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Article

Crystal chemistry and Raman spectroscopy of the johnbaumite–hydroxylellestadite mineral series and associated As- and B-bearing minerals from a pyrometamorphic xenolith of the Upper Chegem Caldera, North Caucasus, Kabardino-Balkaria, Russia

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Abstract

A calcium-silicate xenolith (no. 11) from the ignimbrite of the Upper Chegem Caldera in Kabardino-Balkaria, Russia, has revealed a diverse mineral assemblage with As- and B-bearing phases from the apatite supergroup such as the svabite and johnbaumite–hydroxylellestadite series, in addition to cahnite and datolite. Three distinct zones of variable arsenic content have been investigated. Notably, the outermost altered zone adjacent to the ignimbrite hosts the highest concentration of arsenic and arsenate minerals. A detailed structural analysis using Raman spectroscopy was carried out to investigate the distribution of boron and arsenic in tetrahedral coordination. This has provided the basis for describing a solid-solution system between hydroxylellestadite, svabite and johnbaumite and can be used as a novel technique for identifying apatite-supergroup minerals. One aim of the analysis was to elucidate the origin of various elements and content levels, particularly in relation to the distance from the xenolith–ignimbrite contact. The presence of boron and arsenic, probably derived from ignimbrites, highlights the important role of volcanic rocks as potential contributors of these elements in mineral formation processes.

Keywords: johnbaumite; hydroxylellestadite; svabite; pyrometamorphic rocks; cahnite; boron; arsenic minerals; apatite supergroup; Raman spectroscopy

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Introduction

The xenoliths of the Upper Chegem Caldera ignimbrites in the North Caucasus, Kabardino-Balkaria, Russia, are fascinating objects for modern mineralogy. They combine altered rocks of different lithologies, such as schist, granite, sandstone, siltstone, argillite and limestone (Bogatikov *et al.*, 1992). Most notable are the large carbonate–silicate xenoliths up to 20 m in diameter formed as a result of pyrometamorphism. To date, 11 altered calc-silicate xenoliths containing rare high-temperature and low-pressure mineral assemblages have been found within the ignimbrites (Galuskina *et al.*, 2015). These xenoliths represent rare high-temperature and low-pressure mineral associations containing new and rare minerals formed under sanidinite-facies metamorphism. Among them, more than 20 new minerals have been described in recent years (Galuskin *et al.*, 2015) however for the most recent xenolith (no. 11), found in 2012, there has been only minimal information published on its mineralogy (Galuskina *et al.*, 2015). In particular, this work investigates identification of calcium-arsenate members of the apatite supergroup: svabite, johnbaumite and hydroxylellestadite, and other associated minerals including cahnite and datolite.

Geological setting

The pyrometamorphic calc-silicate rocks are found between the Lakargii and Vorlan peaks in the Upper Chegem Caldera, located in the Baksan Valley in the eastern part of the Elbrus-Kyuygen volcanic region in the North Caucasus, Kabardino-Balkaria, Russia (Bogatikov *et al.*, 1992). A detailed geological setting with maps

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can be found in previous publications e.g. Bogatikov *et al.* (1992) and Gazis (1995).

