Hellandite-(Y)–hingganite-(Y)–fluorapatite retrograde coronae: a novel type of fluid-induced dissolution–reprecipitation breakdown of xenotime-(Y) in the metagranites of Fabova Hoľa, Western Carpathians, Slovakia

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Abstract

Two contrasting reaction coronae were developed around rare earth element (REE) accessory phosphates in Variscan metagranitic rocks, which have been overprinted by Alpine blastomylonitisation from the Fabova Hoľa Massif, in the Veporic Unit, Western Carpathians, Central Slovakia. The Th–U–Pb total EPMA age determination of primary magmatic monazite-(Ce) from the metagranite indicates a Carboniferous (Mississippian, Tournaian) age of 355 ± 1.9 Ma. Monazite-(Ce) breakdown resulted in impressive, though common, fluorapatite ± Th-silicate + allanite-(Ce) + clinzoisite coronae. The alteration of xenotime-(Y) produced a novel type of secondary coronal micro-texture consisting of a massive fluorapatite mantle zone and tiny satellite crystals of hellandite-(Y) [(Ca,REE)4Y2Al□2(B4Si4O12)(OH)2] and hingganite-(Y) [Y2□2Be3Si4O12(OH)2] of ~1–5 μm, and rarely ≤10 μm in size. The localised occurrence of Y–B–Be silicates, which are associated closely with other secondary minerals, suggests the involvement of B and Be during the metasomatic alteration transformation of xenotime-(Y). General reactions for monazite-(Ce) and xenotime-(Y) decomposition, including the fluids involved, can be written as follows: Mnz + (Ca, Fe, Si, Al and F)-rich fluid → FAp + Hld + Hin + Czo; Xtm + (Ca, Fe, Si, Al, F, B and Be)-rich fluid → FAp + Hld + Hin + Czo.

The granitic rocks underwent Early Cretaceous burial metamorphism under greenschist- to lower amphibolite-facies P–T conditions. Subsequently, Alpine post-collisional uplift and exhumation of the Veporic Unit, starting from the Late Cretaceous epoch, was accompanied by a retrograde tectono-metamorphic overprint; the activity of external fluids, caused the formation of secondary coronae minerals around monazite-(Ce) and xenotime-(Y). A portion of B (± Be) should have been liberated from the metagranite feldspars, micas, or xenotime-(Y) enriched in (Nb,Ta)BO4 (schiavinatoite or béhierite) components. However, the principal source of B and Be in fluids necessary for the production of hellandite and hingganite, was probably of external origin from adjacent magmatic, metamorphic, or sedimentary rocks (Permian granites, rhyolites and sedimentary rocks, and Palaeozoic metapelites).

Keywords: hellandite-(Y), hingganite-(Y), Y–B–Be silicate, xenotime-(Y), dissolution–reprecipitation, reaction coronae, metagranite, Fabova Hoľa, Western Carpathians, Slovakia

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parental rock (Wark and Miller, 1993; Bea, 1996; Gratz and Heinrich, 1997; Heinrich et al., 1997; Förster, 1998a, 1998b; Poitras et al., 2002; Pyle et al., 2001; Spear and Pyle, 2002; Wing et al., 2003; Kohn and Malloy, 2004; Ondrejka et al., 2012, 2016; Berger et al., 2008; Janots et al., 2008; Uhler et al., 2009, 2015; Harlov et al., 2011 and references therein). In addition, monazite-(Ce) and xenotime-(Y) are essential for petrochronology (e.g. Parrish, 1990; Montel et al., 1996; Williams et al., 2007; Engi, 2017).

Although these minerals commonly crystallise as primary magmatic or metamorphic accessory phases, younger post-magmatic or metamorphic hydrothermal fluids can cause their partial-to-complete transformation to low-grade neoblasts. For example, the commonly observed breakdown of monazite-(Ce) includes a subsolidus retrograde corona around its partly dissolved core with distinctive concentric mineral zones of apatite ± Th-silicate/oxide, and allanite-(Ce) to REE-rich epidote or clinzoisite (e.g. Broska and Siman, 1998; Finger et al., 1998, 2016; Budzyni et al., 2010; Ondrejka et al., 2012, 2016; Upadhyay and Pruseth, 2012; Lo Pò et al., 2016; Ji et al., 2021). This micro-texture is documented mostly in low- to medium-temperature metagranitoids with primary magmatic monazite-(Ce). However, it can also occur in metapelites if the high-temperature metamorphic monazite-(Ce) destabilises during post Peak metamorphic evolution (Majka and Budzyni, 2006; Finger et al., 2016; Lo Pò et al., 2016). Similar reaction coronae around xenotime-(Y) in granitoids and metapelites (Broska et al., 2005; Majka and Budzyni, 2006; Janots et al., 2008; Majka et al., 2011; Broska and Petrlik, 2015; Budzyni et al., 2018; Hentschel et al., 2020), or the partial compositional alteration of xenotime-(Y) via dissolution–recrystallization resulting in a texture characterised by thorite (ThSiO₄) and uraninite (UO₂) inclusions (Hetherington and Harlov, 2008; Ondrejka et al., 2016), are less frequent. Experiments suggest the significant dissolution, etching, and alteration of monazite-(Ce) and xenotime-(Y) by common metamorphic and igneous fluids, and the formation of porous textures and various secondary phases, are dependent on the P–T–X conditions (Hetherington et al., 2010; Harlov et al., 2011; Harlov and Wirth, 2012; Budzyni et al., 2011, 2017), as well as on the presence of low-T metamorphic or post-magmatic hydrothermal fluids in granitic systems (Budzyni and Kozub-Budzyni, 2015).

In this investigation, partially-decomposed primary magmatic monazite-(Ce) and xenotime-(Y) in mylonitised metagranites from the Variscan basement of the Fabova Hoľa granitic complex in the Veporic Unit, Central Slovakia are reported and interpreted (Fig. 1). Whereas retrograde destabilisation of monazite-(Ce) and remobilisation of light rare earth elements (LREE) results in an impressive corona of fluorapatite ± Th-silicate–allanite–(Ce)–clinzoisite, decomposition of xenotime-(Y) results in a novel type of reaction corona, including fluorapatite, hellandite-(Y) and hingganite-(Y) mineral zones, involving heavy rare earth elements (HREE) + Y, and also B and Be mobility. In this investigation, textural and compositional data, X-ray mapping, Th–U–total Pb age determination of monazite-(Ce) and Raman spectra all contribute to understanding the stability and breakdown products of REE, B and Be accessory minerals, their evolution, and behaviour during fluid-driven processes. Consequently, we describe a possible scenario regarding their origin and fluid sources responsible for their alteration. Moreover, the unusual Y–B–Be silicate reaction corona minerals, hellandite and hingganite, around xenotime-(Y) are documented for the first time.

**Geological setting**

**Regional geology**

The Variscan basement structure of the Western Carpathians is composed of several structural units that are recognisable, even though there has been Alpine, mainly Cretaceous, tectono-metamorphic overprinting (Putiš, 1992). The Alpine structure of the Inner Western Carpathians is related to the evolution of the Cretaceous collisional wedge. The south–north progradation of this wedge has been dated between ca. 130 and 50 Ma according to ⁴⁰Ar–³⁹Ar radiometric age determination of phengitic white mica and muscovite from the thrust-fault shear zones (Putiš et al., 2009b).

The REE accessory minerals investigated occur in mylonitised granites of the Variscan basement, which are included in the Late Cretaceous Veporic Unit of the Inner Western Carpathians (e.g. Plašienka et al., 1997). Calc-alkaline tonalites to granites of I/S-type affinity intruded into the Early Palaeozoic crystalline basement complex of paragneisses, granitic orthogneisses, amphibolites, rare eclogites, calc-silicate marbles and migmatites of the Upper Variscan structural Unit or the Tatra Nappe (Putiš 1992; Bezák 1994; Putiš et al., 2003, 2008, 2009b; Janák et al., 2007). Recent in situ U–Pb radiometric age determination in zircon indicates that their meso–Variscan, Upper Devonian to Carboniferous age interval of emplacement was ~365–350 Ma (Gaab et al., 2005; Broska et al., 2013; Kohút and Larionov 2021).

Granitic rocks also occur in the form of individual small intrusions crosscutting the basement rocks (Ondrejka et al., 2021 and references therein). Similarly, dykes of Permian acidic-to-basic volcanic rocks, together with microgranites, intruded the crustal basement rocks, or occur as intercalations within the Permian sedimentary successions (Kotov et al., 1996; Vozárová et al., 2016). These are covered by Triassic metaquartzites, marbles and calc-schists of the sedimentary cover (Foedera Group) of the Veporic Unit crystalline basement (Plašienka et al., 1997).

Intrusions and lava flows of Miocene calc-alkaline diorites and andesites (~12 Ma; Konečný et al., 2015a, 2015b) belong to the youngest Neo-Alpine magmatic event in the part of the Veporic Unit studied. They also intruded the Variscan granitic rocks of the Fabova Hoľa Massif. These plutonic and volcanic rocks originated as a consequence of subduction of the Outer Western Carpathian basement underneath the Inner Western Carpathians (Pécskay et al., 2006; Lexa et al., 2010).

