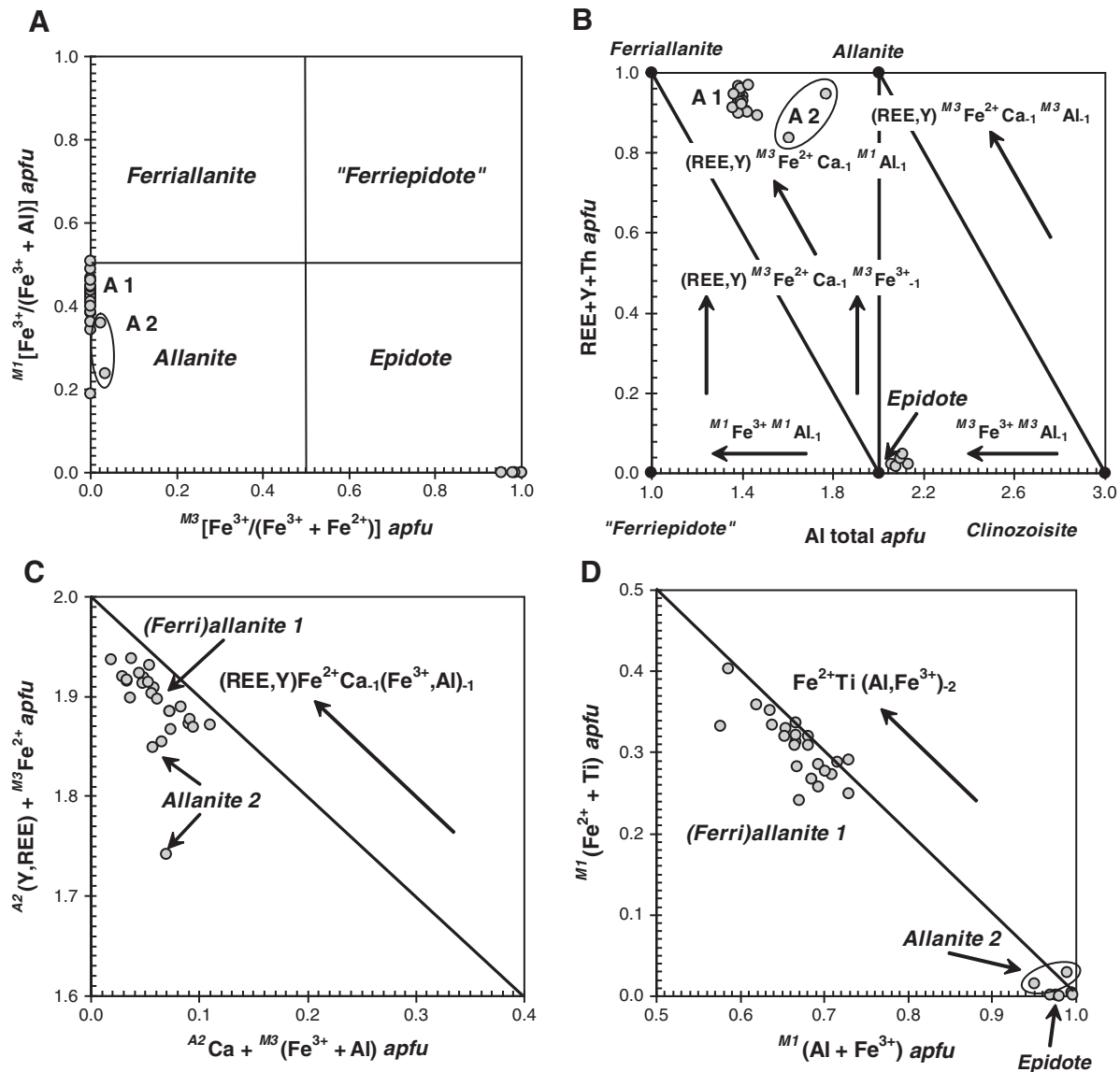


Fig. 3. (A–D) Classification and substitution diagrams of allanite and epidote from the Stupné granite (atomic proportions). Note a different chemical composition of primary (ferri)allanite-(Ce) 1 (A 1) and secondary allanite-(Ce) 2 (A 2). The Fig. 2B is modified diagram of Petřík et al. (1995) and Vlach (2012). Heavy solid lines represent ideal substitution vectors (B–D).

textural relationships are not unambiguous: calcite looks synchronous to younger mineral than synchysite. Calcite is relatively homogeneous with small admixtures of iron (0.5 to 0.9 wt.% FeO), strontium (≤ 0.2 wt.% SrO), and manganese (≤ 0.1 wt.% MnO); Mg content is below detection limit of the electron microprobe. Secondary epidote forms overgrowths around allanite or britholite (Fig. 2B, D), exhibiting very low REE + Y content of ~ 0.02 apfu, while the total Al values are around 2 apfu and approximate epidote end-member composition (Table 1, Fig. 3A–B). In some places, chlorite forms irregular replacement zones on allanite (Fig. 2C) with clinoclase composition of $\text{Fe}/(\text{Fe} + \text{Mg}) = 0.39$ (Table 5). Moreover, acicular aggregates of stilpnomelane partly replace annite (Table 5, Fig. 2K). Titanite occurs as anhedral to subhedral overgrowths on altered allanite together with epidote, calcite, TiO_2 phase (rutile?) and other secondary phases, and it contains appreciable Al, Fe and F (grothite variety), according to $(\text{Al,Fe})^{3+} + (\text{F,OH})^- = \text{Ti}^{4+} + \text{O}^{2-}$ substitution (Table 5). Finally, pseudomorph was detected as irregular replacement domains after primary ilmenite in altered allanite crystals; with its low totals around 94 wt.% indicating potential hydration (Table 5).

