

Fluid-induced chemical and phase heterogeneity in pegmatitic apatite: implications for alteration conditions and anomalous optical biaxiality

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Abstract. This study documents the formation of optically anomalous biaxial apatite resulting from partial fluid-mediated metasomatic alteration of pegmatitic apatite containing a britholite component. The optical anomaly was identified using a refractometer. SEM and EDX data constrain alteration conditions to interaction with acidic, oxidizing, highly saline, Si-bearing fluids at temperatures below 400–500 °C, accompanied by elevated fluorine activity. Pervasive partial metasomatic modification produced patchy compositional zoning and increased porosity within the apatite crystals. Microscale variations in F, OH, and Cl define compositional domains with differing proportions of fluorapatite, hydroxylapatite, and chlorapatite end-members. These chemical differences result in variable light propagation velocities and refractive indices, giving rise to anomalous biaxial optical behavior. Single-crystal X-ray diffraction shows that all crystals retain the hexagonal apatite structure ($P6_3/m$). At the same time, fluid-induced apatite alteration generated non-uniform channel-site occupancies, accompanied by substitution of apatite by britholite along with the formation of vacancies in the calcium positions, and local structural distortions without symmetry lowering. The integration of optical, structural, and chemical data demonstrates that microscale compositional heterogeneity, produced by fluid–apatite interaction, is responsible for the observed optical anomaly.

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INTRODUCTION

Apatite is a key petrogenetic indicator in metamorphic and igneous rocks and related pegmatite. Its generalized crystallochemical formula is $[A(1)_2][A(2)_3](BO_4)_3X$, where A denotes large cations, B – metalloids, and X – halides or oxy-anions (White and Dong, 2003). Owing to its

structural flexibility, apatite allows extensive chemical substitutions and represents an important carrier of phosphorus and rare earth elements, along with zircon, titanite, allanite, and monazite. Fluorine, Cl, and OH readily substitute at the channel X site, and the halogen and trace-element composition of apatite is highly sensitive to physicochemical conditions during crystallization (Roda-Robles *et al.*,

2022). Charge balance is commonly maintained by coupled cation substitutions, mixed X-site occupancies or vacancies, and more rarely by changes in oxygen coordination at the B-site (White and Dong, 2003).

The ideal apatite structure is hexagonal ($P6_3/m$) and optically uniaxial. However, pure hydroxylapatite and chlorapatite crystallize in the subsymmetric monoclinic space group $P2_1/b$ at room temperature and transform to hexagonal symmetry at elevated temperatures (Hughes and Rakovan, 2002, pp. 5–6). Optical anomalies are commonly attributed to internal stress related to compositional heterogeneity and kinetic ordering (Shtukenberg and Punin, 2007, p. 238). Symmetry lowering may arise from misfits in the X-anion sublattice or accommodation of cations with differing size and charge at multiple crystallographic sites (Baikie *et al.*, 2012, p. 1574). Ordering of Cl and OH within anion columns has been proposed as a key mechanism of symmetry reduction in mixed-anion apatites (Hughes *et al.*, 1990). Notably, biaxial optical behavior has been documented in crystals retaining hexagonal symmetry in diffraction studies, indicating that local anion ordering or compositional heterogeneity may decouple optical properties from average crystallographic symmetry (Akizuki *et al.*, 1994; Baikie *et al.*, 2012).

Apatite also records petrogenetic processes not necessarily reflected in bulk-rock composition, preserving evidence of redox variations, in situ fractionation, mineral–fluid interaction, and dissolution–reprecipitation (Teiber *et al.*, 2015; Bruand *et al.*, 2017; Roda-Robles *et al.*, 2022). Zoning is therefore common feature in apatite and reflects complex crystallization and post-crystallization histories. Patchy zoning, in particular, is interpreted as partial metasomatic alteration involving local chemical re-equilibration through dissolution–reprecipitation, a process common for pegmatitic environments where fluids play a dominant role in mineral evolution (Jolliff *et al.*, 1989; Harlov *et al.*, 2005; Harlov, 2015; Roda-Robles *et al.*, 2022, 2024). Such zoning may record melt–fluid exchange processes and local chemical modification of apatite through incorporation of halogens and trace elements, providing valuable insights into the evolution of magmatic–hydrothermal systems (Roda-Robles *et al.*, 2022, 2024).

This study examines post-crystallization alteration of apatite from the Vitosha Mountain (Bulgaria) and its impact on structural and optical properties, emphasizing the link between fluid-mediated chemical heterogeneity and anomalous optical behavior.

GEOLOGICAL SETTING

Vitosha Mountain (Bulgaria) is located in the western part of the Srednogorie tectonic zone, classified as an island-arc system formed during the Cretaceous (Dabovski *et al.*, 1991). The Vitosha pluton, covering approximately 120 km², occupies the central part of the mountain and consist of several magmatic phases arranged broadly from east to west and including gabbro, monzonites (dominant rock), leucosyenites, and aplite granosyenites (Dimitrov, 1942). Mafic microgranular enclaves within monzonites indicate the magma mixing and mingling processes between a basic gabbroic and a more evolved monzonitic melt. Geochemically, the monzonites are intermediate-acidity rocks with an alkaline affinity, consistent with formation in a subduction-related tectonic setting (Antonov *et al.*, 2011b, pp. 21–22). U–Pb zircon dating indicate ages of 81.58 ± 0.23 Ma for gabbro, 80.55 ± 0.40 Ma for monzonite, and 79.67 ± 0.91 Ma for syenites (Atanassova-Vladimirova *et al.*, 2003). The pluton is surrounded by Upper Cretaceous volcanic rocks forming a horseshoe-shaped structure open to the west-northwest (Fig. 1a), with sharp intrusive contacts locally containing xenoliths of the host volcanics. Oligocene sediments locally overlie the intrusive rocks along the western margin of the pluton (Dimitrov, 1942; Zhelev, 1984, 1988; Atanassova-Vladimirova *et al.*, 2003, 2006; Antonov *et al.*, 2011b).

In the monzonites, leucosyenites, and granosyenites of the Vitosha pluton, two facial types of pegmatites are described by S. Dimitrov (1942) – schlieren-like (lenses) and vein-like (dykes). Schlieren-like pegmatites occur among the monzonite rocks, with which they are genetically related, in the form of nests and spots. They were formed the earliest, often with diffuse boundaries within the rocks that accommodate them, zonally arranged, and with miarolitic voids usually in their central parts. They are primarily composed of orthoclase, plagioclase, biotite, and quartz (Dimitrov, 1942; Petrussenko and Karov, 1993; Arnaudova and Arnaudov, 1995). Schlieren-like pegmatites are widely distributed east of the village of Vladaya, between the villages of Murchaev and Kladnitsa, and around the Aleko hut (Dimitrov, 1942). The studied apatite crystals were found in schlieren-like pegmatites in the area of the village of Rudartsi pegmatites (Fig. 1b). Vein-like pegmatites are observed less frequently than schlieren-like pegmatites. They are relatively late and are mainly associated with aplite granosyenites, although they may occur

among monzonite rocks. The mineral composition of vein-like pegmatites is mainly represented by orthoclase, plagioclase and quartz in various ratios (Karov, 2024).

Apatite is a common accessory mineral in both host and vein rocks of the western Vitosha pluton. Centimeter-sized apatite crystals formed during the pegmatitic stage and the onset of the pneuma-

tolitic stage, together with orthoclase, amphibole, magnetite, biotite, tourmaline, titanite, and albite (Dimitrov, 1942). Larger crystals, up to 12 cm in length, have been reported in pegmatites at several localities as Shipeto, Plochata, Lipata quarry, and northwest of the peak Skoparnika (Aslanyan and Ivchinova, 1960/61; Petrusenko and Karov, 1993).