The samples studied were collected in 2016 from different parts of xenolith no. 11 (Fig. 1). This is a recently discovered calcium-silicate xenolith with a diameter of ~5 m. It contains three zones characterised by different mineral compositions (Fig. 2). Zone I is the xenolith core containing periclase (MgO), brucite $(MgOH)_2$, As-bearing hydroxylellestadite, rondorfite $Ca_8Mg(SiO_4)_4Cl_2$, killalaite $Ca_{6.4}(H_{0.6}Si_2O_7)_2(OH)_2$, and Ca–Mg hydrosilicates. It is a cryptocrystalline massive rock showing no lustre with colours ranging from light to dark grey. The middle zone (II) has a more coarse-grained crystalline texture with single crystals visible within the greyish rock mass. It consists of larnite Ca_2SiO_4, rustumite $Ca_{10}(Si_2O_7)_2(SiO_4)(OH)_2Cl_2$, rankinite $Ca_3Si_2O_7$, rondorfite, galuskinite $Ca_7(SiO_4)_3CO_3$, As-bearing hydroxylellestadite, minerals of the edgrewite–hydroxyledgrewite series $Ca_9(SiO_4)_4(F,OH)_2$, kerimasite–elbrusite $Ca_3(Zr,U)_2(SiO_4)(Fe^{3+}O_4)_2$, Sn-bearing lakargiite $Ca(Zr,Sn,Ti)O_3$, wadalite $(Ca,Mg)_6(Al,Fe^{3+})_4((Si,Al)O_4)_3O_4Cl_3$, cuspidine $Ca_8(Si_2O_7)_2F_4$ and secondary minerals: killalaite, hydrogrossular, thaumasite $Ca_3(SO_4)[Si(OH)_6](CO_3)\cdot 12H_2O$, foshagite $Ca_4(Si_3O_9)(OH)_2$, defernite $Ca_6(CO_3)_{1.58}(Si_2O_7)_{0.21}(OH)_7[Cl_{0.50}(OH)_{0.08}(H_2O)_{0.42}]$, and tobermorite $Ca_5Si_6O_{17}\cdot 5H_2O$ (Galuskina *et al.*, 2018). The outer zone (III) is a strongly altered, brittle white part of the xenolith. It consists of hydrogrossular, minerals of the thaumasite–ettringite series, fluorite (CaF_2), Ca–Al hydrosilicate, tobermorite, calcite $(CaCO_3)$, svabite, cahnite and contains relics of cuspidine, perovskite $(CaTiO_3)$, datolite and lakargiite.

Svabite, johnbaumite and hydroxylellestadite

Examination of xenolith no. 11 has revealed the presence of calcium-arsenate members of the apatite supergroup – svabite, $Ca_5(AsO_4)_3F$, johnbaumite, $Ca_5(AsO_4)_3(OH)$, and As-bearing hydroxylellestadite, which were found together with previously unobserved cahnite, $Ca_2[B(OH)_4](AsO_4)$ and datolite, $CaB(SiO_4)(OH)$. Arsenic-bearing minerals have also been reported from other previously discovered xenoliths of the Upper Chegem Caldera, e.g. svabite, As-bearing apatite, and As-bearing hydroxylellestadite by Banasik *et al.* (2012) and the chemical composition and single-crystal X-ray data of B- and As-bearing galuskinite, $Ca_7(SiO_4)_3CO_3$, has been obtained by Lazic *et al.* (2012).

Svabite is a member of the apatite group (the apatite supergroup) (Pasero *et al.*, 2010). The general chemical formula of this supergroup is presented as $^{IX}M1_2{}^{VII}M2_3(^{IV}TO_4)_3X$, and the ideal svabite as $M1 = M2 = Ca$, $T = As$, and $X = F$ (Biagioni *et al.*, 2016). In the rock studied, svabite was confirmed only in the outer part of the xenolith. In the other xenolith zones, OH groups substituted mainly for F at the X site. We have also been able to distinguish another member of the arsenate apatite group – johnbaumite, $Ca_5(AsO_4)_3OH$ (Biagioni and Pasero, 2013). In some cases, we also observed a substitution of As by Si and S at the T site, hence a third mineral of the apatite supergroup – hydroxylellestadite, $Ca_5(SiO_4)_{1.5}(SO_4)_{1.5}OH$, has been recognised in this xenolith. All three of the above mentioned members of the apatite supergroup crystallise in the $P6_3/m$ space group (Onac *et al.*, 2006; Biagioni and Pasero, 2013; Biagioni *et al.*, 2016). They are also topologically similar in that their structure consists of columns of face-sharing $M1$ polyhedra running along **c**. These polyhedra are typically referred to as metaprisms (Pasero *et al.*, 2010) and are connected by TO_4 tetrahedra with channels containing $M2$ cations and X anions (Onac *et al.*, 2006; Biagioni and Pasero, 2013; Biagioni *et al.*, 2016).