5. Discussion and conclusions

5.1. Primary magmatic allanite and apatite

The investigated rock represents metaluminous ($\text{ASI} = 0.92$), biotite alkali-feldspar granite with post-orogenic A-type tendency (Uher and Broska, 1996; Uher et al., 1994). The granite contains relatively widespread accessory allanite-(Ce), with its euhedral crystal shape and textural relationship to the rock-forming alkali feldspars, quartz, and biotite indicating primary magmatic origin of allanite. The investigated allanite shows relatively high titanium concentration; up to 2.9 wt.% TiO_2 (≤ 0.21 apfu Ti). This contrasts with the 1 to 2 wt.% TiO_2 concentration commonly observed allanite from volcanic and plutonic rocks (e.g., Brooks et al., 1981; Catlos et al., 2000; Chesner and Ettlinger, 1989; Jiang et al., 2003; Wood and Ricketts, 2000). The highest Ti contents in allanite, around 5 wt.% TiO_2 , were reported in fayalite-hedenbergite syenite from the Ukrainian Shield (Krivdík et al., 1989), anorogenic granitic rocks in Corsica, France (Poitrasson, 2002), and granitic to syenitic A-type rocks in

Table 2

Representative compositions and structural formulae of fluorapatite (Fap), fluorbritholite-(Y)–(Fbr), britholite-(Y)–(Brt), fluorcalciobricholite (Fcb), and “calciobricholite” (Cbr) from the Stupné granite (wt.%); bd—below detection limit.

	Fap	Fap	Fbr	Brt	Fcb	Cbr		Fap	Fap	Fbr	Brt	Fcb	Cbr
P ₂ O ₅	40.77	37.60	1.57	3.04	7.72	7.18	P	2.918	2.770	0.165	0.313	0.763	0.711
As ₂ O ₅	bd	0.16	0.12	0.08	0.03	0.07	As	0.000	0.007	0.008	0.005	0.002	0.004
SiO ₂	0.20	2.25	23.17	22.40	19.59	19.64	Si	0.017	0.196	2.876	2.721	2.287	2.296
ThO ₂	bd	0.03	5.31	3.63	2.48	2.58	Sum T	2.935	2.973	3.049	3.039	3.052	3.011
UO ₂	bd	bd	0.87	0.88	0.49	0.44	Th	0.000	0.001	0.150	0.100	0.066	0.069
Al ₂ O ₃	bd	0.03	bd	bd	bd	bd	U	0.000	0.000	0.024	0.024	0.013	0.011
Y ₂ O ₃	0.09	1.28	19.34	18.87	16.99	17.06	Al	0.000	0.003	0.000	0.000	0.000	0.000
La ₂ O ₃	0.06	0.48	2.98	3.15	1.20	1.93	Y	0.004	0.059	1.278	1.220	1.056	1.062
Ce ₂ O ₃	0.22	1.45	9.56	9.73	5.46	7.19	La	0.002	0.015	0.136	0.141	0.052	0.083
Pr ₂ O ₃	0.14	0.35	1.81	1.80	1.09	1.28	Ce	0.007	0.046	0.434	0.433	0.233	0.308
Nd ₂ O ₃	0.15	1.37	5.76	5.88	6.50	6.37	Pr	0.004	0.011	0.082	0.080	0.046	0.055
Sm ₂ O ₃	0.13	0.42	1.51	1.58	2.83	2.32	Nd	0.004	0.043	0.255	0.255	0.271	0.266
Eu ₂ O ₃	0.08	0.09	0.30	0.36	0.07	bd	Sm	0.004	0.013	0.065	0.066	0.114	0.093
Gd ₂ O ₃	0.03	0.47	1.95	1.91	3.81	3.23	Eu	0.002	0.003	0.013	0.015	0.003	0.000
Tb ₂ O ₃	bd	0.08	0.39	0.43	0.58	0.51	Gd	0.001	0.014	0.080	0.077	0.147	0.125
Dy ₂ O ₃	0.08	0.27	2.79	2.43	3.52	3.11	Tb	0.000	0.002	0.016	0.017	0.022	0.020
Ho ₂ O ₃	bd	0.17	1.04	0.96	0.49	0.45	Dy	0.002	0.008	0.112	0.095	0.132	0.117
Er ₂ O ₃	0.19	0.15	1.97	1.66	1.95	1.82	Ho	0.000	0.005	0.041	0.037	0.018	0.017
Tm ₂ O ₃	0.06	0.03	0.41	0.41	0.31	0.36	Er	0.005	0.004	0.077	0.063	0.072	0.067
Yb ₂ O ₃	0.00	0.11	1.90	1.91	1.00	1.21	Tm	0.002	0.001	0.016	0.016	0.011	0.013
Lu ₂ O ₃	bd	0.07	0.37	0.42	0.39	0.44	Yb	0.000	0.003	0.072	0.071	0.036	0.043
FeO	0.69	0.16	0.96	0.89	0.73	0.63	Lu	0.000	0.002	0.014	0.015	0.014	0.016
MnO	0.13	0.11	0.31	0.37	0.32	0.00	Fe	0.049	0.012	0.100	0.090	0.071	0.062
CaO	54.64	51.23	14.42	15.75	19.91	20.08	Mn	0.009	0.008	0.033	0.038	0.032	0.000
SrO	0.04	0.03	bd	bd	bd	bd	Ca	4.949	4.774	1.918	2.050	2.490	2.516
PbO	bd	bd	0.14	bd	0.05	0.07	Sr	0.002	0.002	0.000	0.000	0.000	0.000
Na ₂ O	0.12	bd	0.13	0.25	0.21	0.20	Pb	0.000	0.000	0.005	0.000	0.002	0.002
H ₂ O calc.	0.05	0.17	0.51	0.77	0.56	0.76	Na	0.019	0.000	0.031	0.059	0.048	0.045
F	3.63	3.27	1.43	0.94	1.49	1.07	Sum M	5.065	5.027	4.952	4.962	4.949	4.990
Cl	bd	bd	0.06	0.06	0.05	0.05	OH	0.029	0.100	0.426	0.627	0.440	0.594
O = F	–1.53	–1.64	–0.60	–0.40	–0.63	–0.45	F	0.971	0.900	0.561	0.361	0.550	0.396
O = Cl	0.00	0.00	–0.01	–0.01	–0.01	–0.01	Cl	0.000	0.000	0.013	0.012	0.010	0.010
Total	99.96	100.22	100.47	100.15	99.19	99.59	Sum X	1.000	1.000	1.000	1.000	1.000	1.000