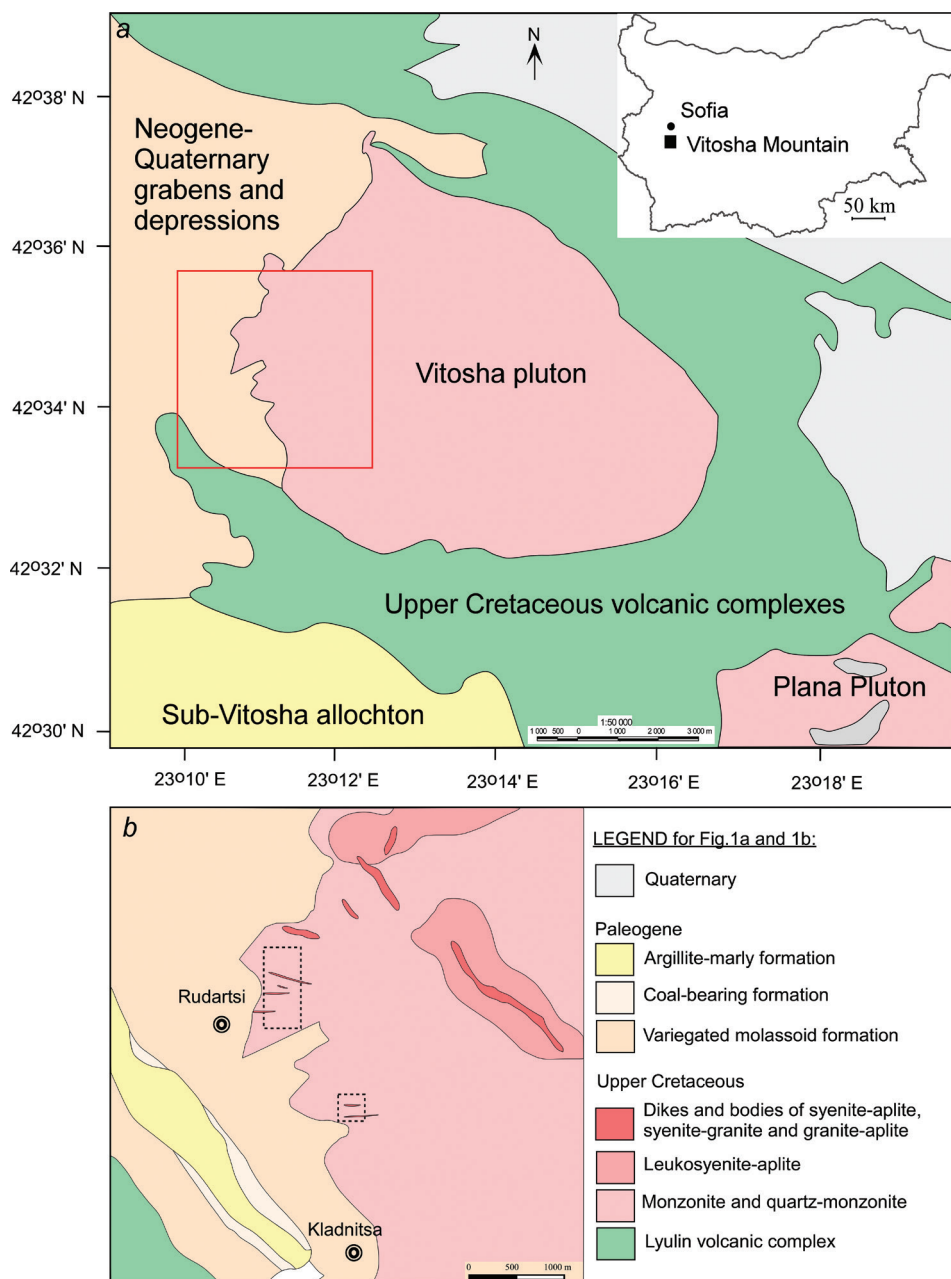


Fig. 1. a) Simplified geological map of Vitosha mountain based on 1:50 000 geological maps (Antonov *et al.*, 2011a, b); the area delineated by a red rectangle is given in Fig. 1b in more detail; b) – fragment of the geological map (Fig. 1a) with additions of the authors (the sampled places for pegmatite apatite are outlined by rectangles). The legend for both maps are the same.

MATERIALS AND METHODS

Materials

For the present study, schlieren-like pegmatites containing apatites were sampled in the western part of the Vitosha pluton, near the village of Rudartsi (the sampling places are delineated as rectangles in Fig. 1b). The outer zones of the pegmatite primarily consist of coarse-crystalline potassium feldspar (K-feldspar), with smaller amounts of plagioclase, quartz, amphibole, magnetite, and accessory minerals such as apatite and titanite. Postmagmatic minerals found in the peripheral areas include biotite and chlorite. The central parts of the pegmatite schlieren are predominantly composed of quartz, along with accessory apatite, epidote, and titanite. The postmagmatic minerals here include fine-grained white mica (sericite). Additionally, prismatic crystals of tourmaline (sclerl) up to 2 cm long have been observed in the rock. More than 30 apatite crystals and crystal fragments (2–30 mm in size) were collected from the schlieren-like pegmatites from the Vitosha pluton for this study.

Methods

The refractive indices of five representative apatite crystals were measured using a refractometer – ER604 by Krüss Optronic, equipped with polarization and a sodium filter that transmits only light of the sodium D-line (589 nm). This instrument operates on the principle of total internal reflection. To ensure optimal contact between the refractometer's hemicylinder and the polished sample surface, a thin layer of standard Anderson liquid ($n_D = 1.79$) was applied. Measurements were taken at the boundary between the dark and light portions of the refractometer's scale, with each sample measured in four orientations, rotated 45° each time.

The specific gravity of the crystals was measured using a specific gravity kit and a scale, calibrated to an accuracy of 0.001. The measurements were conducted on five different samples, and the specific gravity (SG) was calculated using the following formula: $SG = \text{weight of the mineral in air} / (\text{weight of the mineral in air} - \text{weight of the mineral in water})$.

The powder X-ray diffraction (XRD) study of apatite and pegmatite rock-forming minerals was performed at the Geological Institute of the Bulgarian Academy of Sciences using a HUBER Image Plate Guinier Camera G670. This camera operated in asymmetric transmission mode and was equipped

with a Ge monochromator, providing pure $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.540598 \text{ \AA}$). XRD patterns were collected over a $4\text{--}100^\circ$ two theta range with a step size of 0.005° 2θ , 40 kV, 40 mA. The collected X-ray diffraction data were processed using the Match! software package for phase identification, developed by Crystal Impact, Bonn, Germany, and incorporated the ICDD PDF-2 and COD databases.

Single-crystal X-ray diffraction (SCXRD) analyses of apatite crystals were carried out in Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences (IMC-BAS). Data collection experiments were performed on a Bruker D8 Venture diffractometer. The determination of unit cell parameters, data integration, scaling and absorption corrections were performed using the APEX4 software package. The crystal structures were solved by direct methods (SHELXS-97/2013) and refined by full-matrix least-squares methods on F^2 (SHELXL-97/2013). Structural data are available in the Cambridge Structural Database: CSD 2524424, CSD 2524425, CSD 2524426, and CSD 2524427.

The study of the elemental composition, chemical, and phase heterogeneity (SEM and EDX analysis) of apatite was conducted at IMC-BAS using a ZEISS SEM EVO 25 LS, equipped with an EDAX TRIDENT analytical system, at an accelerating voltage of 18 kV and a beam current of 2–3 nA. Observations of the texture and zoning of the apatite were conducted using a strongly enhanced backscattered electron (BSE) imaging technique. EDX analyses of apatite were carried out at selected points using an EDAX SDD Apollo 10 EDS detector and Genesis V 6.2 software with ZAF correction method, and reference standards – monazite (for P), diopside (Ca, Mg, Si), albite (Na), sanidine (Al, K), anhydrite (S), tugtupite (Cl), NdF_3 (F, Nd), LaF_3 (La), CeF_3 (Ce), rhodonite (Mn), and hematite (Fe). All EDX analyses were made on an oriented polished section of apatite crystal with the c-axis positioned perpendicular to the electron beam as recommended by Goldoff *et al.* (2012) to ensure constant $\text{K}\alpha$ X-ray count rates for F and Cl.