In the outer zone of xenolith no. 11 svabite is associated with boron-rich minerals such as cahnite and datolite. Cahnite, a relatively rare mineral in nature, has a structure comparable to that of zircon, with $(AsO_4)^{3-}$ and $[B(OH)_4]^{1-}$ tetrahedra alternately occupying the Si site, and CaO_8 polyhedra between them instead of ZrO_8 (Prewitt and Buerger, 1961). Also present in this zone are low-temperature spheroidal mineral aggregates. These are noteworthy because they consist mainly of fine crystalline bultfonteinite, which contains arsenic in its structure (~3.67–6.40 wt.% As_2O_5), calcite and fluorite. A similar low-temperature association has been described previously from xenolith no. 1 in the Upper Chegem Caldera (Zadov *et al.*, 2013).

This work provides spectroscopic data on the chemical composition of apatite-supergroup minerals and associated As- and B-bearing phases from xenolith no. 11 of the Upper Chegem Caldera, North Caucasus, Kabardino-Balkaria, Russia. This study continues the emerging technique of using Raman data to distinguish between individual group members and supergroups of minerals (Leissner *et al.*, 2015; Watenphul *et al.*, 2016; Bersani *et al.*, 2019; Varlamov *et al.*, 2020). We focused primarily on the Raman scattering arising from vibrations associated with TO_4 tetrahedra, as focussing on modes related to the sites within the structural channels would not yield the expected results because the bands associated with vibrations of the OH group showed very low intensity (Supplementary materials, Fig. S1).

Experimental methods

The chemical composition and crystal morphology of the minerals studied were investigated using a Phenom XL analytical scanning electron microscope (Faculty of Natural Sciences, University of Silesia, Poland). More detailed chemical analyses were carried out using a CAMECA SX100 electron microprobe (Institute of Geochemistry, Mineralogy, and Petrology, University of Warsaw, Poland). Energy-dispersive spectroscopy (EDS) and wavelength-dispersive spectroscopy (WDS) element-distribution maps were also made using the electron microprobe analyser. The following lines and standards were used: Ca$K\alpha$, Si$K\alpha$ – diopside; S$K\alpha$ – baryte; P$K\alpha$, F$K\alpha$ – apatite BB2; V$K\alpha$ – V_2O_5; As$L\alpha$ – GaAs; and Cl$K\alpha$ – tugtupite. The accelerating voltage was 15 kV, and the beam diameter was 10 μm.

Infrared reflectance spectra were measured using a Bio-Rad FTS-6000 spectrometer equipped with a Bio-Rad UMA-500 microscope with a mercury cadmium telluride (MTC) detector cooled to 77 K with liquid nitrogen. Spectra were obtained in the 6000–700 cm^{-1} range with a resolution of 4 cm^{-1}. A spectrum of a gold-covered reference slide was collected as a background, and the spectrum of the sample was recorded by accumulating 1248 scans. The reflectance data were converted to standard absorption spectra using Kramers-Krönig transformations. Measurements were performed on *in situ* grains.

Raman measurements were carried out using a WITec CRM alpha 300R confocal Raman microscope equipped with an air-cooled solid-state laser ($\lambda = 532$ nm) and a CCD camera. The excitation laser radiation was delivered to the microscope via a polarisation-maintaining single-mode optical fibre (50 μm in diameter). Data were acquired using an Olympus MPLAN 100×/0.9NA air objective. The Raman scattered light was focused onto a multimode fibre (50 μm in diameter) and monochromator

Figure 1. (a) Xenolith no. 11 is distinguished by its light colour in contrast to the dark ignimbrite of the Upper Chegem Caldera, Kabardino-Balkaria, Russia; (b) contact of the xenolith with the ignimbrite, where B- and As-bearing minerals have been found; (c) the larnite zone (zone II) is the most developed zone in the xenolith containing green–yellow rondorfite crystals.

with a 600 line/mm grating. The Raman signal was verified using a silicon sample by checking the Si position (520.7 cm^{-1}). All individual Raman spectra were collected in the 200–4000 cm^{-1} range with a spectral resolution of 3 cm^{-1}.