Graciosa Province in Brazil (Vlach and Gualda, 2007). Generally, high Ti content in primary allanite (>0.1 apfu) is a typical feature of both volcanic and plutonic rocks of A-type affinity related to extensional tectonic settings, while relatively low Ti-in-allanite contents (<0.1 apfu) are characteristic of volcanic and plutonic rocks related to compressive tectonic settings as demonstrated by Vlach and Gualda (2007). Titanium entry into the investigated allanite is controlled by substitution mechanisms involving $^{M1}(\text{Ti}^{4+} + \text{Fe}^{2+}) = 2^{M1}(\text{Al}, \text{Fe}^{3+})$ (Fig. 3D) and possibly also $^{M1}\text{Ti}^{4+} + \text{O}^{2-} = ^{M1}(\text{Al}, \text{Fe})^{3+} + \text{OH}^-$. These substitutions suggest a strong influence of oxygen fugacity in allanite formation (Gieré and Sørensen, 2004). Moreover, the alteration of Ti-rich primary magmatic allanite-(Ce) is also favorable for liberation of Ti and formation of secondary, post-magmatic TiO₂ phase, and titanite in the Stupné granite. This is well documented by their irregular shape and textural relationships (Fig. 2C, H).

Euhedral, primary magmatic fluorapatite from the Stupné granite reveals elevated Y and other REE: 1.2 to 6.8 wt.% (Y + REE)₂O₃, 0.04 to 0.23 apfu Y + REE (Table 2). This enrichment in Y and other REE is a characteristic feature of magmatic fluorapatite from alkaline-rich magmatic rocks. While fluorapatite from A-type granites contains up to ~4 wt.% REE₂O₃ (Broska et al., 2004; MacDonald et al., 2013; Wang et al., 2001), the highest concentrations of (Y,REE)₂O₃ have been reported in fluorapatite from non-granitic, highly alkaline magmatic rocks: up to ~19 wt.% in the Pajarito syenite, New Mexico, USA (Roeder et al., 1987), up to 20 wt.% from foyaites and syenites of the Ilímaussaq intrusion, Greenland (Rønsbo, 1989), and up to 21 wt. % in the Oldoinyo Lengai carbonatite, Tanzania (Dawson, 1993). Consequently, the ability of apatite to accept Y + REE is proportional to Na and K alkaline concentration in the parental magma with its strong potential to dissolve rare earth elements.

5.2. Composition and formation of britholite group minerals

Identified britholite group minerals (BGM) in the Stupné granite comprise fluorbritholite-(Y), britholite-(Y), and fluorcalciobricholite together with its currently unapproved hydroxyl-dominant analogue (“calciobricholite”), close to the $\text{Ca}_3(\text{Y}, \text{REE})_2(\text{SiO}_4)_2(\text{PO}_4)_3(\text{OH})$ formula. However, such “calciobricholite” compositions have rarely been reported in alkaline granites and their skarn aureole in Scotland (MacDonald et al., 2013; Smith et al., 2002). BGM are locally enriched in actinide elements, particularly in Th and less in U which are the regular source of their metamictization. Thorium content in britholite-(Ce), fluorbritholite-(Ce), and fluorcalciobricholite compositions with Ce > Y can reach ~3 to 23 wt.% ThO₂ or 0.06 to 0.68 apfu (Contini et al., 1993; Della Ventura et al., 1999; Melluso et al., 2010; Oberti et al., 2001; Orlandi et al., 1989; Pekov et al., 2007). In contrast, BGM compositions with Y > Ce contain notably lesser Th (up to ~2 wt.% ThO₂; Griffin et al., 1979; Payette and Martin, 1986; Pekov et al., 2011; Smith et al., 2002). Therefore, the studied fluorbritholite-(Y) from Stupné granite containing up to 5.2 wt. % ThO₂ (0.15 apfu Th) represents the highest Th content yet reported in naturally occurring Y-dominant britholites [fluorbritholite-(Y), britholite-(Y), Y > Ce “calciobricholite”].

The chondrite-normalized REE diagrams of primary fluorapatite enriched in Y and REE versus secondary BGM from the Stupné granite (Fig. 5) show their very similar flat patterns with LREE ≈ HREE; the only different feature is an absence of Eu anomaly in fluorapatite versus a strong negative Eu anomaly in BGM (Eu/Eu* = 0.2 to 0.6). Such negative Eu anomaly is comparable with other britholite occurrences (Oberti et al., 2001); it indicates a partial removal of Eu and their possible deposition (in the Eu²⁺ form) into REE carbonates with slightly positive Eu anomalies (Fig. 8) during origin of BGM. Consequently, the BGM overgrowths most likely originated by post-magmatic partial dissolution