RESULTS

Powder XRD analysis of pegmatite minerals

The powder XRD analysis shows that the collected apatites are good match for fluorapatite ICDD 96-900-1880 (Fig. 2); plagioclase is identified as albite ICDD 10-0393, amphibole – as calcium-magnesium-iron amphibole ICDD 45-1371, potassium feld-

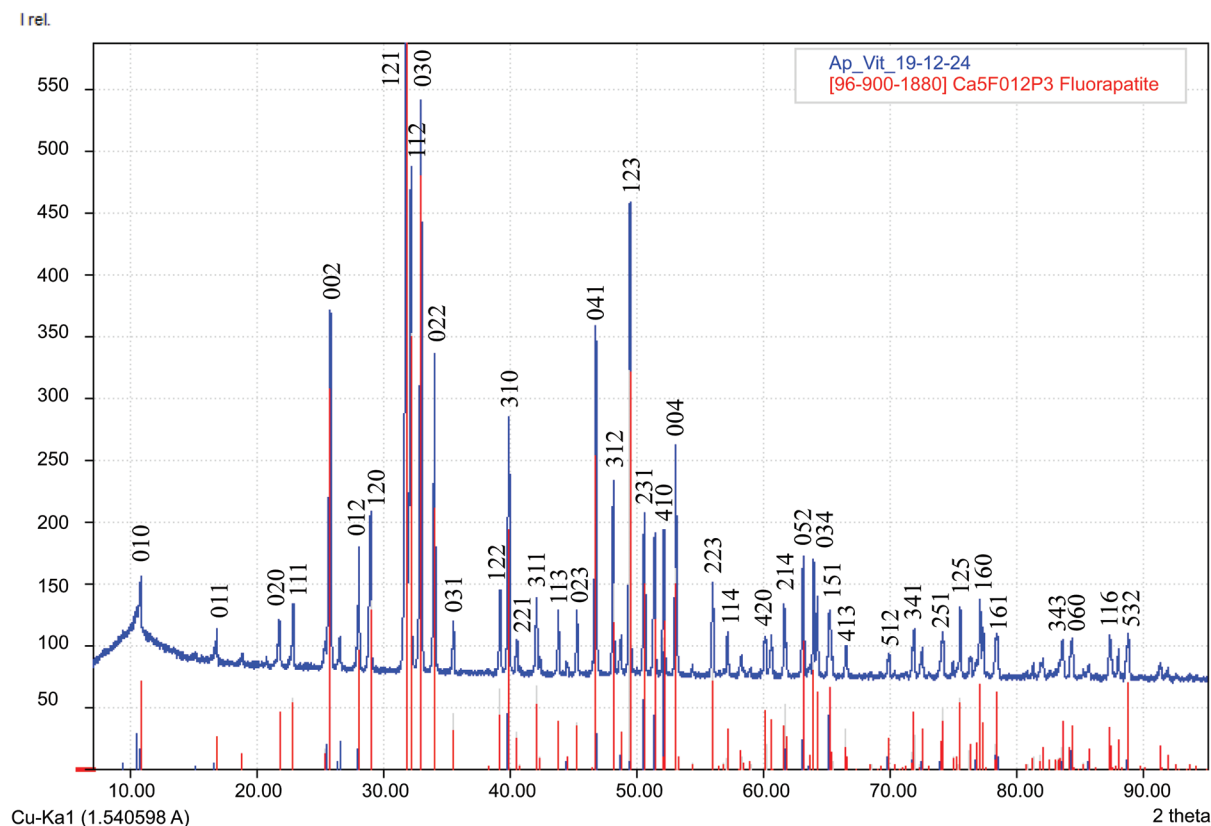


Fig. 2. XRD pattern of the studied apatite.

spar – as orthoclase ICDD 19-0003, and titanium mineral – as anatase ICDD 21-1272.

Apatite morphology and physical properties

The apatite is pale green, ranging from translucent to almost opaque (Fig. 3a). A color zonation is observed in the sections perpendicular to the *c*-axis of the crystals: the central part of the sections has a more intense green color (Fig. 3b), while the periphery is almost white (Fig. 3c). The habit of apatite crystals is prismatic with dominant simple forms for most of the studied samples: hexagonal prisms m $\{10\bar{1}0\}$ and a $\{11\bar{2}0\}$, hexagonal dipyramid x $\{10\bar{1}1\}$, and basal pinacoid c $\{0001\}$. An example of the morphology of apatite crystals is shown in Fig. 3c.

The specific gravity of the studied apatite varies between 2.90 and 3.15, corresponding to the lower boundary of the typical range reported for apatite (Deer *et al.*, 1992).

The measurements of refractive indices were carried out on the prismatic faces, parallel to the optical axis of the apatite crystals. The values for

higher refractive index range from 1.632 to 1.646 and for the lower refractive index range from 1.630 to 1.641. All crystals show an anomalous biaxial optical character. The birefringence ranges from 0.004 to 0.008 (Table 1).

SEM-EDX study

Figure 4a shows a collage of multiple BSE images taken from a fragment (7.8×8.2 mm) of a representative apatite crystal. The vertical axis of the fragment coincides with the crystallographic *c*-axis of apatite. Several features of the internal microstructure typical of pegmatite apatite from the Vitoshka pluton can be seen in this image: (1) the presence of numerous unevenly distributed elongated cavities of varying sizes parallel to the *c*-axis; (2) the presence of two types of zoning – growth zoning and strongly dominant patchy zoning; (3) the presence of mineral inclusions of varying nature and genesis.

The growth zoning is preserved in individual sections of large apatite crystals in the form of apatite subcrystals up to 0.5 mm in size (Fig. 4b, c) and is visible in BSE images as alternating dark (DGZ)

and bright (BGZ) growth zones indicating difference in their chemical composition. Their outlines are well-defined, coinciding with the faces of the whole crystal. The growth zoning reflects the primary conditions of crystallization of apatite in peg-

matite (temperature, chemical fluctuations in melt and volatiles, *etc.*).

The major part of the apatite crystals exhibits patchy zoning – internal, spatially heterogeneous chemical segregation within the crystal (Fig. 4a, e, f).

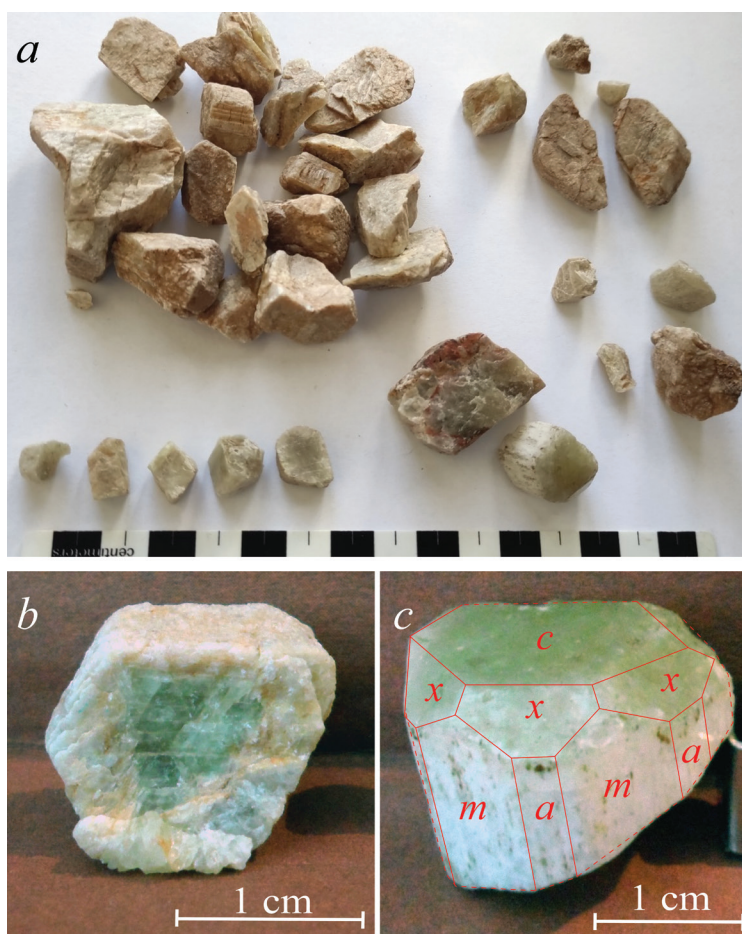


Fig. 3. Morphology and color of apatite: a) general appearance of apatite; b) color zoning; c) morphology of apatite crystals: hexagonal prisms m {1010} and a {1120}, hexagonal dipyramid x {1011}, and basal pinacoid c {0001}.

Table 1
Refractive indices of the studied apatites

Sample No	Rays	Refractive index measurements at four orientations				Birefringence ($n_o - n_e$)
		First	Second	Third	Fourth	
1	n_o	1.641	1.641	1.642	1.642	0.004
	n_e	1.638	1.639	1.641	1.641	
2	n_o	1.638	1.636	1.635	1.636	0.006
	n_e	1.634	1.632	1.632	1.632	
3	n_o	1.643	1.645	1.645	1.646	0.007
	n_e	1.641	1.640	1.639	1.641	
4	n_o	1.638	1.635	1.633	1.632	0.008
	n_e	1.632	1.633	1.630	1.630	
5	n_o	1.638	1.635	1.633	1.632	0.008
	n_e	1.632	1.632	1.630	1.630	

In BSE images the patchy zoning was observed as localized areas or domains of different brightness and composition. The dark (DPZ) and bright (BPZ) patchy zones are irregularly shaped and are randomly distributed throughout the crystal volume, but often exhibit elongation approximately parallel to the crystallographic c-axis.