**Petrographic characterisation of the metagranitic rocks**

The Veporic crystalline basement south of the Late Cretaceous Pohoreľa tectonic line consists mostly of metagranitoids (tonalites, granodiorites and porphyric-to-homogeneous granites) of the meso–Variscan Vepor pluton (Kohút et al., 2008). Relics of magmatic minerals, such as quartz, plagioclase, K-feldspar, biotite, muscovite, fluorapatite, zircon and REE accessory minerals occur in the newly formed or recrystallised mineral assemblage of quartz, albite, Ti-poor biotite, celadonite-rich muscovite (‘phengite’), chlorite, epidote, clinzoisite, calcite, titanite, rutile, and several tiny euhedral garnets that define the mylonitic foliation (Putiš, 1994). The lineation of the mylonitic foliation is defined by newly formed biotite, chlorite, and sericitic phengite in a roughly E–W (to NW–ESE) direction. There are common transitions from granitic and tonalitic protomylonites to augen granite–gneisses (mylonites) and phyllonites (blasto(mylonites). These micro-structures indicate the ductile behaviour of quartz
and the semi-ductile behaviour of feldspars in the mylonites. They reflect mostly the last top-to-the E(ESE) extensional deformation along the ductile low-angle normal faults in the basement and cover rocks during post-metamorphic exhumation (Putiš, 1994).

The mylonitisation processes had an isochemical-to-allochemical character with increasing deformation in two different stages. The first stage of deformation, which was the transition from protomylonite to mylonite, usually is of an isochemical character, with restricted chemical changes. During the second stage, which was the transition from mylonite to ultramylonite/blastomylonite, local deformation occurred with the loss of Ca and Na and the gain of K, Mg (± Fe) in the mylonite/blastomylonite due to higher ductile strain localisation and increased fluid activity. The most immobile elements appear to be Si, Ti and Al (Putiš et al., 1997a).

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The basement mylonites reflect deformational conditions of ∼400–500°C at depths of 20–25 km (Putiš et al., 1994; Putiš et al., 1997a, 1997b). The exhumation age of the granitoid rocks has been determined from the newly formed phengite at ∼100–85 Ma (Maluski et al., 1993; Dallmeyer et al., 1993, 1996; Putiš et al., 2009b). Post-collisional exhumation is constrained by zircon fission track ages of 88 to 62 Ma from the Veporic tectonic units (Plašienka et al., 2007; Vojtko et al., 2016). The apatite fission track ages of 63–55 Ma and apatite (U–Th)/He ages of 62–31 Ma from the southern Veporic Unit (Vojtko et al., 2016) suggest the upper crustal level of the exhumation and cooling to temperatures below ca. 250°C (zircon fission tracks), 125°C (apatite fission tracks) or to ca. 70°C [apatite (U–Th)/He], respectively.

Analytical methods

The minerals were sampled from natural outcrops and investigated in polished thin sections of metagranites (15 rock samples). The petrography of the samples was investigated using a polarised optical microscope.

The composition of the minerals was determined by electron probe microanalysis (EPMA) in wavelength-dispersive spectrometry (WDS) mode and X-ray elemental mapping, using a JEOL JXA–8530 F field emission electron microprobe at the Earth Science Institute of the Slovak Academy of Sciences in Banská Bystrica, Slovakia. An accelerating voltage of 15 kV and a...
beam current of 40–20 nA was used with other relevant analytical conditions chosen according to the mineral type. The typical spot beam diameter varied from 2 to 8 µm; a more focused ≤1–3 µm beam was used for some Y–B–Be silicates, and occasionally for secondary and heterogeneous fluorapatite. The EPMA was calibrated using natural and synthetic standards (Supplementary table S1), and raw counts were converted to wt.% of oxides using a full ZAF matrix correction. Corrections of line interferences for Nd→Ce, Eu→Nd, Eu→Pr, Gd→Ho, Tm→Sm, Nd→Ce, Lu→Dy, Lu→Ho, U→Th, K→U and V→Ti followed Åmli and Griffin (1975). Element amounts of <0.01 wt.% are below the detection limit.

Monazite Th–U–total Pb age determination was performed using a Cameca SX–100 microprobe at the State Geological Institute of Dionýz Štúr in Bratislava. Operating conditions consisted of 15 kV accelerating voltage, 180 nA beam current and a 3 µm beam diameter. The PAP matrix correction factors were used (Supplementary table S1). Analytical lines free of overlap were selected preferentially. Mutual interferences among the REE were corrected using empirical correction factors. The PbLα line is overlapped by LaLα, LaLγ, LaLβ, ThLα, ThLβ, ThLγ, ThLβ→Lγ, ThLγ→Lβ, YLα, YLβ, YLγ lines. The weak interference by the LaLα line is overlapped by LaLα, LaLγ, LaLβ, ThLα, ThLβ, ThLγ, ThLβ→Lγ, ThLγ→Lβ, YLα, YLβ, YLγ lines. The weak interference by the LaLα line was ignored. The UMB line is overlapped by NdLα, NdLβ, NdLγ, NdLβ→Lγ, NdLγ→Lβ, TbLα, TbLβ, TbLγ, TbLβ→Lγ, TbLγ→Lβ, YbLα, YbLβ, YbLγ, YbLβ→Lγ, YbLγ→Lβ lines.

Further details and description of the age determination procedure (MARCS) can be found in Konečný et al. (2018).

Raman analysis was performed with a Horiba Jobin-Yvon LabRAB-HR 800 spectrometer in the Earth Science Institute of the Slovak Academy of Sciences, Banská Bystrica, Slovakia. The spectrometer is equipped with a Czerny-Turner monochromator with a 600 gr/mm grating and a Peltier-cooled Synapse CCD detector. The operating conditions consisted of 10–25 acquisitions that lasted 600 s or 1000 s per spectral window and processed using LabSpec 5 (Horiba) and PeakFit11 software packages (PeakFit11 Software Inc.). The Raman spectra were also obtained using a Thermo Scientific DXR3xi Raman Imaging microscope at the Slovak Natural History Museum, Bratislava. Several lasers were used during the investigation, mainly a 532 nm doubled Nd: YVO4 DPSS excitation laser, a 1064 nm laser, 100 × objective, a 25 µm collection pinhole and an EMCCD detector. Approximately 80 spectra were acquired from the mineral phases investigated at a laser power of 10–20 mW for between 0.5 and 2 s (20 scans for a cycle). The processing of spectra (including fitting by Voigt functions) was carried out using the Thermo Fisher Scientific OMNIC v. 9.11 software package.

Sample description and accessory mineral assemblage

We investigated 15 polished thin sections of mylonitised metagranitic rocks from the Fabova Hola Massif Vepor pluton, in the Slovak Ore Mountains (Veporick Unit). They usually contain accessory monazite-(Ce) with secondary reaction coronae of fluorapatite + allanite-(Ce) to epidote or clinozoisite. However, sample FAH-3 also contains accessory xenotime-(Y) with different, newly described fluorapatite + ellanite-(Y) + hingganite-(Y) reaction coronae. This sample is described in detail. FAH-3 was collected from a small, natural outcrop in the Hronec valley, ~500 m south from the Klátne gamekeeper’s lodge on the western slope of Klátne Grúň hill, (48°47′41″N 19°56′26″E).

The rock studied (FAH-3) represents a foliated blastomylonitised porphyric metagranite. The texture is grano-lepidoblastic with blastomylonitic foliation. The primary magmatic minerals include quartz-1, plagioclase, K-feldspar, biotite-1 and muscovite-1, with accessory zircon, fluorapatite, monazite-(Ce), xenotime-(Y) and Fe–Ti oxides (ilmenite–magnetite). In addition, FAH-3 contains a newly-formed and recrystallised mineral assemblage, which includes quartz-2, albite, phengitic muscovite, epidote to clinozoisite, Ti-depleted biotite-2 and muscovite-2.

Quartz-1 forms anhedral crystals with distinct undulatory extinction and is rimmed by fine-grained aggregates of recrystallised quartz-2. Subhedral plagioclase (oligoclase with An25–14) is replaced extensively by fine-crystalline white mica aggregates (sericitisation) and irregular rim zones of secondary albite (~An0). White-to-grey K-feldspar (98 mol.% orthoclase/microcline, 2 mol.% albite, 1 mol.% celsian on average) forms large euhedral phenocrysts (up to 4 cm in size) locally, with Carlsbad twinning and inclusions of plagioclase and biotite-1. Biotite-1 has an anhite–dominant composition [Fe/(Fe + Mg) = 0.55–0.57;
Primary fluorapatite (apatite-1) and zircon are the dominant accessory phases. Apatite-1 forms large, scattered euhedral-to-subhedral crystals up to 300 μm in size and associated with moderately chloritised biotite, quartz, albite and K-feldspar, together with accessory monazite-(Ce), xenotime-(Y) and their breakdown products. Zircon forms large euhedral prismatic crystals up to 300 μm in size (occasionally up to 500 μm), usually in association with apatite-1 and enclosed in biotite-1. Zircon has regular, magmatic oscillatory zoning, rare inherited xenocrystic cores and locally present inclusions of thorite and coffinite.