The surface Raman imaging was performed in an area 140 µm × 110 µm using 280 × 220 pixels (= 61,600 spectra) with an integration time of 33 ms per spectrum and a sample movement accuracy of ±0.5 µm. All spectra were collected in the 150–4000 cm^{-1} range at 10 mW on the sample and 3 cm^{-1} spectral resolution. The output data were manipulated by performing a baseline correction using the 3rd-degree auto-polynomial function and subjected to an automatic cosmic ray removal procedure. A sum filter was first used to produce element-distribution images, while a K-means cluster analysis (Manhattan distance) was performed using WITec *ProjectFive Plus* Software (version 5.3, WITec Wissenschaftliche Instrumente und Technologie GmbH, Ulm, Germany) to show the area of occurrence of each phase. Finally, a band fitting analysis using a Lorentz–Gauss function with the minimum number of components was performed on the averaged spectrum originating from the individual sample using the *GRAMS*

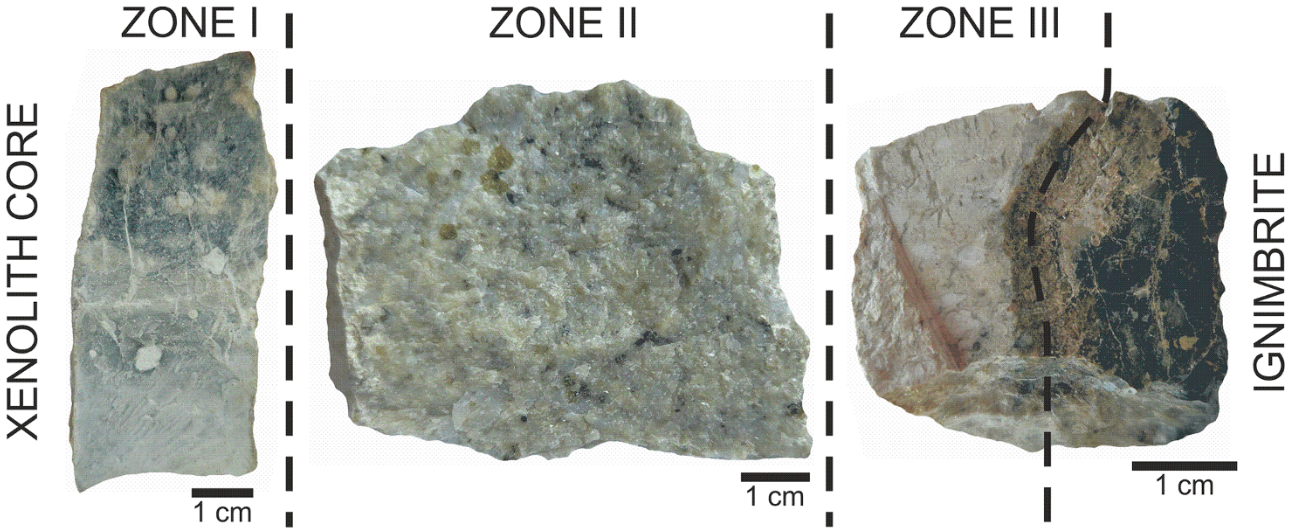

Figure 2. Photo of representative samples of zones I, II and III of the xenolith and its contact with the ignimbrite.