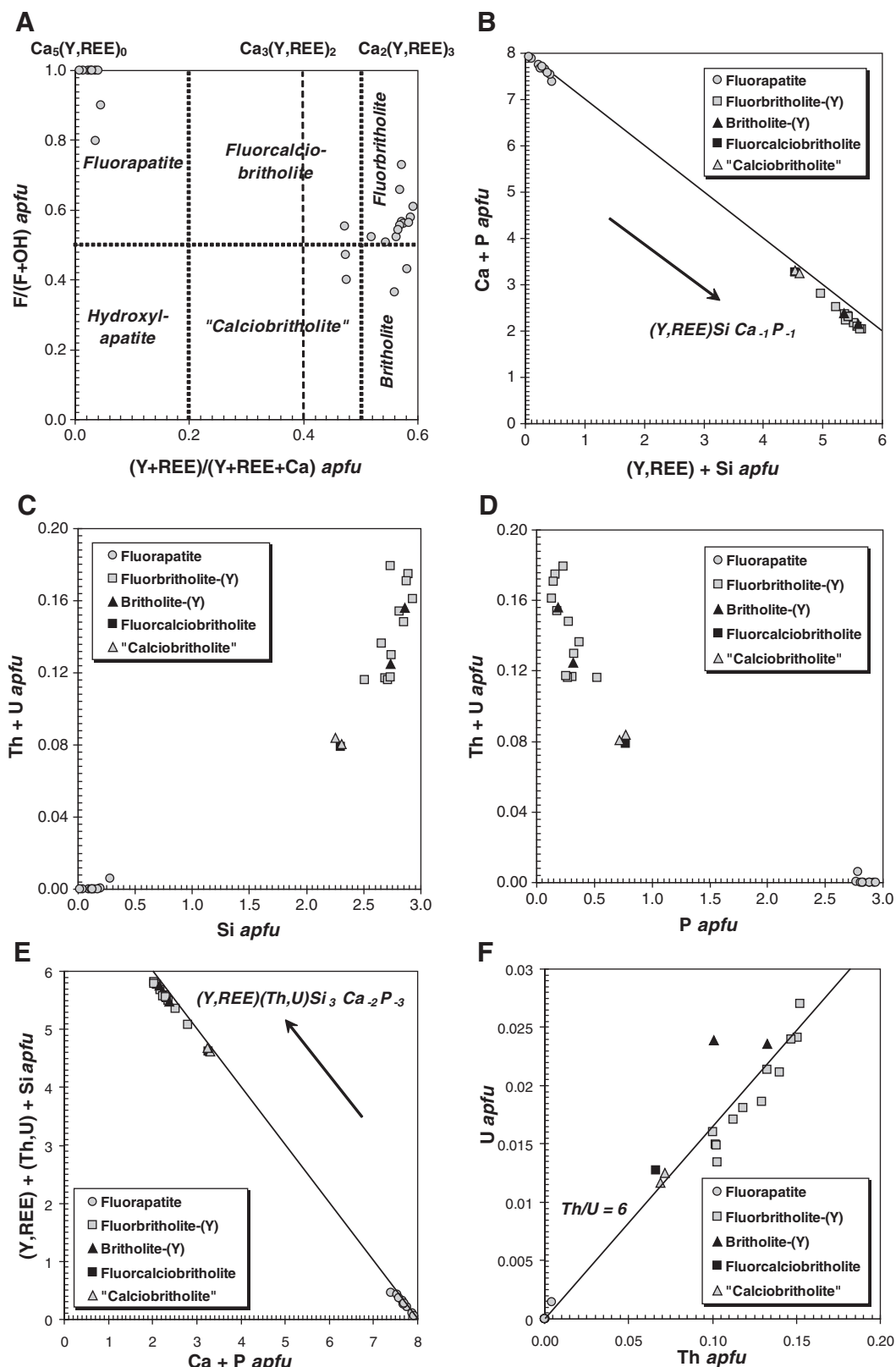


Fig. 4. (A–F) Classification and substitution diagrams of fluorapatite and britholite-group minerals from the Stupné granite (atomic proportions).

and metasomatic replacement of parental fluorapatite in an aqueous fluorine-bearing fluid environment; and most likely rich in alkaline cations (Na^+ and K^+) which is a typical feature of A-type granitic suites (e.g., Bonin, 2007; Whalen et al., 1987).

Occurrences of primary magmatic BGM are limited to peralkaline granites and syenite pegmatites (e.g., Griffin et al., 1979; Larsen, 1996; Pekov et al., 2007, 2011; Vilalva et al., 2013) or peralkaline rhyolitic rocks (Min et al., 2006; Payette and Martin, 1986). Formation of BGM is

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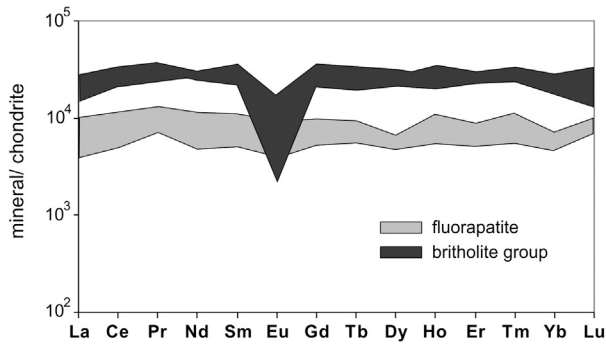


Fig. 5. REE patterns of fluorapatite and britholite-group minerals from the Stupné granite normalized to the CI chondrite (Barrat et al., 2012).