Representative whole-rock compositions are in Table 1. In general, the granites investigated have high SiO₂ (67–75 wt.%), Al₂O₃ (14–17 wt.%) and Na₂O + K₂O – CaO (4–8 wt.%) values and low, but varying TiO₂ (0.05–0.5 wt.%), and P₂O₅ (0.04–0.2 wt.%) values, together with moderate FeO_oxi/(FeO_oxi + MgO) (0.70–0.79). Their A/CNK and A/NK ratios range from 1.0 to 1.2 and 1.2 to 1.6, respectively, corresponding to a peraluminous composition. Trace-element geochemistry shows enrichment in Ba (390 to 1180 ppm) and Sr (230 to 400 ppm), as well as varying REE+Y, Th and U contents. The concentration of light elements also shows enrichment, especially in B (~15 to 20 ppm; Marsina et al., 1999) and Be (2 to 4 ppm). In general, they show a S-type or hybrid S/I-type affinity and are characterised by calc-alkaline compositions and low contents of Mg, Ca, Sr, Ba, Zr and REE when compared with I-type granites (cf. Broska and Uher, 2001; Broska et al., 2004).

Minerals of the reaction coronae

Fluorapatite–allanite-(Ce)–clinozoisite corona around monazite-(Ce)

The primary magmatic monazite-(Ce) is a relatively abundant accessory mineral of the FAH-3 metagranite sample. It is distributed equally throughout the host metagranite, and it is usually enclosed in chloritised biotite-1 or albite, with the association of zircon and apatite-1. Close overgrowths and intergrowths of primary monazite-(Ce) with apatite-1 are common. The monazite is mostly preserved as partly-dissolved relics up to 200 μm in size (occasionally up to 500 μm), usually in association with apatite-2 and enclosed in biotite-1. Zircon forms subhedral, distinctly foliated cores and locally present inclusions of thorite and coffinite. The secondary epidote-group minerals have a large variation in REE+Y, Th and U contents (2.24 wt.% SiO₂, 0.2 apfu Si) suit the presence of Th-silicate nano-inclusions.

Secondary epidote-group minerals have a large variation in REE+Y and Th (0.02–1.00 apfu) and total AI values (1.57–2.47 apfu), thus indicating that varying amounts of allanite–ferriallanite and clinozoisite–epidote solid-solution components are present (Table 2). In general, clinozoisite has Fe³⁺ enrichment in the M3 position and a lower AI content, which indicates a significant epidote component. In general, the composition of the epidote-group minerals solid solution is controlled by a dominant A²REE + M³Fe²⁺ ↔ A³⁺Ca + M³(Fe, Al)³⁺ substitution mechanism.

Fluorapatite–hellandite-(Y)–hingganite-(Y) corona around xenotime-(Y)

Primary xenotime-(Y) is a relatively scarce, accessory mineral, but, when present, it always occurs as solitary crystals that are >100 μm in size in albite or biotite and surrounded by a secondary reaction corona. The reaction coronae around the primary xenotime-(Y) has an inner zone of typically highly-porous secondary fluorapatite (apatite-2b), which is analogous to the monazite coronae, though differs distinctly in the REE minerals of the outer zone. This novel type of secondary reaction micro-texture consists of Y–B–Be silicate minerals instead of the expected allanite-(Y) and/or HREE+Y-rich epidote. These Y–B–Be phases are represented by hingganite-(Y) [(Ca₆REE₃Y₂Fe₄Si₂O₁₀(OH)₂] and hingganite-(Y) [Y₂Fe₂Si₂O₆(OH)₂]. Both minerals occur as numerous tiny anhedral to subhedral satellite crystals and/or chain-like aggregates and intergrowths (usually ~1–5 μm, occasionally ≤10 μm in size) positioned between the apatite-2 and the clinozoisite zone (Fig. 2e–h). The presence of these minerals is also confirmed by X-ray compositional mapping, including B (Fig. 5) and Raman spectra (see section on Raman spectroscopy).
Fig. 2. Back-scattered electron (BSE) images of a mylonitised metagranite and coronae around REE accessory phosphate minerals. (a) An assemblage of rock-forming minerals including quartz-1 (Qz 1), biotite-1 (Bt 1) to chlorite (Chl), feldspars (Fs), locally replaced by fine-crystalline white mica and clinozoisite (Czo). Accessory minerals are apatite-1 (Ap 1), zircon (Zrn) and monazite-(Ce) (Mnz). (b) Typical retrograde corona around monazite-(Ce) (Mnz) surrounded by polygonal apatite-2a (Ap 2a) + bright huttonite inclusions (Ht) and epitaxial intergrowths of allanite-(Ce) (Aln) to clinozoisite (Czo) in biotite-1 (Bt 1). (c) Lopsided corona with an asymmetric tail of allanite-(Ce)-clinozoisite (Aln-Czo) trailing outwards from the monazite-(Ce) (Mnz) in close association with apatite-1 (Ap 1). The other secondary minerals are apatite-2a (Ap 2a) and titanite (Ttn). The host rock-forming minerals are biotite-1 (Bt 1) to chlorite (Chl). (d) A tiny collar of allanite-(Ce) + monazite-(Ce) relics outlining the euhedral habit of the former intergrown apatite-1 (Ap 1) and monazite-(Ce) (Mnz). The other secondary minerals are apatite-2a (Ap 2a) + Th-silicate huttonite (Ht) and clinozoisite (Czo). The host rock-forming mineral is biotite-1 (Bt 1). (e) Secondary corona with preserved xenotime-(Y) relic (Xtm) in the central part surrounded
analyses shows a HREE>LREE slope \( \text{LaN/YbN} = 0.001 \) (Fig. 3). The relatively low, though homogeneous, distribution of B is confirmed by X-ray compositional mapping (Fig. 5). This systematic presence of B together with a slightly increased signal of Nb + Ta in xenotermite-(Y), indicates the possible, but very limited schiavinatoite \( \text{[NbBO}_{4}\text{]}^{\text{2}} \) + behierite \( \text{[TaBO}_{4}\text{]} \) substitution mechanism: \( \text{[Nb,Ta} \text{BY)} \text{[O}_{\text{8}}\text{]} \) in the hingganite-(Y) composition (Table 4) shows a dominance of Y (26.7–33.4 wt.% \( \text{Y}_{\text{2}}\text{O}_{3} \)) over other HREE compositions and a higher HREE\(_{2}\text{O}_{3}\) and an especially higher Y\(_{2}\text{O}_{3}\) content (average value 0.80 wt.; 0.03 apfu HREE + Y), although the LREE content is below the EPMA detection limit. In contrast, the measured concentrations of Th and U in apatite-2b are lower than apatite-2a, with \( \leq 0.5 \) wt.% (Th, U)\(_{2}\text{O}_{3} \) (\( \leq 0.01 \) apfu Th and U) (Table 2).

The hingganite-(Y) compositions (Table 4) show a predominance of Y (22.9–27.8 wt.% \( \text{Y}_{2}\text{O}_{3} \)) over other HREE compositions (1.5–19.5 wt.% \( \text{REE}_{2}\text{O}_{3} \)); 0.92 apfu REE) and have an atomic ratio of Y/(Y + REE) = 0.70–0.81. Among the REE, hingganite-(Y) has HREE>LREE, which is also visible in the – ratio of Y/(Y + REE) = 0.70 (Fig. 3). Additionally, Ca is the other significant cation at the A site (4.5–10.6 wt.% \( \text{CaO} \); 0.36–0.79 apfu Ca), which indicates the significant presence of datolite \( \text{[Ca}_{2}\text{B}_{3}\text{Si}_{2}\text{O}_{8}\text{(OH)}_{2}] \) and homilite \( \text{[Ca} \text{P}_{2}\text{B}_{2}\text{Si}_{2}\text{O}_{8}\text{]} \) molecules (Fig. 7). Hingganite-(Y) has a dominant vacancy (0.49–0.65 pfu) over the M site cations, especially the Fe content, which is markedly low (5.5–7.8 wt.% \( \text{FeO} \); 0.34–0.50 apfu Fe) with a Fe/(Fe + vacancy) atomic ratio of 0.34–0.51. Conversely, hingganite-(Y) has a negligible and usually zero Al content at the M site, thereby indicating a strong Al and Fe distinction between hingganite-(Y) and xenotermite-(Y). Whereas hingganite-(Y) has an almost constant B content (cf. Oberti et al., 2002; Miyawaki et al., 2015), the B concentration in hingganite-(Y) from the Fabova Hola metagranite is controlled by the datolite \( \text{CaB(REE)}_{2}\text{B}_{1}\text{Fe}_{1} \); substitution with \( \text{B/(B} + \text{Be)}_{\text{calc}} = 0.0–0.38 \). It has an intermediate solid solution between the Be-dominant \([\text{hingganite-(Y)–gadolinite-(Y)}]\), and B-dominant (homilite, datolite) end-members of the gadolinite-group minerals.