Table 1. Chemical composition of the selected apatite-supergroup minerals

	Hydroxylellestadite				Johnbaumite		Svabite
Analyses #	1	2	3	4	5	6	7
Wt.%							
SO_3	23.44	20.38	15.20	11.20	5.44	4.32	3.27
P_2O_5	0.29	0.40	7.16	8.15	11.03	10.98	9.57
V_2O_5	n.d.	n.d.	n.d.	0.46	0.90	0.94	n.d.
SiO_2	17.58	15.28	11.43	8.39	4.16	3.26	2.41
As_2O_5	0.55	6.21	9.50	17.14	25.96	28.90	33.68
CaO	55.60	53.20	54.03	51.35	49.27	49.14	47.59
Cl	1.39	1.72	1.10	1.03	1.45	1.52	0.37
F	0.27	0.52	1.31	1.34	0.96	0.80	1.59
H_2O*	1.30	1.03	0.83	0.76	0.77	0.81	0.69
–O=F+Cl	0.43	0.61	0.80	0.80	0.73	0.71	0.75
Total	100.00	98.13	99.77	99.02	99.20	100.00	98.41
Calculated on 8 cations per formula unit							
S	1.48	1.34	0.99	0.76	0.39	0.31	0.24
P	0.02	0.03	0.52	0.63	0.88	0.88	0.79
V	n.d.	n.d.	n.d.	0.03	0.06	0.06	n.d.
Si	1.48	1.34	0.99	0.76	0.39	0.31	0.24
As	0.02	0.29	0.50	0.82	1.28	1.44	1.73
T site	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Ca	5.00	5.00	5.00	5.00	5.00	5.00	5.00
M site	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Cl	0.20	0.26	0.16	0.16	0.23	0.24	0.06
F	0.07	0.14	0.36	0.38	0.29	0.24	0.49
OH	0.73	0.60	0.48	0.46	0.48	0.52	0.45
X site	1.00	1.00	1.00	1.00	1.00	1.00	1.00

Note: * – calculated on the basis of charge balance; n.d. – not detected; # – location of point analysis is shown on Fig. 3.

software package (version 9.2, Thermo Fisher Scientific, Waltham, MA, USA).

Chemical analysis to detect and image boron in the investigated phases was performed using time-of-flight secondary ion mass spectrometry (ToF–SIMS). ToF-SIMS studies are complementary to EDX studies in that they can detect all elements within the detection limits in the ppm range (Hagenhoff, 2000; Fearn, 2015; Siljeström *et al.*, 2017). A ToF-SIMS 5 mass spectrometer equipped with a reflectron-type analyser and a liquid metal ion gun (Bi_3^+, 30 keV and ~0.3 pA) was used to analyse two regions containing the mineral. The area analysed was adapted to the size of the mineral grain in the material examined and was ~320 μm × 320 μm and 270 μm × 270 μm, respectively. The surface of the sample areas was cleaned in the spectrometer with a caesium gun immediately prior to measurements. Positive mass spectra were collected using the Spectroscopy and Fast Imaging Modes of operation. The spectra were calibrated using CH_3^+, $C_2H_3^+$, $C_3H_3^+$ and $C_3H_5^+$ ions for positive polarity. The *SurfaceLab6* software was