usually connected with late- to post-magmatic or hydrothermal alteration processes in diverse alkaline rocks, for example, in alkali syenitic ejecta (Della Ventura et al., 1999), REE-enriched pegmatite segregations (Arden and Halden, 1999), carbonate-amphibole-clinopyroxene rocks (Zaitsev and Chakhmouradian, 2002), REE-rich mineralized zones associated with potassic alkaline to subalkaline volcanic to plutonic rocks (Harlov et al., 2003), or carbonatites and related skarn deposits (Ahijado et al., 2005). Moreover, (fluor)britholite-(Y) occurs as either a discrete phase or as an alteration product after allanite-(Ce) of calcic endoskarn in contact aureole of Beinn an Dubhaich alkaline granite at Skye in the United Kingdom (Smith et al., 2002). BGM overgrowths on apatite crystals have been reported from several occurrences (Della Ventura et al., 1999; Larsen, 1996; MacDonald et al., 2013; Melluso et al., 2010; Zaitsev and Chakhmouradian, 2002). Contrasting, fluid-driven transformation of fluorbritholite-(Y) to secondary fluorapatite, thalénite-(Y) and

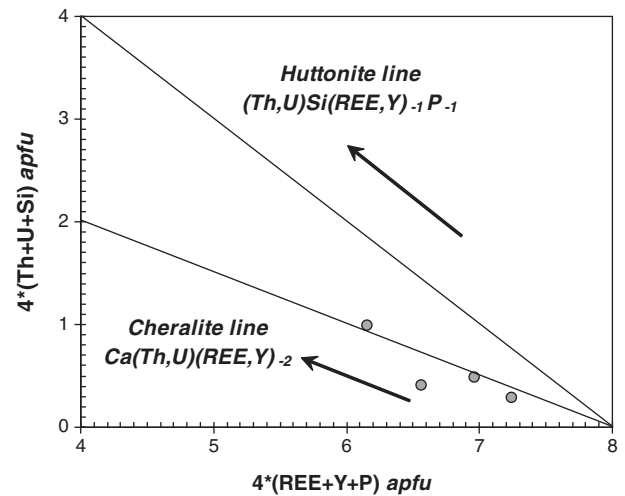


Fig. 6. Substitution diagram of monazite from the Stupné granite (atomic proportions).

tombarthite-(Y) was described from Reiarssdal granitic pegmatite, Norway (Griffin et al., 1979). Britholites in granitic rocks are uncommon but have been described as late-magmatic crystals in alkaline granites from Scotland and Northern Ireland in the United Kingdom (MacDonald et al., 2013) and in hydrothermally altered S-type, tin-bearing granites of the Ervedosa area in Portugal (Gomes and Neiva, 2000). Moreover, low-temperature britholite-(Ce) and britholite-(La) in association with synchysite-(Ce), cerite-(Ce), goethite, hollandite, and barite precipitated during late-stage supergene alteration processes in Virulundo carbonatite, Angola (Torró et al., 2012). The above-mentioned post-magmatic and commonly low-temperature origin of BGM is in accordance with textural relationships in the Stupné granite. Investigated britholite overgrowths on fluorapatite (Fig. 2F) indicate secondary, probably hydrothermal-metamorphic, fluid-driven partial dissolution of primary fluorapatite and precipitation of BGM, an example of the dissolution-reprecipitation process (Putnis, 2002).

Table 3

Representative compositions and structural formulae of monazite-(Ce) from the Stupné granite (wt.%), bd—below detection limit.

Anal. no.	1	2	3	Anal. no.	1	2	3
SO ₃	0.08	0.06	0.10	S	0.002	0.002	0.003
P ₂ O ₅	23.60	24.13	26.61	P	0.831	0.855	0.917
As ₂ O ₅	0.10	0.16	0.16	As	0.002	0.004	0.003
SiO ₂	2.86	0.80	0.34	Si	0.119	0.033	0.014
ZrO ₂	1.03	0.06	0.07	Al	0.022	0.006	0.000
HfO ₂	0.08	bd	bd	Sum B	0.977	0.899	0.937
ThO ₂	13.47	7.24	6.13				
UO ₂	0.07	0.02	0.04	Zr	0.021	0.001	0.001
Al ₂ O ₃	0.46	0.11	bd	Hf	0.001	0.000	0.000
Y ₂ O ₃	1.49	1.01	1.49	Th	0.127	0.069	0.057
La ₂ O ₃	7.75	8.92	9.97	U	0.001	0.000	0.000
Ce ₂ O ₃	20.75	24.01	26.43	Y	0.033	0.022	0.032
Pr ₂ O ₃	3.42	3.82	4.34	La	0.119	0.138	0.150
Nd ₂ O ₃	8.81	9.41	11.55	Ce	0.316	0.368	0.394
Sm ₂ O ₃	1.32	1.26	1.96	Pr	0.052	0.058	0.064
Eu ₂ O ₃	0.62	0.69	0.89	Nd	0.131	0.141	0.168
Gd ₂ O ₃	1.03	1.01	1.51	Sm	0.019	0.018	0.027
Tb ₂ O ₃	0.09	0.15	0.18	Eu	0.009	0.010	0.012
Dy ₂ O ₃	0.38	0.42	0.64	Gd	0.014	0.014	0.020
Ho ₂ O ₃	0.14	0.10	0.25	Tb	0.001	0.002	0.002
Er ₂ O ₃	0.22	0.12	0.22	Dy	0.005	0.006	0.008
Tm ₂ O ₃	0.06	0.16	0.08	Ho	0.002	0.001	0.003
Yb ₂ O ₃	0.13	0.15	0.19	Er	0.003	0.002	0.003
Lu ₂ O ₃	0.07	0.03	0.16	Tm	0.001	0.002	0.001
FeO	0.68	1.37	0.50	Yb	0.002	0.002	0.002
CaO	5.00	8.33	3.85	Lu	0.001	0.000	0.002
SrO	1.33	1.31	1.12	Fe	0.024	0.048	0.017
BaO	0.63	0.62	0.58	Ca	0.223	0.374	0.168
PbO	0.22	bd	0.09	Sr	0.032	0.032	0.026
Total	95.89	95.49	99.46	Ba	0.010	0.010	0.009
				Pb	0.003	0.000	0.001
				Sum A	1.148	1.318	1.170