### Raman spectra of hingganite-(Y) and xenotermite-(Y)

The presence of B- and Be-bearing silicate phases in the breakdown products was determined from their Raman spectra. The Raman spectra of the hingganite-(Y) can be divided into several regions with relatively intensive bands and these vary due to different crystal orientations (Fig. 8a). In the region between 100 and 400 cm\(^{-1}\), the most prominent peaks are at 189 cm\(^{-1}\) (with a peak on the shoulder at 153 cm\(^{-1}\)) and 324 cm\(^{-1}\). The region of 400 to 800 cm\(^{-1}\) includes several overlapping, less-intensive bands with two prominent peaks at 453 and 639 cm\(^{-1}\). The third most intensive peak, together with 189 and 639 cm\(^{-1}\), is located at 917 cm\(^{-1}\) with two shoulder peaks at 969 and 998 cm\(^{-1}\). In the high-frequency region, there is a sharp peak at 3546 cm\(^{-1}\) located on the broad band spreading between 3100 and 4000 cm\(^{-1}\). All \( \mu \)-Raman depolarised spectra of randomly oriented hingganite-(Y) crystals (FAH-3) correspond to their minor compositional variations. In the low-frequency region (200–1000 cm\(^{-1}\)), the spectra show numerous peaks superimposed on an increased background luminescence. The most dominant features are in the regions of 250–370, 500–550, and 560–750 cm\(^{-1}\) (Fig. 8b–d), in addition to the complexes of numerous, less-intensive bands. Two relatively sharp peaks at 3454 and 3662 cm\(^{-1}\) located on top of the broad band are present in the high-frequency region (Fig. 8d).

### Table 1. Whole-rock compositions of the Fabova Hola metagranate (sample FAH-3).

| Sample | FAH-3 |
|--------|--------|
| \( \text{SiO}_{2} \) (wt. %) | 69.91 |
| \( \text{TiO}_{2} \) | 0.40 |
| \( \text{Al}_{2}\text{O}_{3} \) | 15.54 |
| \( \text{FeO}_{\text{tot}} \) | 2.29 |
| \( \text{MnO} \) | 0.06 |
| \( \text{CaO} \) | 0.95 |
| \( \text{Na}_{2}\text{O} \) | 1.78 |
| \( \text{K}_{2}\text{O} \) | 4.27 |
| \( \text{P}_{2}\text{O}_{5} \) | 3.38 |
| \( \text{L}_{2}\text{O}_{3} \) | 0.90 |
| \( \text{Total} \) | 99.63 |
| \( \text{Be} (\text{ppm}) \) | 1.12 |
| \( \text{Co} \) | 1.45 |
| \( \text{Ga} \) | 21 |
| \( \text{MgO} \) | 0.95 |
| \( \text{MnO} \) | 1.69 |
| \( \text{Na}_{2}\text{O} \) | 1.78 |
| \( \text{K}_{2}\text{O} \) | 4.27 |
| \( \text{P}_{2}\text{O}_{5} \) | 3.38 |
| \( \text{L}_{2}\text{O}_{3} \) | 0.90 |
| \( \text{Total} \) | 99.63 |
| \( \text{Nb} \) | 10.1 |
| \( \text{U} \) | 0.79 |
| \( \text{Y} \) | 2.98 |
| \( \text{Zn} \) | 49 |
| \( \text{Zr} \) | 1.7 |
| \( \text{La} \) | 33 |
| \( \text{Nd} \) | 2.9 |
| \( \text{Tb} \) | 0.58 |
| \( \text{Yb} \) | 1.12 |
| \( \text{Lu} \) | 0.16 |

* Boron content from Marsina et al. (1999).
Table 2. Representative EPMA compositions of monazite-(Ce), xenotime-(Y), fluorapatite and epidote-group minerals (in wt.% and apfu). Abbreviations are as follows: monazite-(Ce) (Mnz), xenotime-(Y) (Xtm), fluorapatite (Ap), allanite-(Ce) (Aln), epidote (Ep), clinzoisite (Czo).

| Mnz | Mnz | Xtm | Xtm | Ap 2a | Ap 2a | Ap 2b | Ap 2b | Aln | Ep | Czo |
|-----|-----|-----|-----|-------|-------|-------|-------|-----|----|-----|
| Wt.% | | | | | | | | | | |
| SO₃ | 0.03 | 0.04 | 0.00 | 0.00 | 0.01 | 0.01 | 0.00 | 0.01 | SiO₂ | 30.66 | 36.91 | 38.80 |
| P₂O₅ | 29.72 | 28.73 | 35.31 | 34.80 | 40.78 | 41.13 | 41.57 | 40.95 | TiO₂ | 0.41 | 2.44 | 0.15 |
| As₂O₅ | 0.18 | 0.00 | 0.01 | 0.05 | 0.00 | 0.06 | 0.02 | 0.00 | ThO₂ | 0.25 | 0.00 | 0.01 |
| Na₂O | n.a. | n.a. | 0.04 | 0.03 | n.a. | n.a. | n.a. | n.a. | UO₂ | 0.01 | 0.00 | 0.00 |
| Ta₂O₅ | n.a. | n.a. | 0.00 | 0.00 | n.a. | n.a. | n.a. | n.a. | Al₂O₃ | 15.99 | 19.83 | 26.82 |
| SiO₂ | 0.42 | 0.78 | 0.32 | 0.56 | 0.42 | 0.52 | 0.51 | 0.38 | Y₂O₃ | 0.00 | 0.09 | 0.04 |
| Th₂O₅ | 4.01 | 8.39 | 0.10 | 0.69 | 0.62 | 0.01 | 0.08 | 0.14 | La₂O₃ | 6.44 | 0.16 | 0.02 |
| UO₂ | 0.11 | 0.70 | 1.75 | 1.37 | 0.01 | 0.04 | 0.03 | 0.07 | CeO₂ | 12.81 | 0.32 | 0.05 |
| Al₂O₃ | 0.00 | 0.00 | 0.00 | n.a. | n.a. | n.a. | n.a. | n.a. | PrO₂ | 1.20 | 0.15 | 0.10 |
| Y₂O₃ | 1.05 | 2.98 | 42.95 | 43.13 | 0.11 | 0.49 | 0.71 | 0.50 | Nd₂O₃ | 4.63 | 0.21 | 0.05 |
| La₂O₃ | 13.79 | 19.55 | 0.01 | 0.02 | 0.68 | 0.04 | n.a. | n.a. | SmO₂ | 0.44 | 0.07 | 0.02 |
| CeO₂ | 29.10 | 24.08 | 0.09 | 0.05 | 1.47 | 0.21 | n.a. | n.a. | EuO₂ | 0.26 | 0.39 | 0.27 |
| PrO₂ | 3.34 | 3.11 | 0.01 | 0.03 | 0.09 | 0.12 | n.a. | n.a. | GdO₂ | 0.11 | 0.10 | 0.08 |
| Nd₂O₃ | 12.85 | 11.73 | 27.7 | 0.46 | 0.75 | 0.22 | n.a. | n.a. | TbO₂ | 0.00 | 0.03 | 0.04 |
| Sm₂O₃ | 2.05 | 2.92 | 0.56 | 0.10 | 0.06 | 0.08 | 0.03 | DyO₂ | 0.00 | 0.03 | 0.02 |
| Eu₂O₃ | 0.09 | 0.12 | 0.02 | 0.01 | n.a. | n.a. | n.a. | n.a. | Ho₂O₃ | 0.05 | 0.00 | 0.00 |
| Gd₂O₃ | 1.18 | 1.84 | 1.35 | 1.61 | 1.12 | 0.07 | 0.00 | 0.17 | Er₂O₃ | 0.00 | 0.19 | 0.15 |
| Tb₂O₃ | 0.07 | 0.20 | 0.57 | 0.57 | n.a. | 0.09 | 0.00 | 0.00 | Tm₂O₃ | 0.01 | 0.04 | 0.04 |
| Dy₂O₃ | 0.34 | 0.81 | 5.41 | 5.61 | n.a. | 0.11 | 0.10 | 0.11 | Yb₂O₃ | 0.05 | 0.06 | 0.05 |
| Ho₂O₃ | 0.04 | 0.05 | 1.06 | 1.15 | n.a. | 0.00 | 0.00 | 0.00 | Lu₂O₃ | 0.01 | 0.07 | 0.00 |
| Er₂O₃ | 0.33 | 0.45 | 3.77 | 3.98 | n.a. | 0.28 | 0.07 | 0.05 | Fe₂O₃ | 2.52 | 12.28 | 7.75 |
| Tm₂O₃ | 0.11 | 0.12 | 0.75 | 0.67 | n.a. | 0.02 | n.a. | n.a. | FeO | 10.53 | 2.19 | 0.74 |
| Yb₂O₃ | 0.10 | 1.64 | 3.47 | 3.05 | n.a. | 0.06 | 0.09 | 0.06 | MgO | 0.15 | 0.00 | 0.00 |
| Lu₂O₃ | 0.07 | 0.14 | 1.09 | 0.97 | n.a. | 0.02 | 0.05 | 0.09 | SmO₂ | 0.27 | 0.27 | 0.20 |
| FeO | 0.04 | 0.00 | 0.20 | 0.23 | 0.59 | 0.49 | 0.25 | 0.45 | Pbo | 0.04 | 0.00 | 0.00 |
| MnO | n.a. | n.a. | n.a. | n.a. | 0.04 | 0.12 | 0.00 | 0.00 | BaO | 0.00 | 0.01 | 0.01 |
| PbO | 0.07 | 0.16 | 0.12 | 0.09 | 0.02 | 0.00 | 0.01 | 0.05 | SrO | 0.00 | 0.43 | 0.22 |
| BaO | n.a. | n.a. | n.a. | n.a. | 0.00 | 0.00 | 0.04 | 0.08 | CaO | 10.73 | 22.55 | 23.28 |
| SrO | 0.01 | 0.03 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | Na₂O | 0.00 | 0.00 | 0.00 |
| CaO | 0.91 | 1.44 | 0.33 | 0.36 | 51.53 | 53.71 | 54.18 | 53.68 | F | 0.16 | 0.00 | 0.00 |
| Na₂O | n.a. | n.a. | n.a. | n.a. | 0.02 | 0.05 | 0.00 | 0.01 | Cl | 0.00 | 0.01 | 0.01 |
| F | n.a. | n.a. | n.a. | n.a. | 3.51 | 3.68 | 3.72 | 3.65 | O<F | -0.08 | 0.00 | 0.00 |
| Cl | n.a. | n.a. | n.a. | n.a. | 0.02 | 0.02 | 0.02 | 0.02 | O<Cl | 0.00 | 0.00 | 0.00 |
| O=F | - | - | - | - | -1.48 | -1.55 | -1.57 | -1.54 | H₂O | 1.54 | 1.85 | 1.92 |
| O<Cl | - | - | - | - | - | - | - | - | Total | 99.18 | 100.65 | 100.86 |
| H₂O* | - | - | - | - | 0.05 | 0.02 | 0.00 | 0.02 | Total | 99.48 | 99.93 | 99.96 |
| Total | 100.01 | 99.45 | 99.20 | 99.26 | 99.80 | 99.80 | 99.96 | 99.88 | | | |