Regardless of the type of zoning the all analyzed parts of apatite can be specified as fluor-hydroxy-

lapatite with a minor chlorapatite component (Fig. 5 and Table 2). Moreover, lighter areas of apatite with patchy zoning (BPZ) clearly contain more chlorine (Figs 5, 6). The two types of apatite zoning demonstrate similar variations in chemical composition where the lighter zones (BGZ and BPZ) are enriched with the britholite component (Table 2, Fig. 6) which reflect the “britholite substitution” in apatite: $\text{Si}^{4+} + \text{REE}^{3+} \leftrightarrow \text{P}^{5+} + \text{Ca}^{2+}$ (Pan and Fleet,

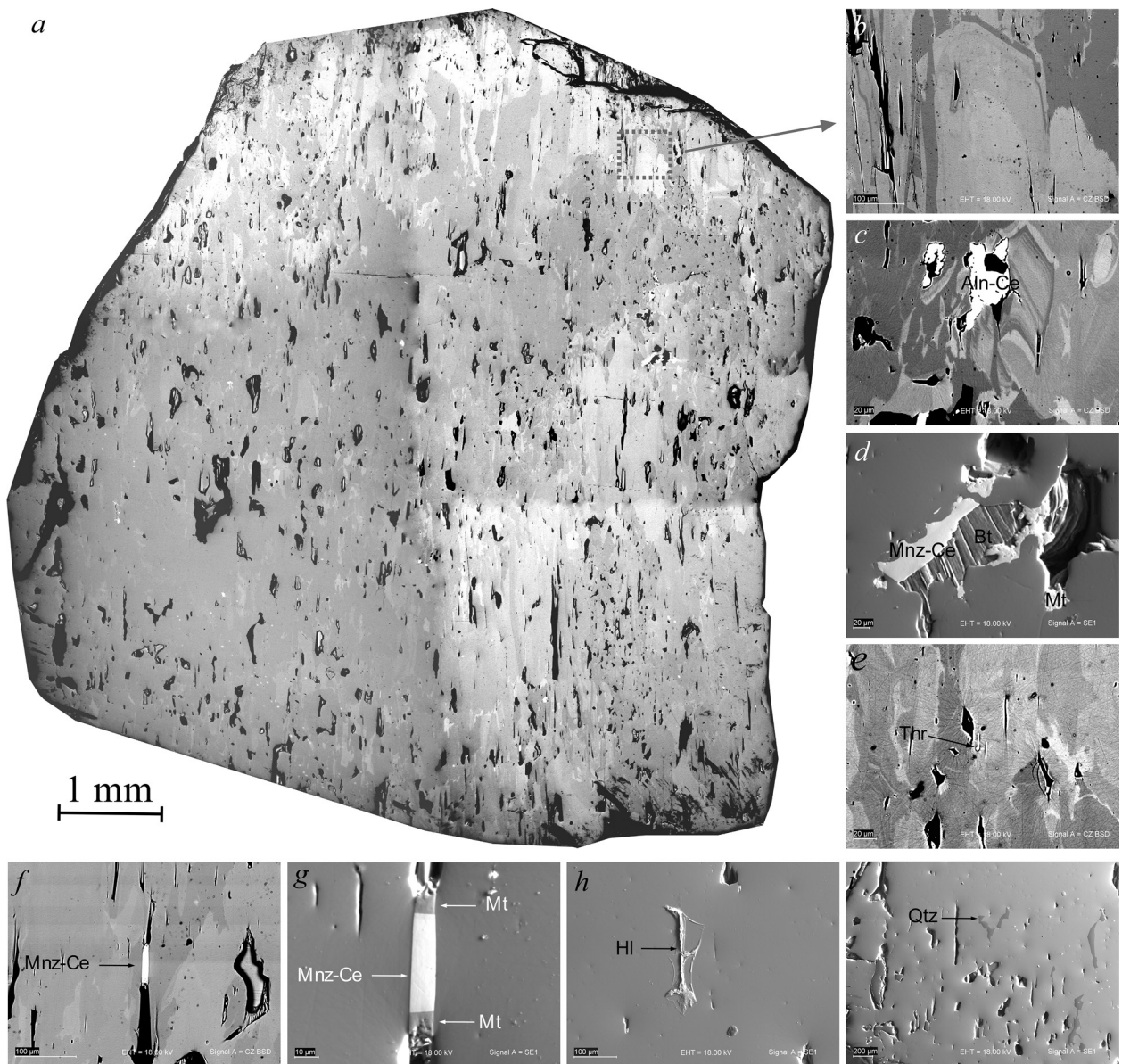


Fig. 4. SEM images of apatite: *a*) a collage of multiple backscattered electron (BSE) images from a fragment (7.8×8.2 mm, vertical axis parallel to the c-axis) of an apatite crystal, showing the typical microstructure of the apatites studied (dissolution cavities, patchy and zonal growth zoning, mineral inclusions); *b*) growth zoning of apatite subcrystal; *c*) growth zoning and allanite-Ce inclusion (Aln-Ce); *d*) inclusions of biotite (Bt), monazite-Ce (Mnz-Ce) and magnetite (Mt); *e*) patchy zoning and thorianite (Thr); *f*) and *g*) monazite-Ce inclusion with magnetite; *h*) halite-sylvite inclusions; *i*) quartz inclusions. Mineral symbols are according to Warr (2021).

2002; Rønsbo, 1989). The dark areas (DGZ and DPZ) compared to the lighter ones (BGZ and BPZ) are poorer in Si, La, Cl, Ce and Nd, and richer in F (Fig. 6). Cerium, irrespective of type of zoning, is the dominant rare earth element while La and Nd are present in lower concentrations and may be below the detection limit of the method. The content of the britholite component (Bri, mol%) in DGZ reaches up to 0.67%, while in BGZ it is almost twice as high 1.06% (Table 2). The quantity of the britholite component (Bri, mol%) in the DPZ reaches 0.54%, while in the BPZ, it is nearly double, reaching 1.12% (Table 2). Primary inclusions located in the areas of growth zoning in the studied apatite are allanite-Ce (Fig. 4c), biotite (Fig. 4d), and thorionite (Fig. 4e).

Throughout the volume of apatite crystals, dissolution textures are observed in the form of microscopic pits and dissolution channels developing along the “c” axis of apatite, indicating post-magmatic fluid-mineral interaction (Fig. 4a, f–i). Dissolution cavities typically contain post-magmatic minerals such as monazite-Ce and magnetite (Fig. 4f, g). The composition of monazite includes Ce_2O_3 – 32.5 wt%, La_2O_3 – 19.2 wt%, Nd_2O_3 – 10.5 wt% and ThO_2 – 1.2 wt%, which qualitatively reflects the presence of rare earth elements (Ce, La, Nd) + Th in primary apatite. Monazite-Ce inclusions develops

only in reacted areas of apatite that are depleted in REE, silicon, and chlorine, and appear darker in BSE images.

Sodium-potassium chloride inclusions with the composition (in wt%): K – 29.2, Na – 16.6, and Cl – 54.2, were observed precipitated in some dissolution cavities (Fig. 4h). Positive forms of alkali chlorides on the polished surface of apatite (Fig. 4h) suggest the possibility of their formation during the irradiation of apatite with an electron beam in the vacuum of scanning microscope. In addition to monazite, halite-sylvite, and magnetite, quartz (Fig. 4i) was also found in the dissolution pits and channels.