5.3. Allanite alteration

The alteration of primary magmatic allanite-(Ce) to ferriallanite-(Ce) crystals in the Stupné granite and formation of the secondary mineral assemblage, mainly REE carbonates and calcite (Fig. 2B–D, H), represent an excellent example of metasomatic replacement by corrosive aqueous fluid infiltration. Transformation of allanite to secondary REE carbonate minerals (mainly bastnäsite, synchysite and parisite) has been described in numerous cases in various magmatic and metamorphic rocks (e.g., Berger et al., 2008; Buda and Nagy, 1995; Buda et al., 2014; Budzyń et al., 2010; Förster, 2000; Gieré, 1996; Hirtopanu et al., 2013; Littlejohn, 1981; Meintzer and Mitchell, 1988). However, such alteration of allanite is usually connected with absence of calcite, common precipitation of clay minerals (kaolinite, montmorillonite), and in some cases also with thorite, fluorite, and magnetite (Berger et al., 2008; Buda and Nagy, 1995; Gieré, 1996; Littlejohn, 1981). In contrast, our studied allanite was replaced mainly by calcite and synchysite, and rarely also by bastnäsite, monazite, epidote, chlorite (clinocllore), and Ti-minerals: titanite, TiO₂ phase, and pseudorutile. Such extensive carbonation of allanite is relatively rare in nature. One similar case was described in the Soutz granite, France, where secondary association comprising calcite + synchysite-(Ce) + bastnäsite-(Ce) + illite + anatase + quartz was formed (Middleton et al., 2013). Moreover, textural relationships indicate a partial replacement of allanite-(Ce) by calcite in the Ditrau alkaline massif (Hirtopanu et al., 2013). Conversely, Wing et al. (2003) described a decarbonation reaction producing

Table 4
Representative compositions and structural formulae of synchysite-(Ce)–(Syn-F), “hydroxylsynchysite-(Ce)”–(Syn-OH), parisite-(Ce)?–(Par?), and bastnäsite-(Ce)–(Bas) from the Stupné granite (wt.%); bd—below detection limit.

	Syn-F	Syn-F	Syn-OH	Par?	Bas		Syn-F	Syn-F	Syn-OH	Par?	Bas
SO ₃	0.06	bd	0.03	0.04	bd	S	0.002	0.000	0.001	0.003	0.000
P ₂ O ₅	0.04	bd	0.06	0.08	bd	P	0.002	0.000	0.003	0.006	0.000
As ₂ O ₅	0.11	0.11	0.09	0.14	0.15	As	0.003	0.003	0.002	0.007	0.003
CO ₂ calc.	27.37	28.44	27.46	24.33	20.49	C	1.977	1.893	1.970	2.970	0.993
SiO ₂	0.23	1.42	0.33	0.11	0.11	Si	0.012	0.069	0.017	0.010	0.004
TiO ₂	0.16	0.12	0.04	bd	0.05	Sum B	1.996	1.965	1.993	2.996	1.000
ThO ₂	2.86	1.40	2.15	1.14	0.88						
Al ₂ O ₃	0.06	0.58	0.10	0.05	bd	Ti	0.006	0.004	0.002	0.000	0.001
Y ₂ O ₃	1.50	1.77	2.65	0.60	0.23	Th	0.034	0.016	0.026	0.023	0.007
La ₂ O ₃	8.87	8.84	8.51	12.28	20.61	Al	0.004	0.033	0.006	0.005	0.000
Ce ₂ O ₃	18.02	19.04	18.83	26.70	34.60	Y	0.042	0.046	0.074	0.029	0.004
Pr ₂ O ₃	3.22	2.09	3.40	4.56	5.86	La	0.173	0.159	0.165	0.405	0.270
Nd ₂ O ₃	8.36	8.20	9.23	10.68	10.64	Ce	0.349	0.340	0.362	0.874	0.450
Sm ₂ O ₃	0.82	0.42	1.22	0.79	bd	Pr	0.062	0.037	0.065	0.149	0.076
Eu ₂ O ₃	0.55	bd	0.65	0.73	0.80	Nd	0.158	0.143	0.173	0.341	0.135
Gd ₂ O ₃	1.05	1.10	1.44	0.77	0.76	Sm	0.015	0.007	0.022	0.024	0.000
Tb ₂ O ₃	0.08	0.05	0.14	0.06	0.12	Eu	0.010	0.000	0.012	0.022	0.010
Dy ₂ O ₃	0.39	0.53	0.65	0.13	0.00	Gd	0.018	0.018	0.025	0.023	0.009
Ho ₂ O ₃	0.19	0.00	0.41	bd	bd	Tb	0.001	0.001	0.002	0.002	0.001
Er ₂ O ₃	0.14	0.37	0.22	0.18	0.17	Dy	0.007	0.008	0.011	0.004	0.000
Tm ₂ O ₃	0.21	0.17	0.21	0.15	0.20	Ho	0.003	0.000	0.007	0.000	0.000
Yb ₂ O ₃	0.13	0.18	0.21	0.06	0.16	Er	0.002	0.006	0.004	0.005	0.002
Lu ₂ O ₃	0.11	bd	0.11	bd	0.08	Tm	0.003	0.003	0.003	0.004	0.002
FeO	0.98	4.68	0.21	0.18	0.06	Yb	0.002	0.003	0.003	0.002	0.002
MnO	bd	bd	bd	bd	0.09	Lu	0.002	0.000	0.002	0.000	0.001
CaO	18.38	17.27	17.27	10.88	0.52	Fe	0.043	0.191	0.009	0.013	0.002
SrO	0.23	0.17	0.13	bd	bd	Mn	0.000	0.000	0.000	0.000	0.003
BaO	0.15	0.34	0.12	0.06	0.07	Ca	1.042	0.902	0.972	1.042	0.020
PbO	bd	bd	bd	0.09	bd	Sr	0.007	0.005	0.004	0.000	0.000
H ₂ O calc.	0.62	1.42	1.96	1.55	1.44	Ba	0.003	0.006	0.002	0.002	0.001
F	4.64	3.47	1.87	3.78	5.85	Pb	0.000	0.000	0.000	0.002	0.000
Cl	0.04	0.05	bd	0.03	0.03	Sum A	1.986	1.928	1.951	2.971	0.996
O = F	−1.95	−1.46	−0.79	−1.59	−2.46						
O = Cl	−0.01	−0.01	0.00	−0.01	−0.01	OH	0.220	0.461	0.689	0.927	0.341
Total	97.62	100.79	98.91	98.55	101.47	F	0.776	0.535	0.311	1.069	0.657
						Cl	0.004	0.004	0.000	0.005	0.002
						Sum X	1.000	1.000	1.000	2.001	1.000
						O	6.000	6.000	6.000	9.000	3.000
						F/(F + OH)	0.779	0.537	0.311	0.536	0.658