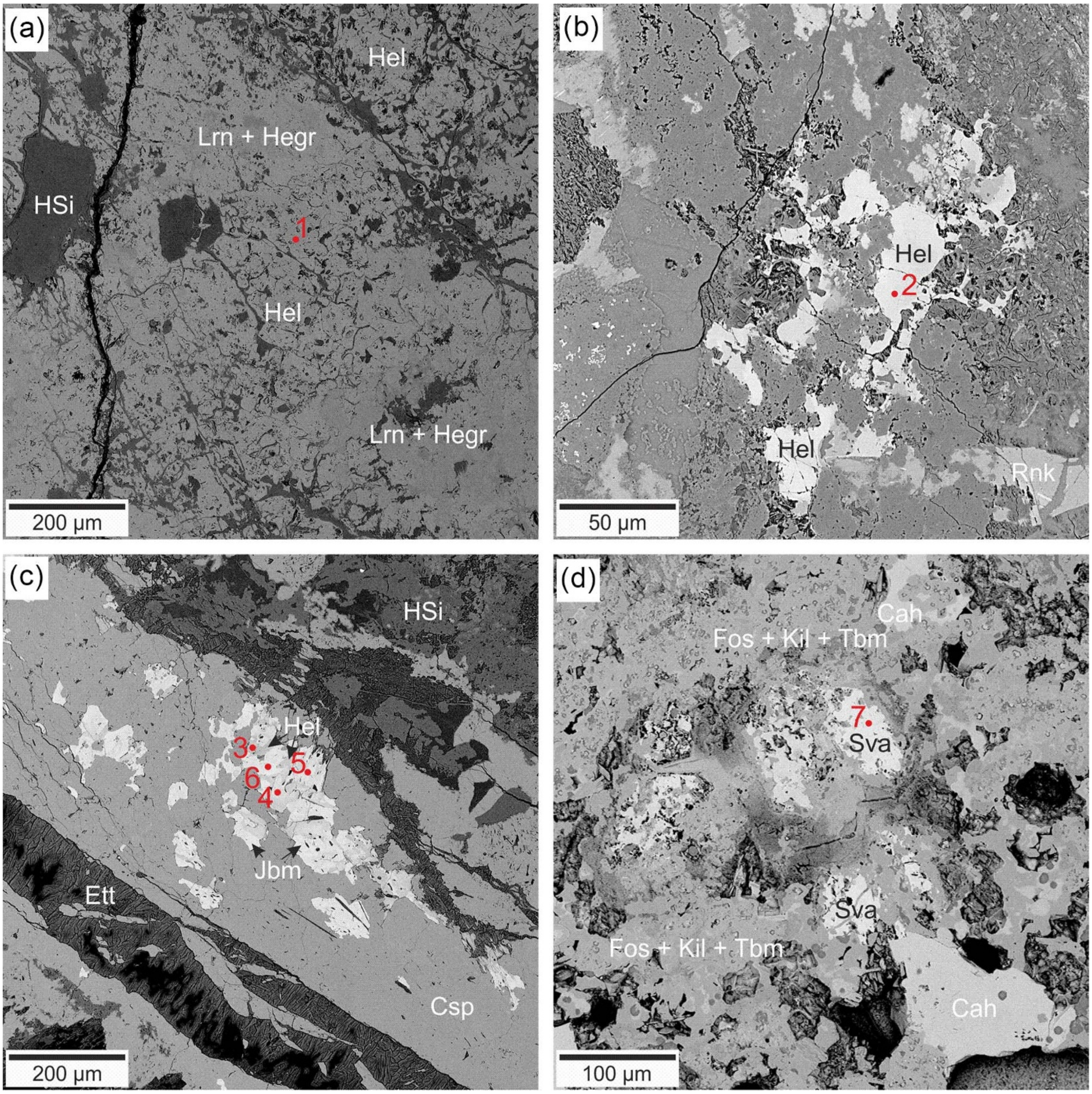

Figure 3. BSE image of As-bearing minerals from different zones of xenolith no. 11. (a, b) Zone I; (c, d) zone III. The red dots indicate the points of analysis in Table 1. Mineral abbreviations: Csp – cuspidine; Cah – cahnite; Ett – ettringite; Fos – foshagite; Hel – hydroxylellestadite; Hegr – hydroxyledgrewite; Hsi – unidentified hydrosilicates; Jbm – johnbaumite; Kil – killalaite; Lrn – larnite; Rnk – rankinite; Sva – svabite; and Tbm – tobermorite.

used for data analysis. Distribution maps were reconstructed from the mass spectra in post-measurement analysis.

Results

Minerals of the apatite supergroup

Minerals belonging to the apatite supergroup within xenolith no. 11, formed irregular, elongated grains of varying sizes, reaching up to 100 μm. They typically formed aggregates (up to 1.0 mm in diameter) of several crystals. Both the single crystals and their aggregates were usually chemically homogeneous. The only exceptions to this rule were the aggregates found in the cuspidine veins, characterised by variable compositions within the T (As ↔ Si/S) and X (OH ↔ F) sites. Despite the homogeneity of the individual apatite supergroup minerals in the xenolith studied, their chemical composition varied throughout the xenolith zones. During the research, the following minerals of the apatite supergroup were identified in the rock studied: hydroxylellestadite (zone I, II and cuspidine veins in zone III), svabite (zone III), and johnbaumite (cuspidine veins in zone III). The results of the chemical analyses of these minerals are summarised in Table 1.