Single crystal X-ray diffraction analysis

To explain the optically anomalous biaxial behavior of the studied apatite, we investigated the crystal structure of four crystals with dimensions of approximately $0.1 \times 0.1 \times 0.1$ mm. They were all found to crystallize in the hexagonal space group $P6_3/m$ with typical apatite structure. The apatite crystal structure is composed by phosphate tetrahedra and two types of calcium polyhedra connected to form channels parallel to (001). The polyhedral network is positively charged, and this charge is balanced by OH^- , F^- or Cl^- ions within the channels (Hughes and Rakovan, 2002). This arrangement is highly

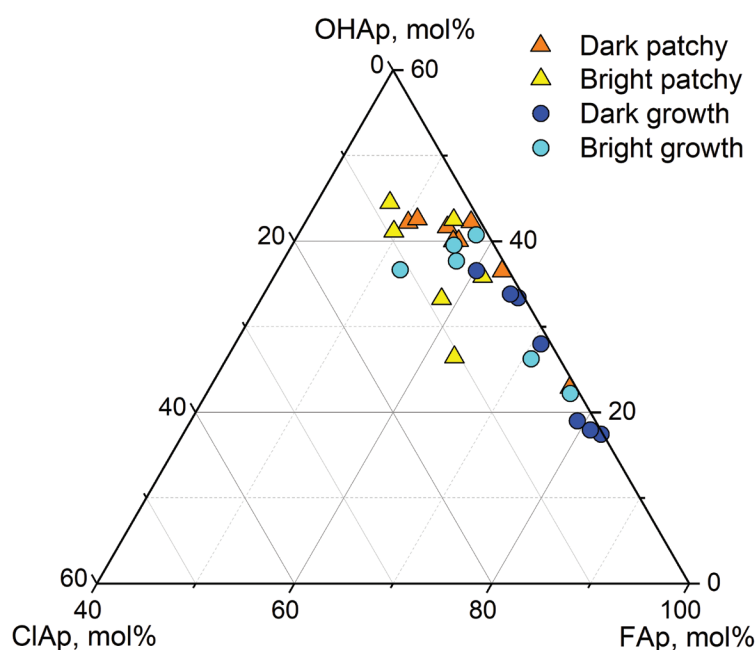


Fig. 5. Ternary FAP–OHAp–ClAp diagram with plotted EDX analyses. FAP – fluorapatite, OHAp – hydroxylapatite, ClAp – chlorapatite.

Table 2
 Elemental composition of apatite according to EDX analysis (wt.%) (BGZ – bright growth zones, BPZ – bright patchy zones and DPZ – dark patchy zones, FAp – fluorapatite, OHAp – hydroxylapatite, ClAp – chlorapatite)

Oxides	1	2	3	4	6	9	10	14	15	16	17	18	19	20	7	8	27	28	29	30	31	32	33	34	38	39	40	
	BPZ	DPZ	BPZ	DPZ	BPZ	DPZ	BPZ	DPZ	BPZ	DPZ	DPZ	DPZ	BPZ	DPZ	BPZ	BGZ	DGZ	BGZ	DGZ	BGZ	DGZ	BGZ	DGZ	DGZ	DGZ	BGZ	DGZ	
CaO	54.36	55.03	54.56	54.59	54.48	55.28	54.54	54.72	54.23	54.64	55.20	54.75	54.21	54.8	54.18	54.53	54.60	54.43	54.57	54.10	53.92	54.66	54.42	54.70	54.79	54.25	54.30	
La ₂ O ₃	0.12	0.05	0.20	0.1	0.23	0.19	0.16	0.16	0.23	0.15	0.07	0.00	0.10	0.11	0.15	0.23	0.08	0.22	0.15	0.33	0.23	0.00	0.00	0.08	0.10	0.24	0.05	
Ce ₂ O ₃	0.40	0.12	0.33	0.23	0.45	0.22	0.35	0.18	0.35	0.26	0.12	0.14	0.36	0.35	0.62	0.43	0.15	0.56	0.34	0.55	0.50	0.14	0.10	0.12	0.11	0.50	0.26	
Nd ₂ O ₃	0.20	0.14	0.14	0.2	0.26	0.00	0.22	0.06	0.12	0.100	0.00	0.12	0.23	0.15	0.14	0.19	0.12	0.22	0.11	0.20	0.08	0.00	0.19	0.07	0.18	0.05	0.13	
P ₂ O ₅	40.93	41.86	41.41	41.27	40.91	41.84	41.20	41.22	41.19	41.11	41.56	41.71	40.64	41.52	41.34	41.43	42.02	41.39	41.76	41.67	41.06	41.82	41.39	41.99	41.78	41.45	41.40	
SiO ₂	0.39	0.03	0.21	0.16	0.27	0.06	0.23	0.08	0.24	0.16	0.15	0.15	0.33	0.19	0.30	0.30	0.04	0.31	0.17	0.32	0.31	0.20	0.23	0.13	0.17	0.38	0.20	
Cl	0.21	0.05	0.73	0.51	0.18	0.05	0.59	0.43	0.65	0.25	0.23	0.27	0.55	0.07	0.36	0.28	0.13	0.20	0.23	0.33	0.06	0.04	0.07	0.09	0.02	0.08	0.07	
F	2.26	2.35	2.34	1.87	2.03	2.87	2.16	1.89	1.83	2.02	2.11	2.09	1.74	2.11	1.94	2.10	2.96	2.64	2.24	2.15	2.83	2.46	2.63	2.43	3.08	2.16	3.00	
H ₂ O ^a	0.63	0.65	0.47	0.74	0.75	0.41	0.58	0.75	0.72	0.73	0.71	0.71	0.77	0.75	0.64	0.70	0.34	0.46	0.65	0.67	0.39	0.59	0.49	0.60	0.31	0.72	0.32	
O=(F+Cl)	1.00	1.00	1.15	0.90	0.90	1.22	1.04	0.89	0.92	0.91	0.94	0.94	0.86	0.90	0.99	0.95	1.27	1.16	0.99	0.98	1.21	1.05	1.12	1.04	1.30	0.93	1.28	
Total	98.50	99.28	99.24	98.77	98.66	99.70	98.99	98.60	98.64	98.51	99.21	99.00	98.03	99.15	98.68	99.24	99.17	99.27	99.23	99.34	98.17	98.86	98.40	99.17	99.24	98.90	98.45	
Crystal chemical formulae calculated on the basis of 25 O (24 O + O (= 2 (F, Cl, OH)))																												
Ca	9.969	9.971	9.952	9.986	9.993	9.999	9.969	10.021	9.938	10.014	10.025	9.951	10.007	9.967	9.897	9.924	9.902	9.910	9.910	9.834	9.910	9.921	9.947	9.908	9.938	9.883	9.932	
La	0.009	0.003	0.012	0.006	0.014	0.012	0.011	0.011	0.014	0.009	0.003	0.000	0.006	0.006	0.009	0.014	0.006	0.014	0.009	0.020	0.015	0.000	0.000	0.006	0.014	0.003	0.018	
Ce	0.026	0.009	0.020	0.014	0.028	0.015	0.023	0.011	0.023	0.017	0.009	0.009	0.023	0.023	0.040	0.028	0.009	0.035	0.020	0.034	0.032	0.009	0.006	0.009	0.006	0.031	0.018	
Nd	0.011	0.009	0.009	0.011	0.017	0.000	0.014	0.003	0.008	0.006	0.000	0.009	0.014	0.008	0.009	0.011	0.006	0.014	0.006	0.011	0.006	0.000	0.012	0.003	0.012	0.003	0.009	
M-cat.	10.015	9.991	9.992	10.018	10.053	10.025	10.018	10.047	9.984	10.045	10.036	9.968	10.049	10.004	9.954	9.978	9.922	9.974	9.944	9.899	9.962	9.930	9.965	9.926	9.961	9.931	9.961	
P	5.931	5.995	5.967	5.965	5.929	5.978	5.952	5.966	5.965	5.953	5.963	5.989	5.926	5.965	5.966	5.957	6.021	5.955	5.993	5.984	5.962	5.999	5.978	6.009	5.987	5.967	5.983	
Si	0.067	0.006	0.035	0.027	0.047	0.009	0.039	0.013	0.041	0.028	0.026	0.026	0.057	0.033	0.051	0.051	0.007	0.053	0.028	0.054	0.054	0.034	0.040	0.021	0.029	0.064	0.034	
X-cat.	5.998	6.001	6.002	5.992	5.976	5.987	5.991	5.979	6.006	5.981	5.988	6.015	5.983	5.998	6.017	6.008	6.028	6.008	6.021	6.038	6.015	6.033	6.019	6.031	6.017	6.031	6.017	
Cl	0.060	0.014	0.211	0.147	0.052	0.013	0.169	0.125	0.187	0.074	0.067	0.078	0.161	0.020	0.219	0.081	0.036	0.058	0.065	0.095	0.019	0.013	0.020	0.024	0.004	0.024	0.020	
F	1.223	1.256	1.260	1.009	1.098	1.529	1.166	1.024	0.990	1.093	1.132	1.122	0.949	1.135	1.048	1.128	1.583	1.417	1.203	1.151	1.537	1.319	1.420	1.300	1.647	1.161	1.621	
OH	0.717	0.730	0.529	0.844	0.850	0.458	0.665	0.852	0.823	0.833	0.801	0.800	0.890	0.845	0.733	0.791	0.380	0.525	0.731	0.754	0.444	0.668	0.560	0.676	0.349	0.815	0.359	
FAp, mol%	61.15	62.79	62.99	50.44	54.89	76.45	58.29	51.17	49.50	54.66	56.60	56.09	47.43	56.76	52.41	56.41	79.18	70.86	60.17	57.56	76.85	65.95	70.99	64.99	82.33	58.05	81.03	
OHAp, mol%	35.85	36.50	26.45	42.20	42.49	22.89	33.25	42.59	41.15	41.64	40.05	40.01	44.50	42.25	36.64	39.55	19.00	26.25	36.56	37.70	22.20	33.40	28.00	33.80	17.45	40.75	17.95	
ClAp, mol%	3.00	0.71	10.56	7.37	2.62	0.65	8.46	6.24	9.35	3.69	3.35	3.90	8.07	0.99	10.95	4.04	1.82	2.89	3.27	4.74	0.94	0.64	1.01	1.21	0.22	1.20	1.02	
Ap, mol%	98.88	99.90	99.42	99.55	99.22	99.85	99.35	99.79	99.32	99.53	99.57	99.58	99.05	99.46	99.15	99.15	99.88	99.11	99.53	99.11	99.11	99.43	99.33	99.65	99.51	98.94	99.44	
Brt, mol %	1.12	0.10	0.58	0.45	0.78	0.15	0.65	0.21	0.68	0.47	0.43	0.42	0.95	0.54	0.85	0.85	0.12	0.89	0.47	0.89	0.89	0.57	0.67	0.35	0.49	1.06	0.56	