Contents of U are below detection limits.

allanite and apatite from monazite + chlorite + plagioclase + calcite + quartz. The bastnäsite or synchysite replacement of primary allanite also indicates a relatively high alkaline environment (Littlejohn, 1981; Meintzer and Mitchell, 1988) and the highly oxidizing nature of the fluids (Hanson et al., 2012).

The presence of secondary carbonate minerals (calcite, bastnäsite, synchysite) replacing primary allanite in the Stupné granite indicates a relatively low-temperature, post-magmatic overprint of the rock by hydrothermal-metamorphic, metasomatic aqueous fluids rich in fluorine and carbon in the form of CO₃^{2−}, HCO₃[−] or CO₂; depending on

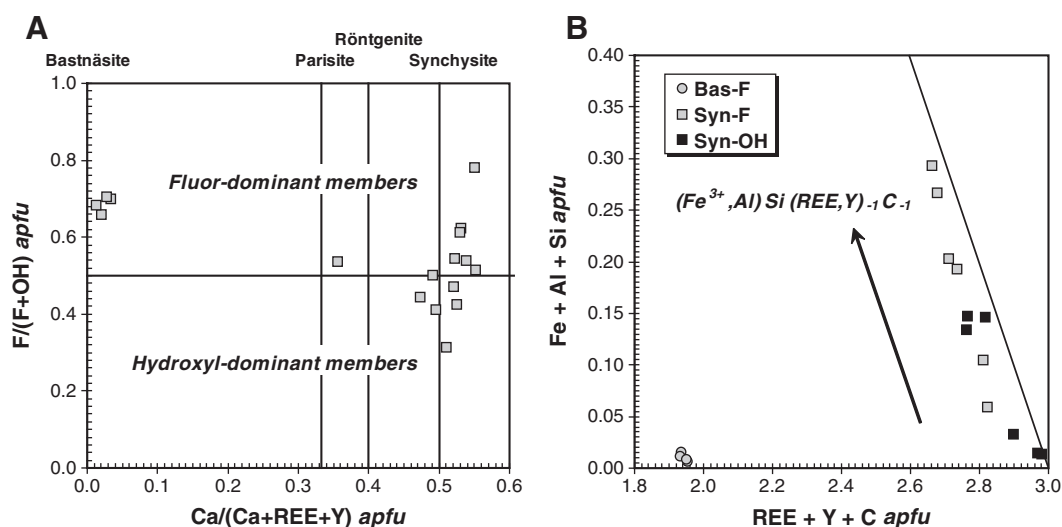


Fig. 7. (A, B) Classification and substitution diagrams of REE carbonate minerals from the Stupné granite (atomic proportions). Mineral abbreviations: Bas-F—bastnäsite-(Ce), Syn-F—synchysite-(Ce), and Syn-OH—“hydroxylsynchysite-(Ce).”

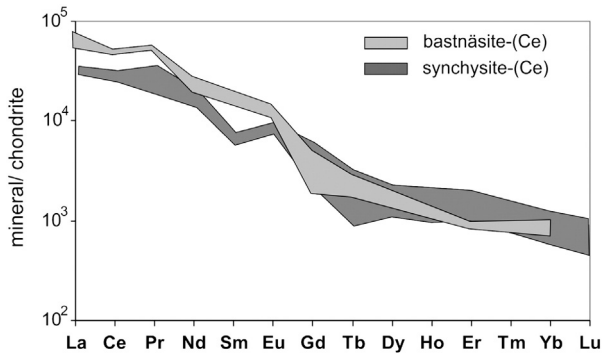


Fig. 8. REE patterns of synchysite and bastnäsite from the Stupné granite normalized to the CI chondrite (Barrat et al., 2012).

fluid pH (Gieré, 1996). Destabilization of primary biotite (annite) by stilpnomelane and partial dissolution of fluorapatite most likely released sufficient fluorine for bastnäsite and synchysite precipitation, however with insufficient fluorine fugacity for fluorite crystallization. The source of the carbon-rich fluids remains unclear, with degassing of deeper magmatic reservoirs or influx and heating of meteoric water interacting with carbonate/organic-rich sedimentary rocks providing possible sources (Middleton et al., 2013). The presence of britholite + synchysite paragenesis (Torró et al., 2012) indicates a possibility of contemporaneous origin of both fluorapatite and allanite alteration mechanisms.