(Continued)
Table 2. (Continued.)

|       | Mnz | Mnz | Xtm | Xtm | Ap 2a | Ap 2a | Ap 2b | Ap 2b | Eu³⁺ | Aln | Ep | Czo |
|-------|-----|-----|-----|-----|-------|-------|-------|-------|-------|-----|----|-----|
| Pb³⁺  | 0.001 | 0.002 | 0.001 | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.009 | 0.011 | 0.007 |
| Ba³⁺  | -    | -    | -    | -    | 0.000 | 0.000 | 0.001 | 0.003 | 0.003 | 0.003 | 0.003 | 0.002 |
| Sr²⁺  | 0.000 | 0.001 | 0.000 | 0.000 | 0.000 | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 | 0.001 | 0.001 |
| Ca²⁺  | 0.038 | 0.061 | 0.012 | 0.013 | 4.830 | 4.884 | 4.936 | 4.921 | Dy³⁺ | 0.000 | 0.001 | 0.001 |
| Na⁺   | -    | -    | -    | -    | 0.003 | 0.009 | 0.000 | 0.002 | 0.001 | 0.000 | 0.000 |
| ΣB, ΣM | 0.998 | 1.012 | 0.993 | 1.001 | 5.000 | 5.000 | 5.000 | 5.000 | Er³⁺ | 0.000 | 0.005 | 0.004 |
| OH⁻   | 917  | -    | -    | -    | 0.028 | 0.010 | 0.000 | 0.010 | 0.000 | 0.000 | 0.000 | 0.000 |
| F⁻    | -    | -    | -    | -    | 0.972 | 0.988 | 1.000 | 0.988 | Yb³⁺ | 0.001 | 0.002 | 0.001 |
| Cl⁻   | -    | -    | -    | -    | 0.002 | 0.002 | 0.002 | 0.002 | Lu³⁺ | 0.000 | 0.002 | 0.000 |
| ΣX    | -    | -    | -    | -    | 1.000 | 1.000 | 1.003 | 1.000 | Pb⁴⁺ | 0.001 | 0.000 | 0.000 |
| X_{hit} | 0.017 | 0.031 | -    | -    | -    | -    | -    | -    | Ba³⁺ | 0.000 | 0.000 | 0.000 |
| X_{chrl} | 0.058 | 0.111 | -    | -    | -    | -    | -    | -    | Sr²⁺ | 0.000 | 0.020 | 0.010 |
| X_{mnz} | 0.925 | 0.859 | -    | -    | -    | -    | -    | -    | Ca³⁺ | 0.122 | 0.962 | 0.953 |
|        |       |       |       |       |       |       |       |       |       |       |       |       |

*H₂O contents calculated on the basis of ideal stoichiometry. n.a. = not analysed, - = not calculated. 0.00 wt.% values indicate below the detection limit.

Discussion and conclusions

Raman spectra interpretation

Raman spectra of the investigated hingganite-(Y) were interpreted in context with published data, including that of isostructural datolite and gadolinite (Frost et al., 2013; Goryainov et al., 2015; Thomas and Davidson, 2017; Škoda et al., 2018; Paulmann et al., 2019; Gorelova et al., 2020; Tomašić et al., 2020) and were also compared with spectra of macroscopic gadolinite samples. Škoda et al. (2018) assigned bands in the region of 200–750 cm⁻¹ to bending modes of Si–O and Be–O, stretching vibrations of REE–O and Fe–O, as well as to lattice vibrations. According to Hofmeister et al. (1987), modes below 350 cm⁻¹ in silicates are generally considered to be translations. The Raman band at 3546 cm⁻¹ is attributed to stretching vibrations of OH⁻ units in the mineral structure (Fig. 8a).

Part of the bands in the region from 450 cm⁻¹ to 650 cm⁻¹ could be assigned to bending vibrations of the layer formed by (SiO₄)₄⁻ and (BeO₄)₂⁻ tetrahedra and were also detected in the spectra of macroscopic samples (Gorelova et al., 2020). Raman peaks at 969 cm⁻¹ and 917 cm⁻¹ (in the range of 969–992 and 906–917 cm⁻¹ in the fitted spectra) are assigned to stretching vibrations of Si–O and Be–O in tetrahedral coordination (Škoda et al., 2018; Gorelova et al., 2020). The presence of a peak at 917 cm⁻¹ correlates well with the fitted spectra of the macroscopic gadolinite samples. Weak Raman bands in the range of 650–800 cm⁻¹ correspond to Be–O stretching vibrations (Hofmeister et al., 1987).

However, not all the bands can easily be attributed to known causes, according to the published data (Leite et al., 2001; Škoda et al., 2018; Gorelova et al., 2020). The Raman spectra of all the measured mineral phases, compositionally corresponding to hingganite-(Y), are essentially obscured by strong photoluminescence, as both broad and narrow bands. Even a minor lanthanoid content in the structure may cause intense luminescence (Panczer et al., 2012; Lenz et al., 2015; Gaft et al., 2005; de Bettencourt-Dias, 2014). Taking into consideration the concentrations of Gd, Dy, Eu, Yb, Lu and Tm (Table 4), there is a strong indication that some of features in the spectra are in fact photoluminescence bands. Some of these bands can be present in the range of 453–562 cm⁻¹ in the 532 nm spectrum of hingganite-(Y). If recalculated to wavelength, 540–550 nm bands could correspond to luminescence bands that were caused by the ⁴S₉/₂→⁴I₁₅/₂ electronic transition in Er³⁺ (Bodyl et al., 2009; de Bettencourt-Dias, 2014).

The presence of 3546 cm⁻¹ correlates well with the hingganite-(Y) composition, which contains the OH⁻ group located at the ⁵f₅ site, in contrast to gadolinite, which contains O at ⁵f₅ (Bačík et al., 2017). However, the peak is located on the top of the strong broad band (Fig. 8a), which was recalculated, considering that the 532 nm excitation has a centre at ca. 660 nm...
and therefore, can be interpreted as a luminescence band induced by the $^{5}F_{9/2} \rightarrow ^{7}H_{15/2-9/2}$ electronic transition in Dy$^{3+}$ (de Bettencourt-Dias, 2014).

The stacked spectra of hingganite-(Y) measured with 532 nm and 633 nm excitation show several overlapping peaks that might be attributed to Raman scattering. The shape and band intensities of individual spectra vary due to different crystal orientation. The position of the broad bands partly matches the spectrum of hingganite-(Ce) (RRUFF ID: R061013, Lafuente et al., 2015), where the tetrahedrally coordinated T site is vacant. The high number and broadening of the bands results from a varying composition. In the Raman spectra, as in the gadolinite-group minerals, stretching vibrations of REE-O and Fe-O and lattice vibrations are observed in the spectral region 200–750 cm$^{-1}$ (Leite et al., 2001; Škoda et al., 2018). The vibrations in the 320–600 cm$^{-1}$ region may be attributed to out-of-plane and in-plane bending vibrations of the (SiO$_4$)$^{3-}$ tetrahedron. Hofmeister et al. (1987) assigned the wavenumbers of the Si-O and Be-O vibrations in phenakite (Be$_2$SiO$_4$), which is a mineral with (SiO$_4$)$^{3-}$ and (BeO$_4$)$^{6-}$ tetrahedra and roughly analogous to the layers of tetrahedra in hellandite. The observed bands above 875 cm$^{-1}$ thus correspond to Si-O antisymmetric stretching vibrations. Raman bands at 780–810 cm$^{-1}$ and 768–778 cm$^{-1}$ may possibly relate to Si-O and Be-O stretching vibrations, respectively. The band intensity at 662 cm$^{-1}$ (in 633 nm excited spectrum) can be explained by photoluminescence of Dy$^{3+}$, which occurs in some minerals at ~660 nm (Gaft et al., 2005; de Bettencourt-Dias, 2014). This luminescence band results from the $^{5}F_{9/2} \rightarrow ^{7}H_{15/2-9/2}$ electronic transition in Dy$^{3+}$, similarly as in hingganite-(Y) (de Bettencourt-Dias, 2014). In the range of 2500–4000 cm$^{-1}$ spectra possess continuum background topology.