In the relatively unaltered area of the xenolith (zone I), hydroxylellestadite with minor arsenic substitutions (0.55–6.21 wt.% As_2O_5, Fig. 3a, b, Table 1, #1–2) was identified. Analyses of apatite supergroup minerals located further from the xenolith core revealed gradual changes in the occupancy of the T and X positions within their structure (Fig. 4b). Additionally, a significant increase in arsenic content in the tetrahedral position was observed in minerals from the outermost and most altered

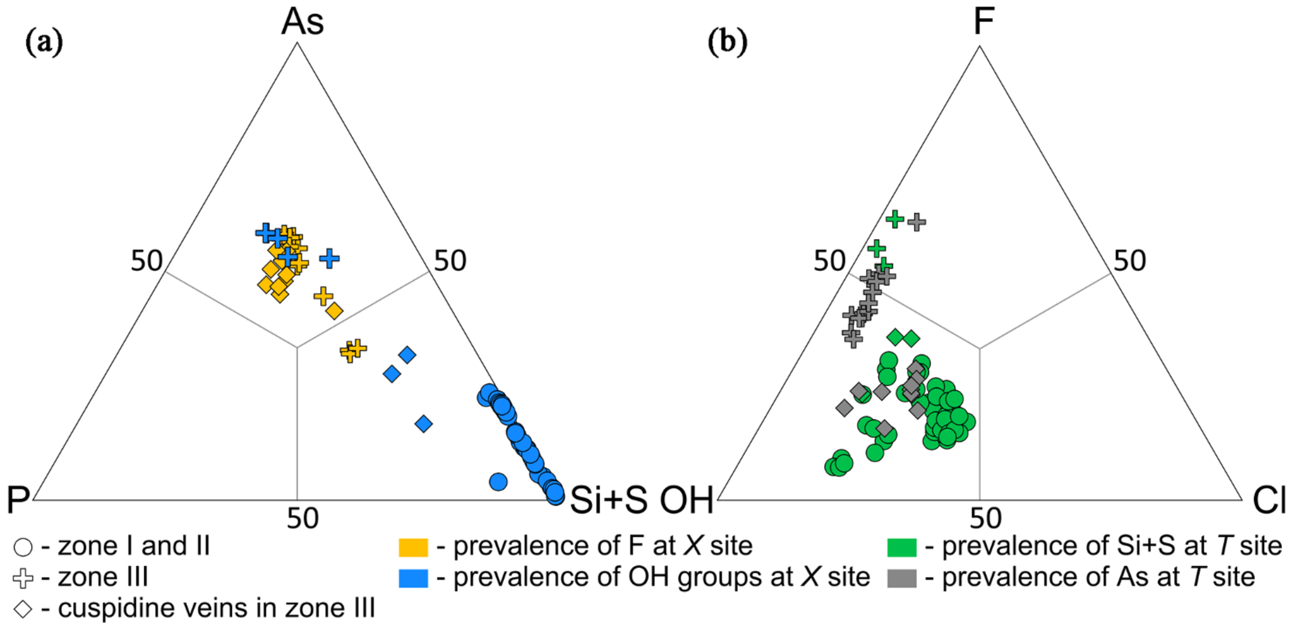

Figure 4. Ternary diagram of (a) cations at the *T* site and (b) anions at the *X* site in the solid-solution system between hydroxylellestadite, johnbaumite and svabite. Symbols used in the diagram: circles – analyses made in the zones I and II, crosses – analyses made in the zone III, diamond – analyses made in the cuspidine veins in zone III. Colours used in the diagram: (a) blue – prevalence of OH groups at the *X* site, yellow – prevalence of F at the *X* site; and (b) green – prevalence of Si+S at the *T* site, grey – prevalence of As at the *T* site.

part of the xenolith (zones II and III) (Fig. 4a). Another notable observation was the simultaneous increase in fluorine content at the expense of hydroxyl groups (Fig. 4). Consequently, in the highly weathered outer part of the xenolith, the apatite supergroup mineral was identified as svabite (zone III) (Fig. 3d; Table 1, #7). Cuspidine veins containing aggregates composed of apatite supergroup minerals were also noted in the outer part of the xenolith (zone III) (Figs 3c and 5). Within these veins two members of the apatite supergroup can be distinguished: hydroxylellestadite (Table 1, #3–4) and johnbaumite (Table 1, #5–6).