^a Calculated assuming the (F, Cl, OH) site is filled

favorable for atomic substitution in the structure and compensating anion groups. The studied samples are typical representatives of natural fluorapatites, in which part of the fluorine atoms are replaced by hydroxyl groups. As can be seen in Table 3, different degrees of substitution affect the parameters of

the unit cell and, accordingly, the positions of the atoms. Figure 7 schematically presents the position of fluorine atoms and hydroxyl groups in relation to calcium atoms in the studied apatites. The distances from the corresponding anion to the plane formed by the three calcium atoms are given in Table 3. The

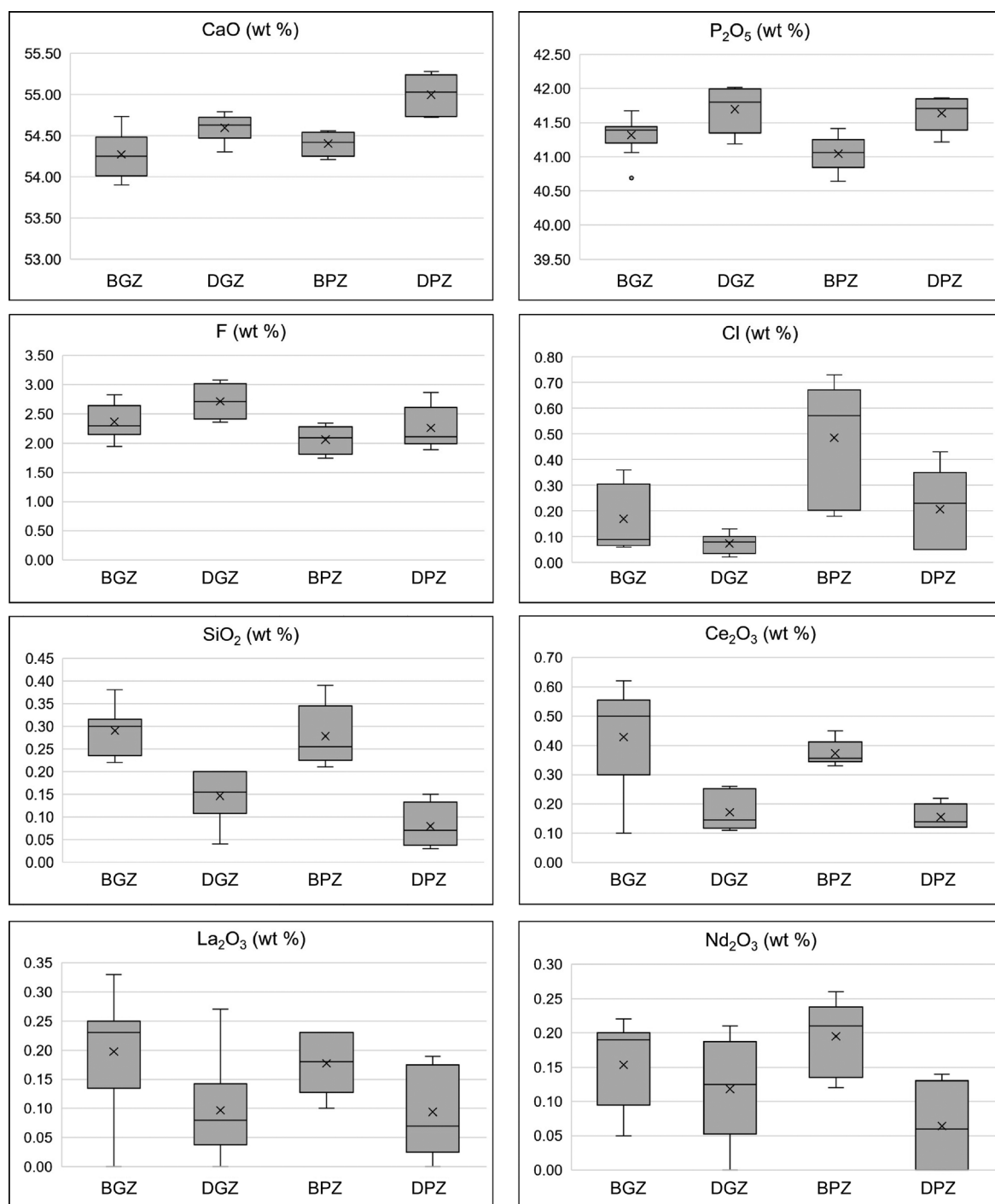


Fig. 6. Box-plot distributions of apatite composition for bright growth zones (BGZ), dark growth zones (DGZ), bright patchy zones (BPZ), and dark patchy zones (DPZ).

apatite framework is preserved in all samples despite variations in chemical composition. The first three crystals correspond to $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH},\text{F})_2$ with variable OH⁻/F⁻ ratios (Table 3). An increase in fluorine content is accompanied by an expansion of the *a* lattice parameter and the unit-cell volume, whereas the *c* parameter remains nearly constant. The largest unit-cell volume observed in the F-rich sample confirms the stabilizing role of fluorine within the apatite channel (Hughes *et al.*, 1989). The fourth crystal, $\text{Ca}_{9.07}\text{Ce}_{0.03}(\text{P}_{5.72}\text{Si}_{0.28})\text{O}_{24}(\text{OH})_{0.89}\text{F}_{1.18}$, exhibits a more complex substitution pattern involving heterovalent substitutions of Ce³⁺ for Ca²⁺ and Si⁴⁺ for P⁵⁺. The slightly shorter average P–O bond lengths observed in this sample further support partial incorporation of SiO₄ tetrahedra into the apatite structure, as reported for Si-bearing apatites (Hughes *et al.*, 1991). The P–O bond lengths in all crystals fall within the typical range for well-ordered PO₄ tetrahedra (Elliott, 1994). The decrease in F–OH distances from the F-rich to the chemically substituted apatite reflects increasing positional disorder within the channel site, consistent with mixed OH/F occupancy (Sudarsanan *et al.*, 1972). Despite these local variations, the rotation angle ϕ of the PO₄ tetrahedra remains nearly constant at approximately 23°, demonstrating that the apatite framework accommodates chemical substitutions without significant distortion of the tetrahedral network (Hughes *et al.*, 1989).

DISCUSSION

The obtained results allow discussion of several aspects of the mineralogy of apatite from the Vitoshka

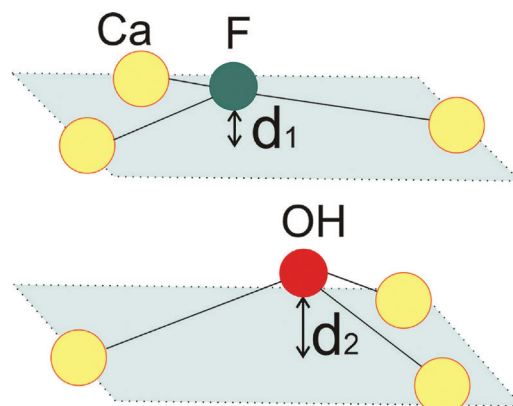


Fig. 7. Schematic representation of the position of fluorine atoms and hydroxyl groups relative to calcium atoms.

pluton, including the type of alteration, the physicochemical conditions of alteration, and their influence on the optical properties of crystals.