The strong broad band below the two intensive lines at 3454 cm$^{-1}$ and 3662 cm$^{-1}$ was only detected with 532 nm excitation. The relatively sharp bands could be attributed to OH$^{-}$ vibrations. Della Ventura et al. (2002) described spectral bands in this region as an expression of a wide variety of OH$^{-}$ environments due to local short-range disorder at the next-nearest-neighbour cation sites bonded to O5. However, the broad band with a position similar to the 532 nm spectrum of hingganite-(Y) can also result in the $^{5}F_{9/2} \rightarrow ^{7}H_{15/2-9/2}$ electronic transition in Dy$^{3+}$ (de Bettencourt-Dias, 2014).

On the basis of our interpretations, Er and Dy are the main sources of photoluminescence features in the spectra of both hingganite-(Y) and hellandite-(Y). This correlates perfectly with the chemical data. Erbium and Dy are the most abundant REE together with Gd and Yb. However, the most prominent photoluminescence band of Gd$^{3+}$ ($^{5}F_{7/2} \rightarrow ^{5}S_{7/2}$) is in the UV region around 315 nm, and the most emissive $^{5}F_{9/2} \rightarrow ^{5}H_{5/2}$ electronic transition of Yb$^{3+}$ manifests itself in the NIR region around 980 nm (de Bettencourt-Dias 2014). The ranges of measurement were 535 to 675 nm and 640 to 855 nm for the 532 and 633 nm excitations, respectively. The content of other REE with possible photoluminescence bands in the measured region (Pr, Sm, Eu, Tb, Ho and Tm; de Bettencourt-Dias, 2014) are lower, usually below 0.5 oxide wt.%. Therefore, these REE may contribute to the dominant photoluminescence features, or to an increase in the background, however they do not manifest in a resolvable photoluminescence band.

Crystal chemistry of contrasting coronae formation and breakdown reactions

The metamorphic-hydrothermal breakdown of monazite-(Ce) to the secondary fluorapatite–allanite-(Ce)–clinozoisite corona is a widely reported process in granitic, gneissic and metapelitic lithologies during post-magmatic cooling, or low- to high-grade prograde/retrograde metamorphic conditions (Broska and Siman, 1998; Finger et al., 1998, 2016; Broska et al., 2005; Majka and Budzyn, 2006; Petrík and Konečný, 2009; Ondrejka et al., 2012, 2016; Regis et al., 2012; Upadhay and Pruseth, 2012; Lo Pò et al., 2016; Hentschel et al., 2020). It has also been experimentally replicated (Budzyn et al., 2011, 2017). The analogous breakdown of xenotime-(Y) is not as common as monazite, but, when present, it usually results in similar corona structures, with an inner zone of fluorapatite (commonly HREE+Y-rich) and/or an outer zone of HREE-bearing epidote-group minerals, albeit in much smaller amounts (Broska et al., 2005; Majka and Budzyn, 2006; Janots et al., 2008; Broska and Petrík, 2015; Budzyn et al., 2018; Hentschel et al., 2020). Experiments involving xenotime-(Y) replacement indicate that the reaction products are roughly similar to those found in natural occurrences over a wide $P$–$T$ range, and reflect the relatively high mobilisation of HREE+Y into the apatite-supergroup minerals (fluorapatite, fluorcalcicbritholite) or epidote, which depends on the CaO/Na$_2$O ratio (Budzyn and Kozub-Budzyn, 2015; Budzyn et al., 2017). These experiments also suggest that the reactivity of xenotime-(Y) is temperature-dependent, and that the stability of xenotime-(Y) and HREE+Y-rich epidote is strongly controlled.
by pressure (Budzyń et al., 2017). These results suggest that xenotime-(Y) is more stable than monazite-(Ce) due to a lesser mobility of HREE+Y compared with LREE during low- to medium-grade metamorphism.

The effects of retrograde metamorphism during, and after, deformation on primary magmatic monazite-(Ce) and xenotime-(Y) are distinctive in the Fabova Hola metagranites. Similar corona reaction zones around monazite-(Ce) and
xenotime-(Y) usually suggest that they were most probably formed contemporaneously, and that the mechanism of their formation was similar (cf. Broska et al., 2005; Majka et al., 2011). In some cases, the fluorapatite–hingganite-(Y) coronae, as a product of fluid-induced breakdown of xenotime-(Y) and beryl, have been described from the Skoddefjellet pegmatite, Svalbard (Majka et al., 2011), whereas the partial replacement of xenotime-(Y) by hingganite-(Y) and Y-rich allanite-(Ce) was documented in the Pilawa Górna pegmatite, Poland (Budzyń et al., 2018). Alteration of primary monazite-(Ce) and xenotime-(Y) resulted in the formation of discrete grains of secondary hingganite-(Y) to hingganite-(Nd) in association with secondary Sr,S-rich monazite-(Ce) in the Bacúch metamorphic magnetite deposit, Veporic Unit, Slovakia (Pršek et al., 2010), only ∼13 km NW from the FAH-3 metagranite sample. All of these examples indicate a substantial supply of Be during the xenotime (± monazite) breakdown. However, in our example, the REE remobilisation during alteration of the primary monazite-(Ce) and xenotime-(Y) resulted in a slightly different secondary assemblage. Whereas LREE released from the altered monazite-(Ce) were transported through the apatite-2a zone and accumulated in an allanite-(Ce) zone, the HREE and Y from xenotime-(Y) were transported the same distance, though precipitated as hellandite-(Y) and hingganite-(Y) (Fig. 9). The reported corona assemblage, which includes Y–B–Be silicates and most notably hellandite-(Y), represents a new type of breakdown micro-texture with the involvement of light elements (B and Be) in the reaction, which have not been reported previously. The metamorphic/metasomatic replacement during blastomylonitisation including fluids rich in B and Be can be expressed by the following generalised reactions:

\[\text{Mnz} + (\text{Ca, Fe, Si, Al and Y})-\text{rich fluid} \rightarrow \text{FAp} + \text{Ht} + \text{Aln} + \text{Czo};\]

\[\text{Xtm} + (\text{Ca, Fe, Si, Al, F, B and Be})-\text{rich fluid} \rightarrow \text{FAp} + \text{Hld} + \text{Hin} + \text{Czo}.\]

Hellandite-(Y), which is a relatively rare borosilicate mineral, occurs mostly as a late-magmatic to hydrothermal mineral of

| Wt.% | FAH-3a | FAH-3j | Apfu |
|------|--------|--------|------|
| SiO₂ | 23.83  | 24.01  | 23.71 |
| TiO₂ | 0.24   | 0.26   | 0.02  |
| ThO₂ | 0.00   | 0.05   | 0.01  |
| UO₂  | 0.07   | 0.10   | 0.09  |
| B₂O₃* | 13.60 | 13.91  | 13.73 |
| Y₂O₃ | 26.63  | 26.56  | 26.81 |
| La₂O₃ | 0.03  | -      | 0.04  |
| Ce₂O₃ | 0.01  | 0.01   | 0.04  |
| Pr₂O₃ | -     | -      | 0.09  |
| Nd₂O₃ | 0.02  | 0.09   | 0.07  |
| Sm₂O₃ | -     | 0.05   | 0.19  |
| Eu₂O₃ | 0.00  | 0.00   | 0.00  |
| Gd₂O₃ | 1.99  | 1.94   | 1.90  |
| Tb₂O₃ | 0.04  | -      | -     |
| Dy₂O₃ | 2.60  | 2.59   | 2.33  |
| Ho₂O₃ | 0.23  | 0.35   | 0.15  |
| Er₂O₃ | 2.88  | 2.75   | 2.68  |
| Tm₂O₃ | 0.22  | 0.21   | 0.18  |
| Yb₂O₃ | 2.91  | 3.02   | 2.31  |
| Lu₂O₃ | 0.54  | 0.63   | 0.47  |
| Fe₂O₃ | 0.85  | 0.68   | 0.68  |
| Mn₂O₃** | 0.00 | 0.00   | 0.17  |
| MnO**  | 0.58  | 0.44   | 0.28  |
| CaO   | 15.93 | 15.94  | 16.46 |
| H₂O*** | 1.81  | 1.91   | 1.86  |
| Total | 99.86 | 100.32 | 99.12 |

*a₂O₃ content calculated on the basis of ideal stoichiometry ** The partition of total Mn between Mn³⁺ and Mn²⁺ was calculated from ideal stoichiometry and neutral charge balance. ***H₂O content calculated from charge balance. - = not analysed/calculated. 0.00 wt.% values indicate below the detection limit.