The REE carbonate minerals, such as synchysite, bastnäsite, and parisite, can form over a relatively wide temperature range in magmatic to hydrothermal conditions (Hsu, 1992; Williams-Jones and Wood, 1992). Besides magmatic occurrences in carbonatites and silicate alkaline rocks, bastnäsite and synchysite were commonly found in hydrothermal associations, including Alpine-type fissures (Gieré, 1996), in

basalt amygdules (Augé et al., 2014) as well as in sedimentary authigenic conditions, e.g., in bauxites from karstic depressions (Maksimović and Pantó, 1996) and pelosiderite concretions in coal beds (Szakáll et al., 2002). Similarly, the alteration and breakdown of allanite represents rather a relatively low-temperature event. For example, formation of monazite and rhabdophane at the expense of allanite during retrogression of metapelites from Crete, Greece, took place at $\leq 300^\circ\text{C}$ (Krenn and Finger, 2007), and a replacement of allanite by fluorite, an REE, Th, P-rich phase (probably monazite), and a Th-rich phase (probably thorianite) in the Casto granite (Idaho, USA) was estimated under 200°C by activity of low-salinity hydrothermal fluid (Wood and Ricketts, 2000). Synchysite replacing allanite or parisite were formed under very low-grade metamorphic overprint of Ca-rich graywackes of the Drahany Upland (Czech Republic), at a maximum temperature of $\sim 200\text{--}300^\circ\text{C}$ (Čopjaková et al., 2011). Moreover, the replacement of allanite to calcite, synchysite, bastnäsite, and other secondary phases in the Soultz monzogranite (France) originated under hydrothermal CO_2 -rich fluids at temperatures around 300 to 350°C and pressure ≤ 220 MPa, based on fluid-inclusion study of adjacent carbonate-quartz veins (Dubois et al., 1996; Middleton et al., 2013). Moreover, hypergene very-low temperature weathering (below $\sim 100^\circ\text{C}$) of allanite in presence of groundwater also resulted to formation of bastnäsite (Meintzer and Mitchell, 1988; Vlasov et al., 1964).

The presence of secondary stilpnomelane replacing primary magmatic annite also indicates a relatively low-temperature and pressure conditions of the Stupné granite alteration. Stilpnomelane is an index metamorphic mineral stable from anchimetamorphic to low- and medium-grade regional metamorphism of greenschist to blueschist facies in iron-rich metasedimentary and metavolcanic protoliths, especially in banded iron formations (e.g., Bekker et al., 2010; Li et al., 2000; Miyano and Beukes, 1997). Based on experimental and thermodynamic data, Fe-end member stilpnomelane can persist to a maximum temperature of 500°C and pressures up to $600\text{--}700$ MPa (Miyano and Klein, 1989) or even higher pressure (Massonne and Willner, 2008). However, stilpnomelane is also a product of low P-T retrograde metamorphic transformation of Fe-rich minerals (biotite, almandine) in granitic rocks and pegmatites. For example, such secondary stilpnomelane occurs in the Mont Blanc granite in Swiss Alps (von Raumer, 1969), in Trysil granite, Norway (Heim et al., 1996), in granite pebbles in Menaver conglomerates, England (Dörr et al., 1999), or in granitic pegmatites from Strzegom, Poland, where stilpnomelane formation at temperature of 130 to 300°C was estimated according to the fluid inclusion study (Janeczek, 1989). Therefore, we propose a relatively low-temperature (ca. $\leq 300^\circ\text{C}$) hydrothermal-metamorphic overprint of the Stupné granite. Similar post-magmatic hydrothermal alteration of primary magmatic allanite-(Ce) to secondary monazite-(Ce) and the Nb-Ta-Y-REE minerals is most probably connected with a younger Alpine metamorphic overprint of the Turčok metagranite, a typical member of Permian A-type suite in Western Carpathians (Uher et al., 2009). An analogous alteration process presumably took place also during early Alpine overprint of the Stupné granite, before its final denudation, transport, and deposition of the granite clasts to the marine flysch sediments.

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Table 5
Representative compositions and structural formulae of clinocllore, stilpnomelane, titanite, and pseudorutile from the Stupné granite (wt.%); bd—below detection limit.

	Clinocllore	Stilpnomelane	Titanite	Pseudorutile
SiO ₂	39.03	42.67	31.01	0.16
TiO ₂	0.05	0.00	30.79	56.31
Al ₂ O ₃	13.37	6.70	5.88	0.05
Fe ₂ O ₃ calc.	0.00	3.05	1.00	36.70
FeO	16.78	31.90	bd	0.12
MnO	0.02	1.31	0.04	0.30
MgO	14.84	0.79	bd	bd
CaO	1.37	0.39	28.76	0.14
Na ₂ O	0.03	0.10	bd	
K ₂ O	0.52	1.28	bd	
H ₂ O calc.	10.91	7.36		
F	bd	bd	1.59	
O = F			−0.67	
Total	96.92	95.55	98.40	93.78
Si	3.909	10.429	1.012	0.011
Ti	0.004	0.000	0.756	3.000
Al	1.578	1.930	0.226	0.004
Fe ³⁺	0.000	0.562	0.025	1.957
Fe ²⁺	1.406	6.520	0.000	0.007
Mn	0.002	0.271	0.001	0.018
Mg	2.216	0.288	0.000	0.000
Ca	0.147	0.102	1.006	0.011
Na	0.006	0.047	0.000	
K	0.066	0.399	0.000	
Sum	9.334	20.548	3.026	5.008
H ₂ O mol.		2.000		
OH	8.000	8.000		
F			0.164	
O	10.000	28.000	4.836	9.000
Anions sum	18.000	36.000	5.000	9.000
Fe/(Fe + Mg)	0.39	0.96		

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