Anomalous optical biaxiality

Hexagonal apatite is optically uniaxial negative (Hughes and Rakovan, 2002), with the higher refractive index corresponding to the ordinary ray (n_o) and the lower to the extraordinary ray (n_e). In a refractometer study, the ordinary refractive index should remain constant during four measurements at 45° rotations. However, despite well-developed hexagonal morphology, such constancy was not observed. Instead, both rays propagated at variable velocities in different directions, indicating anomalous biaxial optical behavior in all studied crystals.

Table 3
Selected structural parameters of the studied apatites

Chemical formula	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{0.44}\text{F}_{1.73}$ (1)	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{0.72}\text{F}_{1.36}$ (2)	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{0.70}\text{F}_{1.38}$ (3)	$\text{Ca}_{9.07}\text{Ce}_{0.03}(\text{P}_{5.72}\text{Si}_{0.28})\text{O}_{24}(\text{OH})_{0.89}\text{F}_{1.18}$ (4)
CCDC Deposition number	CSD 2524424	CSD 2524425	CSD 2524426	CSD 2524427
SymGr	P 63/m	P 63/m	P 63/m	P 63/m
a=b (Å)	9.4230(13)	9.39110(10)	9.39160(10)	9.3855(4)
c (Å)	6.8837(15)	6.8805(2)	6.8783(2)	6.8785(3)
V (Å) ³	529.34(19)	525.513(19)	525.401(19)	524.73(5)
Distance PO(Å)	2×1.534, 1.537, 1.541	2×1.533, 1.535, 1.541	2×1.533, 1.534, 1.539	2×1.531, 1.532, 1.539
ϕ	23.02	23.24	23.27	23.27
d1(Å)	0.208	0	0	0
d2(Å)	0.847	0.461	0.468	0.344

Single-crystal X-ray diffraction was performed to assess structural symmetry, as mixed crystals may exhibit symmetry reduction due to variable F, Cl, and OH arrangements at the X site. Similar optical anomalies have been attributed to inhomogeneous impurity incorporation, a type of surface-structural control during growth, which influence trace-element partitioning, atom ordering, and dissymmetrization (Bulka *et al.*, 1980; Akizuki *et al.*, 1994; Rakovan and Reeder, 1994; Shtukenberg *et al.*, 2001; Rakovan, 2002). Growth under non-equilibrium conditions promotes heterogeneous distribution of isomorphous structural units, generating internal strain and kinetic ordering that may produce cascades of optical effects (Shtukenberg and Punin, 2007, pp. 201, 203). Variations in composition, temperature, and stress relaxation thus lead to optical anomalies related to compositional heterometry.

The symmetry and orientation of the optical indicatrix are controlled by the local symmetry of the growing crystal face or by growth steps on that face. Optical deviations resulting from kinetic ordering depend on composition and are typically most pronounced in equimolar solid solutions composed of fully miscible components (Shtukenberg and Punin, 2007). Such effects may create discrepancies between structural and optical symmetry. In apatite with patchy zoning, uneven chemical distribution of chemical elements within a single crystal, produces compositionally distinct domains. Because light velocity depends on optical density and thus on composition and structure, heterogeneity modifies light propagation: whereas homogeneous crystals exhibit constant velocity along a given direction, heterogeneous crystals show slight velocity variations across compositional domains.

The studied apatite displays significant variation in fluorapatite, hydroxylapatite, and chlorapatite proportions within single crystals (Table 2, Fig. 5). These end-members have distinct refractive indices (Anthony *et al.*, 2016), and their uneven distribution likely contributes to the observed biaxial character. Comparable behavior is documented in topaz, where partial substitution of F by OH increases refractive indices while reducing the optic axial angle (2V) and density (Gübelin *et al.*, 1986).

Relationships between structural data, elemental composition, optical anomaly and fluid mediated alteration of apatite

The zoning reflects both primary crystallization and later fluid-driven modification (Fig. 6). Growth zones display narrow, near-symmetric distributions

indicative of stable conditions, whereas patchy domains exhibit broader, positively skewed distributions (notably for Cl and REE), reflecting greater heterogeneity. These features point to open-system, fluid-mediated metasomatism involving redistribution of REE, Si, and halogens via dissolution–reprecipitation or diffusion-assisted exchange. The presence of mixed OH–F occupancies and additional heterovalent “britholite” substitutions involving Si^{4+} for P^{5+} and Ce^{3+} for Ca^{2+} indicates that the apatite structure has accommodated chemically diverse environments. The plotted compositions in coordinates $\text{Ca}+\text{P}$ (apfu) versus $\text{REE}+\text{Si}$ (apfu) (Fig. 8) show that the slope ratio of the fitted lines for the points of patchy zoning ($= 0.82$) and growth zoning ($= 0.88$) differs from the slope ratio of the ideal britholite substitution ($= 1$). This along with structural formula deviations from ideal site occupancies suggest additional charge-compensation mechanisms, including vacancies in the calcium positions, for example, according to the scheme $2\text{REE}^{3+} + \square = 3\text{Ca}^{2+}$ (Pan and Fleet, 2002), which is confirmed by structural studies. Such substitution mechanisms are consistent with fluid-mediated alteration under elevated fluorine activity and oxidizing conditions, as independently constrained by SEM observations and EDX analyses. Experimental studies and data on natural apatite have shown that interaction of apatite with Si-bearing, acidic, high-salinity fluids at temperatures of approximately 400–500 °C promotes coupled substitutions (e.g., $\text{Si}^{4+} + \text{REE}^{3+} \leftrightarrow \text{P}^{5+} + \text{Ca}^{2+}$) and enhances fluorine incorporation into the channel site (Fleet and Pan, 1995; Hughes and Rakovan, 2002; Pan and Fleet, 2002).

SCXRD results show that increasing fluorine expands the a lattice parameter and unit-cell volume, whereas Si and trivalent cation incorporation slightly contracts the framework. These opposing structural effects indicate localized, non-uniform modification of the crystal lattice rather than homogeneous solid-solution behavior. This interpretation is fully consistent with the patchy compositional zoning and increased porosity observed by SEM, which suggest pervasive but spatially heterogeneous fluid–mineral interaction.

Microscale variations in F, OH, and Cl define domains enriched in fluorapatite, hydroxylapatite, or chlorapatite. Although the average symmetry determined by SCXRD remains hexagonal, such domain-scale heterogeneity results in local variations in bond lengths, channel-site geometry, and atomic displacement parameters, particularly along the structural channel parallel to the c axis. Similar channel disorder and X-site positional splitting are

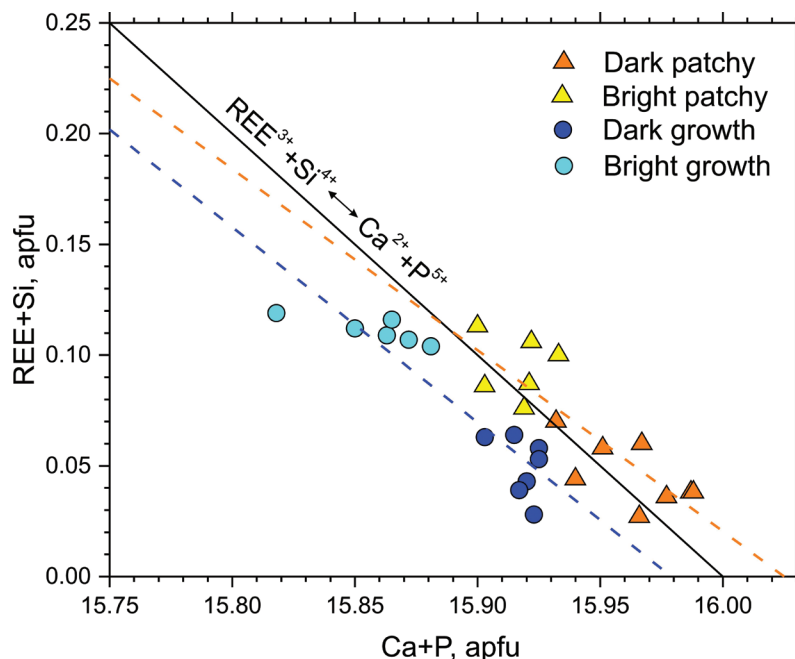


Fig. 8. Plotted compositions of the studied apatites in coordinates Ca+P (apfu) versus REE+Si (apfu)

known from mixed-anion apatites affected by fluids (Sudarsanan *et al.*, 1972; Elliott, 1994).