** Table 3. Representative compositions from EPMA of hellandite-(Y) (in wt.% and apfu).**
**Table 4.** Representative compositions from EPMA of hingganite-(Y) from the gadolinite group (in wt.% and apfu).

| Component | Wt.% 10 | Wt.% 11 | Wt.% 6 | Wt.% 7 | Apfu 10 | Apfu 11 | Apfu 6 | Apfu 7 |
|-----------|---------|---------|-------|-------|--------|--------|-------|-------|
| SiO₂      | 28.17   | 28.59   | 28.24 | 28.41 | 27.15  |        |       |       |
| TiO₂      | 0.15    | 0.21    | 0.18  | 0.27  | 0.02   |        |       |       |
| ThO₂      | 0.03    |         | 0.07  | 0.01  | 0.01   |        |       |       |
| UO₂       | 0.12    | 0.06    | 0.08  | 0.09  | 0.08   |        |       |       |
| B₂O₃⁺      | 4.87    | 5.96    | 3.59  | 6.02  | 2.63   |        |       |       |
| Al₂O₃      | 0.00    | 0.00    | 0.13  | 0.00  | 0.00   |        |       |       |
| Y₂O₃      | 27.78   | 26.69   | 28.69 | 27.41 | 32.16  |        |       |       |
| La₂O₃      | 0.04    |         |       |       |        |        |       |       |
| Ce₂O₃      | 0.02    | 0.06    |       |       | -0.04  |        |       |       |
| Pr₂O₃      | 0.06    |         |       |       | -0.09  |        |       |       |
| Nd₂O₃      | 0.01    | 0.10    | 0.03  | -0.19 |        |        |       |       |
| Sm₂O₃      | 0.03    | 0.19    | 0.01  | -0.18 |        |        |       |       |
| Eu₂O₃      | 0.07    | 0.02    | 0.05  | 0.03  | 0.03   |        |       |       |
| Gd₂O₃      | 2.24    | 2.32    | 2.19  | 1.93  | 3.53   |        |       |       |
| Tb₂O₃      | 0.00    | 0.10    |       |       | -0.19  |        |       |       |
| Dy₂O₃      | 3.09    | 2.90    | 2.82  | 2.32  | 4.24   |        |       |       |
| Ho₂O₃      | 0.58    | 0.30    | 0.35  | 0.38  | 0.37   |        |       |       |
| Er₂O₃      | 2.91    | 2.25    | 2.85  | 2.74  | 2.66   |        |       |       |
| Tm₂O₃      | 0.21    | 0.15    | 0.17  | 0.17  | 0.17   |        |       |       |
| Yb₂O₃      | 2.19    | 1.52    | 2.07  | 2.22  | 1.13   |        |       |       |
| Lu₂O₃      | 0.46    | 0.41    | 0.44  | 0.46  | 0.50   |        |       |       |
| BeO*       | 8.22    | 7.62    | 9.18  | 7.50  | 9.41   |        |       |       |
| FeO        | 7.84    | 7.17    | 6.69  | 6.27  | 6.92   |        |       |       |
| MgO        | 0.03    | 0.03    |       |       |        |        |       |       |
| MnO        | 0.04    | 0.11    | 0.04  | 0.05  | 0.01   |        |       |       |
| CaO        | 9.35    | 10.56   | 10.08 | 9.72  | 5.93   |        |       |       |
| F          | -       |         | 0.04  |       |        |        |       |       |
| F=O        | -       | -       | -0.02 |       |        |        |       |       |
| H₂O**      | 2.20    | 2.40    | 2.46  | 2.61  | 2.33   |        |       |       |
| Total      | 100.69  | 99.69   | 100.52| 98.61 | 99.86  |        |       |       |
| ΣHREE⁵⁺     | 39.68   | 37.00   | 39.76 | 37.66 | 45.38  |        |       |       |
| Σ(Tl,Be)O₂  | 0.15    | 0.06    | 0.16  | 0.10  | 0.08   |        |       |       |

*ΣB₂O₃ and BeO contents calculated from charge balance, **H₂O content calculated on the basis of ideal stoichiometry. - = not analysed/calculated. 0.00 wt.% values indicate below the detection limit.

NYF (Nb–Y–F) granitic pegmatites (Hogarth et al., 1972; Mellini and Merlino, 1977; Ma et al., 1986; Miyawaki et al., 1987, 2015; Pieczka et al., 2015) and in the Predazzo granite, Italy (Emiliani and Gandolfi, 1965; Mellini and Merlino, 1977). In contrast, its occurrence, which has been documented in a late greenschist-facies regional metamorphic assemblage in the form of micro-veins transecting chloritite rock from the Abitibi greenstone belt, Ontario and Quebec, Canada, indicates that Y and B were mobilised during the low-grade metamorphism (Pan et al., 1994). Other members of hellandite-group minerals [general chemical formula: X₄Y₂Z₇(BO₃)₂WO₇; Oberti et al. (2019)] show a strong dominance of Ce over Y and LREE>HREE. They have also been described in alkaline rocks, mainly in miarolitic caverns and vugs of syenitic ejecta in volcanic rocks from Latium, Italy [hellandite-(Ce), mottanite-(Ce) Ca₄Ce₂Al(Be₁₂Ti₄Si₄O₂₄)O₂; ferri-mottanite-(Ce) Ca₄Ce₂Fe²⁺(Be₁₂Ti₄Si₄O₂₄)O₂; ciprianiite Ca₄(ThCa)Al(Be₁₂Ti₄Si₄O₂₄)O₂; Della Ventura et al., 1999, 2002; Oberti et al., 1999, 2019; Perna et al., 2021], or in metasomatic rocks associated with alkaline mafic rocks from the Dara-i-Pioz complex, Tajikistan, and the Hodza-Achkan massif, Kyrgyzstan [tadzhikhite-(Ce) Ca₄Ce₂Ti₄Si₄O₂₄; Reguir et al., 1999; Pautov et al., 2013]. Mottanite-(Ce), ferri-mottanite-(Ce), ciprianiite and some hellandite-(Ce) also contain a notable concentration of Be (1.8–3.0 wt.% BeO; 0.7–1.2 apfu; Della Ventura et al., 2002; Oberti et al., 2019; Perna et al., 2021), which occupies a special tetrahedral site, usually vacant in hellandite-(Y), hellandite-(Ce) and tadzhikhite-(Ce) (e.g. Oberti et al., 2002, 2019).
The crucial factors in controlling the competitive crystallisation of hellandite-(Y) or hingganite-(Y) are most probably the local Al–Fe redistribution and the Fe\(^{2+}/\)Fe\(^{3+}\) ratio; where hellandite-(Y) contains a significant Al content and only minor amounts of Fe\(^{3+}\) (cf. Pan et al., 1994), whereas the gadolinite–hingganite series is Al-free and favours Fe\(^{2+}\) instead of Fe\(^{3+}\) (Tables 3 and 4) (cf. Miyawaki et al., 1984; Demartin et al., 1993, 2001b; Câmara et al., 2008; Báčik et al., 2014). Extremely rare ferri-mottanaite-(Ce), the first Fe\(^{3+}\)-dominant hellandite group mineral from the Vico volcanic province, Italy (Oberti et al., 2019), and ferri-hellandite-(Ce) \([(Ca_3Ce)Ce_2Fe^{3+}\square Si_3B_2O_2\square{(OH)}_2]\) from the Sagåsen larvikite quarry, Mørje, Porsgrunn, Vestfold and Telemark, Norway (Friis et al., 2021), were described only recently. Nevertheless, a second important factor could prevent the crystallisation of Fe\(^{3+}\)-rich hellandite-group minerals; namely the local Be:B ratio. Amounts of Be could rise to give a ratio of 1.5:4 in the hellandite group (Oberti et al., 2019; Della Ventura et al., 2002), and more than 1:1 in the gadolinite-group minerals (Bačik et al., 2017). Our data on hellandite-(Y) do not exclude the presence of Be – some of the Raman bands at 810–790 cm\(^{-1}\) and

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**Fig. 8.** (a) Raman spectra of hingganite-(Y) excited by a 532 nm laser; two different orientations of the crystal (A and B). (b, c, d) Raman spectra of hellandite-(Y) excited by a 532 nm laser for two different crystals and spectrum of hellandite-(Y) excited by a 633 nm laser (dashed line).

**Fig. 9.** Summary sketch of the main stages of monazite/ xenotime metasomatic alteration transformation.
770–768 cm\(^{-1}\) could be attributed not only to Si–O but also Be–O stretching vibrations. However, the presence of sharp O–H peaks at 3454 and 3662 cm\(^{-1}\) indicate a significant proportion of OH\(^-\) groups in the T site cavity. Therefore, we can assume that the possible Be (or Li) occupancy at the T site of hellandite-(Y) is very probably limited, however without accurate measurement, this limit cannot be quantified. Consequently, if the Be:B ratio significantly exceeds 1:1 in the environment, hingganite-(Y) preferentially crystallises and binds Be, Fe\(^{2+}\), and also a small amount of remaining B.

Although allanite-(Ce) and LREE-rich epidote are typical reaction products which accumulate LREE during monazite-(Ce) alteration in common granitic and metapelitic rocks over a wide P–T range, the analogous replacement of xenotime-(Y) produces only a limited amount of allanite-(Y), HREE+Y-rich epidote, and a significant amount of HREE+Y can be accommodated by apatite-supergroup minerals (cf. Broska et al., 2005; Budzyn\, et al., 2017; Hentschel et al., 2020). Moreover, allanite-(Y) and epidote-group minerals, rich in HREE+Y, are very rare in nature and occur mainly in highly evolved felsic rocks, e.g. granitic pegmatites, rare-metal (leuco)granites, and associated metamorphic REE mineralisation veins (e.g. Gieré and Sorensen, 2004; Alekseev et al., 2013, 2016). These data, together with our observations, raise a question regarding the relative stability between LREE-rich epidote-group minerals and HREE+Y-rich epidote-group minerals in magmatic and metamorphic systems, and suggest that the HREE and Y mainly reside in other minerals (Gieré and Sorensen, 2004). A possible explanation for this disparity in the Fabova Hola granite samples is a higher B activity during mylonitisation (~15–20 ppm B in the metagranite; Marsina et al., 1999), which favours the formation of borosilicates instead of epidote-group minerals. A similar scenario for hydrothermal tourmalisation, and its influence on LREE vs. HREE accumulation and allanite formation was proposed by Balashov (1976) and later by Alekseev et al. (2016) regarding allanite-(Ce) and allanite-(Y) paragenesis in a tourmalinite from the Severnyi pluton, Chukchi Peninsula, Russia. The stability of LREE-rich epidote-group minerals vs. HREE+Y-rich gadolinite-group minerals and the HREE +Y-rich (boro)silicate alternatives are also evident in the Strange Lake peralkaline pluton in Canada, where LREE mobility was controlled largely by the stability of ferriallanite-(Ce), whereas HREE was controlled by gadolinite-(Y) (Gysì et al., 2016; Vasyukova and William-Jones, 2019). However, little is currently known regarding the formation of HREE+Y-rich epidote-group minerals vs. HREE +Y-rich gadolinite-group minerals during alteration of natural xenotime-(Y). Moreover, though a few experiments have focused on the relative stabilities of xenotime-(Y)–HREE+Y-rich epidote–HREE+Y-rich fluorapatite in high Ca and Na–Ca environments under different P–T conditions (e.g. Budzyn\, et al., 2017), none have considered a B-(Be) saturated environment.

Crystal-chemical data for secondary (boro)silicates indicate solid solutions with a general Ca–REE+Y substitution trend (Fig. 10). This suggests that a major change in fluid chemistry occurred during hydrothermal alteration of monazite-(Ce) and xenotime-(Y), which was substantially controlled by the activity of Ca. Moreover, the remobilisation and distribution of LREE vs. HREE+Y was controlled by the competition between hydrothermal fluids and the stability of primary REE phosphates, as well as by the stability of secondary LREE epidote-group minerals and HREE+Y gadolinite-group minerals (cf. Gysì et al., 2016). Formation of hellandite-(Y) and hingganite-(Y) in the Fabova Hola metagranite may have resulted from localised heterogeneity in the environment, hingganite-(Y) preferentially crystallises and binds Be, Fe\(^{2+}\), and also a small amount of remaining B.

**Age of primary monazite-(Ce), formation of coronae as a function of P–T conditions, and the relationship to Alpine mylonitisation**

An age of 355 ± 1.9 Ma obtained by in situ Th–U–total Pb EPMA of primary magmatic monazite-(Ce) are consistent with the SIMS zircon U–Pb radiometric age determination of the corresponding I-type granitic rocks from the Tatríc and Veporícky granite units (~350–360 Ma; Broska et al., 2013), including the Sihla type tonalite dated to ca. 355 Ma directly from the Vepor pluvion (Kohút et al., 2008). It represents a primary magmatic age for emplacement of the granite during the main stage of Variscan plutonic activity in the West-Carpathian Tatríc and Veporícky crystalline basement (Poller et al., 2000; Gaab et al., 2005; Burda and Gawęda 2009; Kohút et al., 2008; Broska et al., 2013; Burda et al., 2013a, 2013b; Gawęda et al., 2016; Kohút and Larionov, 2021).

Determining the age from analysis of marginal parts of the monazite-(Ce) grains and isolated tiny monazite-(Ce) relics resulted in a scatter of younger ages (300 to 90 Ma). This less precise age interval indicates a disturbance in Th–U–Pb abundances, which was probably induced during alteration and coronae formation around monazite-(Ce) that resulted in partial-to-total Pb removal and partial resetting of the geochronometer (cf. Harlov et al., 2011; Williams et al., 2011). The exhumation of mylonitised metagranites of the Fabova Hola Complex at ca. 90–85 Ma was constrained by ⁴⁰Ar–³⁹Ar phengite ages from the extensional shear zones (Putíš, 1994; Dallmeyer et al., 1996; Putíš et al., 2009a). The Late Cretaceous to Palaeocene uplift of the Veporícky Unit is also documented by the zircon fission track age of the Sihla tonalite (64.9 ± 4.8 Ma; Plšienka et al., 2007). Deformation here terminated in a brittle–ductile regime, and the opened ‘en-echelon’ or ‘pinch and swell structures’ are still inferred by late- to post-metamorphic mineralisation. The greenschist-facies tectono-metamorphic conditions during the metagranite exhumation and blastomylonitisation may
alernatively constrain the conditions of coronae formation (Putiš, 1994; Putiš et al., 1997b; Janák et al., 2001; Lupták et al., 2000; Jeřábek et al., 2007, 2008a, 2008b). The coronae-bearing domains could be indicators of a channelised fluid flow during the exhumation. These domains are always located in a granitic blastomylonitic groundmass composed of newly formed medium-pressure greenschist-facies minerals, such as quartz-2, albite, chlorite, phengite, biotite-2, epidote, clinozoisite, z-grossular-rich garnet and calcite. Therefore, the estimated P–T conditions of coronae formation are from ca. 450 to 300°C following the exhumation ductile deformation regime and still a high late-metamorphic fluid activity. The outer rims of coronae are frequently ingrowing the hosting deformed biotite-1, being partly altered to phengite and chlorite (Fig. 9). Similarly, the brittle fractures of the neighbouring semiduc- tile feldspars are infilled by quartz, albite and chlorite.

Possible sources of B and Be

The presence of hellandite-(Y) and hingganite-(Y) in the coronae mineral aggregates requires a source of B and Be, which could have been remobilised during fluid-mediated breakdown of xenotime-(Y). Two principal sources of B and Be could be: (1) internal origin from rock-forming or accessory minerals of the host metagranite; or (2) resulting from external sources such as adjacent magmatic, metamorphic and sedimentary rocks.

The B content in common plutonic and metamorphic plagioclase and K-feldspar can usually be up to 100 ppm B, which could be incorporated as the (Na,K)BSiO₃ molecule in the feldspars. Boron could have been leaked into the circulating fluid during the post-magmatic orthoclase to microcline ordering of K-feldspar (Sauerer and Troll, 1990). The tourmaline-free granites. It contributes up to 69 wt.% of the whole B content in the rock (Sauerer and Troll, 1990). The mica-group minerals, especially muscovite, also represent an important carrier of B among granitic rock-forming minerals, where B substitutes for Al in the tetrahedral site as a boromuscovite molecule (Grew, 2002a). The concentration of Be in rock-forming minerals of common two-mica granites is generally very low, usually ≤10 ppm (Kretz et al., 1989).

Alternatively, or even additionally, the potential in situ source of B could be the altered xenotime-(Y) itself. The xenotime contains traces of B, which has been documented by X-ray compositional mapping (Fig. 5i). The incorporation of B into the xenotime-(Y) structure is most probably controlled by coupled heterovalent substitution (Nb, Ta) BY₃P₀, (Nb⁵⁺, Ta⁵⁺ + B³⁺ ↔ Y³⁺ + P⁵⁺), though in a limited range due to a very low Nb content, (close to the detection limit) in the xenotime-(Y). The natural occurrences of schianvatoine (NbBO₃) and béhérite (TaBO₃), together with the Nb-Ta orthoborates with a zircon–xenotime type crystal structure (Mrose and Rose, 1962; Range et al., 1996; Demartin et al., 2001a; Finch and Hanchar, 2003), together with previous indications of B replacing P in xenotime-(Y) (Oftendal, 1964), support the presence of B in the xenotime-(Y) and the existence of a possible limited xenotime-(Y)–schianvatoine–béhérite solid solution as a source of B.

The second possibility represents an external source of B and Be during the Alpine tectono-thermal overprint of the Fabova Hola metagranites The B-bearing environment, necessary for hellandite-(Y) and hingganite-(Y) formation, is supported by the occurrence of abundant newly formed tourmaline neoblasts in the adjacent Variscan Veporic metatonalites and tourmalinites pebbles in the Permian basal conglomerates (Vozárová et al., 2016), as well as in the surrounding Palaeozoic micaceous meta-pelites (cf. Lupták et al., 2000; Janák et al., 2001; Jeřábek et al., 2008b). Schorlitic tourmaline is a mineral commonly found in the Permian Klenevac-type granite, which occurs as several small intrusions in the Veporic Unit (Hraško et al., 2002; Villaseñor et al., 2021).

Consequently, B and Be could have been mobilised during Alpine mylonitisation, and in the associated tectono-thermal fluid that overprinted the in situ rock-forming minerals, especially muscovite and feldspars. These are the principal host phases for B and also Be, considering their high modal abundance in the parent granitic rocks (cf. Domanič et al., 1993; Leeman and Sisson, 1996; London et al., 1996; Grew, 2002a, 2002b; and references therein).

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