These crystal heterogeneities provide a structural explanation for the optically anomalous biaxial behavior observed using a refractometer. Differences in refractive indices among fluorapatite, hydroxylapatite, and chlorapatite end-members are well documented and arise from bonding environments within the channel site. When such domains coexist microscopically within one crystal, light velocities vary among compositional domains and crystallographic directions, effectively breaking ideal uniaxial optical symmetry expected for hexagonal apatite. The resulting optical anisotropy manifests as anomalous biaxial behavior, despite the retention of average hexagonal symmetry.

The SCXRD data confirm that this optical anomaly does not result from symmetry reduction, but from fluid-induced compositional and structural heterogeneity superimposed on an intact hexagonal framework. The integration of crystallographic, chemical, and optical data thus demonstrates that post-magmatic fluid activity plays a decisive role in modifying both the internal microstructure and the optical properties of apatite.

Type of alteration

The conducted studies show that postmagmatic fluids strongly affected apatite from the Vitosh

pegmatites, causing redistribution of chlorine and the britholite component (LREE+Si) and producing patchy zoning – irregular REE-enriched (light/bright) and depleted (dark) domains (Fig. 4a), while preserving crystal morphology. This alteration corresponds to partial metasomatic replacement via coupled dissolution–reprecipitation (Harlov *et al.*, 2011) and is accompanied by formation of post-magmatic monazite-(Ce). Fluid interaction with apatite promotes exchange reactions that redistribute Si and REE, leading to formation of monazite and other REE phosphates (Birski *et al.*, 2019). Numerous studies demonstrate that monazite inclusions in apatite form through fluid-induced dissolution–reprecipitation during metasomatism (Harlov *et al.*, 2002a, b, 2005; Harlov, 2011, 2015). Their elongation parallel to the apatite c-axis (Fig. 4d, f, g) reflects a topotactic reaction in which product orientation is inherited from the host crystal (Harlov *et al.*, 2007).

Dissolution pits and channels constitute ~25% of the crystal volume, as estimated by comparison with petrographic standards (Williams *et al.*, 1985). Their abundance and preferred orientation (Fig. 4a) indicate extensive fluid circulation. Structurally controlled porosity provides pathways linking reaction fronts with external fluids and facilitates replacement (Putnis, 2002, 2009).

REE incorporation during alteration depends on primary apatite composition, fluid chemistry, silica

activity, temperature, and redox conditions (Watson and Green, 1981; Pan and Fleet, 2002). Cerium dominates the REE budget in the studied apatite, followed by La and Nd (Table 2). Under oxidizing conditions, Ce^{3+} is oxidized to Ce^{4+} , enhancing substitution into apatite and influencing Nd incorporation (Pan and Fleet, 2002, p. 39; Al-Shahrabalee and Jaber, 2023). Association of tetravalent Ce with Th indicates oxidized, low-temperature conditions (Anenburg *et al.*, 2018).

Halogen diffusion is faster parallel to the c-axis than perpendicular to it (Brenan, 1993). Fluorine and chlorine partitioning between minerals and hydrothermal fluids in systems containing apatites depends strongly on temperature, pressure, fluid composition, and coexisting F–Cl-bearing phases (Zhu and Sverjensky, 1991), such as micas, amphiboles, and tourmaline in the studied pegmatites.

Despite partial REE incorporation into newly formed monazite, the altering fluids were likely not REE-rich. Furthermore, in apatite, rare-earth element diffusion is significantly slowed when coupled substitutions are required for charge balance; when REE^{3+} must move in concert with Si^{4+} (e.g., $\text{REE}^{3+} + \text{Si}^{4+} \leftrightarrow \text{Ca}^{2+} + \text{P}^{5+}$), diffusivities are more than an order of magnitude lower than for simple isovalent exchange (Cherniak, 2000).

Chemico-physical conditions of the alteration process

Primary apatite from the Vitoshka pluton crystallized during the pegmatitic stage and early pneumatolitic stage at $\sim 600^\circ\text{C}$ (Dimitrov, 1942; London *et al.*, 2020). The preservation of anatase constrains subsequent alteration to temperatures below this threshold, as transformation to rutile typically begins at $\sim 600\text{--}700^\circ\text{C}$ (Hanaor and Sorrell, 2011).

REE mobility during alteration was governed by dissolution of apatite coupled with precipitation of monazite-(Ce), a process enhanced by increasing fluid salinity (Chappell *et al.*, 2023). Monazite formation during late hydrothermal alteration results from topochemical fluid–rock interaction and occurs over wide P–T ranges, provided that fluids are H_2O -dominated (Harlov and Förster, 2003). Dissolution channels likely initiated at $\sim 400\text{--}500^\circ\text{C}$, forming elongated features parallel to the c axis and persisting at lower temperatures, consistent with experimental etching textures in fluorapatite (Betkowski *et al.*, 2016). Dissolution rates increase in acidic, saline fluids (Chappell *et al.*, 2023).

The britholite component (up to $\sim 1\%$; Table 2) serves as a sensitive petrogenetic indicator of low-

temperature alteration under elevated fluorine activity. High F^- concentrations promote substitution of Ca^{2+} by REE^{3+} , whereas other ligands (Cl, S) play a subordinate role in REE mobilization (Krenn *et al.*, 2012; Zozulya *et al.*, 2019, p. 16). In alkali F- or Cl-bearing fluids, apatite shows enhanced REE incorporation (Krenn *et al.*, 2012), and LREE fluoride and chloride complexes can fractionate REE during hydrothermal transport at $150\text{--}400^\circ\text{C}$ (Migdisov *et al.*, 2009; Williams-Jones *et al.*, 2012). In pegmatitic systems, especially under highly saline, Na-rich conditions, apatite participates actively in fluid–mineral mass transfer. Chlorine-rich brines enhance the mobility of metals, silica, and REE over broad P–T ranges (Harlov and Förster, 2003; Mair *et al.*, 2017). Sodium-potassium chloride inclusions in dissolution pits (Fig. 4h) and silica redeposition along fluid pathways corroborate the involvement of silica and saline NaCl–KCl fluids in enhancing apatite solubility and controlling REE availability during secondary phase formation.

The experimentally established transformation of monazite to vitusite and the formation of britholite symplectites at $\sim 600^\circ\text{C}$ (Betkowski *et al.*, 2016) imply that the absence of these phases in the studied apatite constrains alteration temperatures to below this threshold.

CONCLUSION

This study demonstrates that the optically anomalous biaxial behavior of the investigated apatite is the result of post-magmatic fluid-mediated partial alteration of the mineral rather than a primary symmetry-lowering crystallization process. Single-crystal X-ray diffraction confirms that all examined crystals retain the hexagonal apatite structure with space group $P6_3/m$, indicating preservation of the fundamental apatite framework despite significant chemical and textural modification.

SEM observations and EDX analyses reveal pervasive interaction with acidic, oxidizing, high-salinity, and Si-bearing fluids at temperatures below $400\text{--}500^\circ\text{C}$, accompanied by elevated fluorine activity and the involvement of F- and Cl-bearing mineral phases. These fluid–mineral interactions produced patchy compositional zoning, increased porosity, and coupled heterovalent substitutions involving Si, REE, and channel-site anions (F, OH, Cl). The single-crystal structural data record these processes through systematic variations in unit-cell parameters, channel-site geometry, and tetrahedral bond lengths, while still reflecting an average hexagonal symmetry.

Microscale heterogeneity in the proportions of fluorapatite, hydroxylapatite, and chlorapatite end-members generates local differences in refractive indices and light propagation velocities. The coexistence of these compositional domains within individual crystals effectively disrupts the ideal uniaxial optical behavior expected for hexagonal apatite, resulting in anomalous biaxial optical properties detected by refractometer. The combined optical, structural, and chemical dataset provides a coherent explanation for the observed optical anomaly.

These results highlight the exceptional sensitivity of apatite to post-magmatic fluid activity and demonstrate that optical anomalies may serve as

reliable indicators of metasomatic modification, even where average crystallographic symmetry is preserved. More broadly, the study emphasizes the importance of combining crystallographic, microstructural, chemical, and optical approaches when interpreting the origin and evolution of complex apatite compositions in fluid-rich geological environments.

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