The Raman study of arsenic substitutions at the *T* site in the structure of apatite supergroup minerals and their synthetic equivalents is an important problem, commonly discussed in the literature (Frost *et al.*, 2007; Banasik *et al.*, 2012; Gianfagna *et al.*, 2014; Giera *et al.*, 2016; Song *et al.*, 2018; Lempart *et al.*, 2019). The minerals found in the xenolith no. 11 mean that changes in compositions combined with results from Raman spectroscopy allow a mutual correlation between the $SiO_4/SO_4–AsO_4$ ratio of these minerals (Fig. 6).

A closer look at the spectra collected from the samples analysed revealed the most intense bands associated with symmetric stretching vibrations of SO_4 ν_1 (1006 cm^{-1}) and SiO_4 ν_1 (856 cm^{-1}) are characterised by the ellestadite-group minerals (Środek *et al.*, 2018). The band at ca. 860 cm^{-1} is additionally interpreted as symmetric stretching vibrations of AsO_4 ν_1 when As is present at the *T* site (Gianfagna *et al.*, 2014), while the band at ca. 961 cm^{-1} originates from symmetric stretching vibrations of the PO_4 ν_1 as in As-free members (Antonakos *et al.*, 2007; Giera *et al.*, 2016). However, this band can also be related to the asymmetric stretching vibrations of AsO_4 ν_3 in As-bearing phases (Song *et al.*, 2018). A broad and low-intensity band around 1141 cm^{-1} corresponds to asymmetric stretching vibrations of SiO_4, SO_4 and PO_4 ν_3 (Antonakos *et al.*, 2007; Comodi *et al.*, 2016; Środek *et al.*, 2018). The low-lying bands correspond to the deformational ν_4 vibrations of the SO_4 group (630 cm^{-1}), SiO_4 group (538 cm^{-1}) and PO_4 group (581 cm^{-1}) (Antonakos *et al.*, 2007; Środek *et al.*, 2018). In the range of 500–400 cm^{-1} low-intensity bands appear related to ν_2 vibrations of PO_4, SO_4 groups, and ν_4 vibrations of AsO_4 groups (Gianfagna *et al.*, 2014; Banno *et al.*, 2016, Środek *et al.*, 2018). The maximum at 467 cm^{-1} is most probably related to ν_2 vibrations of SO_4 groups (Banno *et al.*, 2016, Avdontceva *et al.*, 2021), and the band at 426 cm^{-1} to ν_4 vibrations of AsO_4 groups (Gianfagna *et al.*, 2014). The bands at 368 and 325 cm^{-1} are due to ν_2 vibrations of AsO_4 (Frost *et al.*, 2007) and SiO_4 (Onac *et al.*, 2006), respectively.

The Raman spectra of the minerals of the hydroxylellestadite–johnbaumite–svabite series reveal a gradual change in band intensity corresponding to the vibrations of anions occupying the *T* site. As a result, we found a correlation between the decrease in intensity of the SO_4-related bands and the simultaneous increase in arsenic content in the mineral composition. It is worth noting that the intensity of the band at 860 cm^{-1} does not decrease with decreasing silica content due to the overlapping nature of the symmetric stretching vibrations of SiO_4 and AsO_4. However, changes in the shape of the band indicated a structural deformation, confirming the Si↔As substitution.

As- and B-bearing minerals associated with the apatite supergroup minerals

In this work we have identified several B- and/or As-bearing minerals in addition to the apatite-supergroup minerals, such as cahnite, datolite and the low-temperature bultfonteinite, $Ca_2(HSiO_4)F{\cdot}H_2O$. The highest B and As contents of borate and arsenate minerals were detected in the outer, altered zone adjacent to the ignimbrite (Fig. 1b). The core and middle

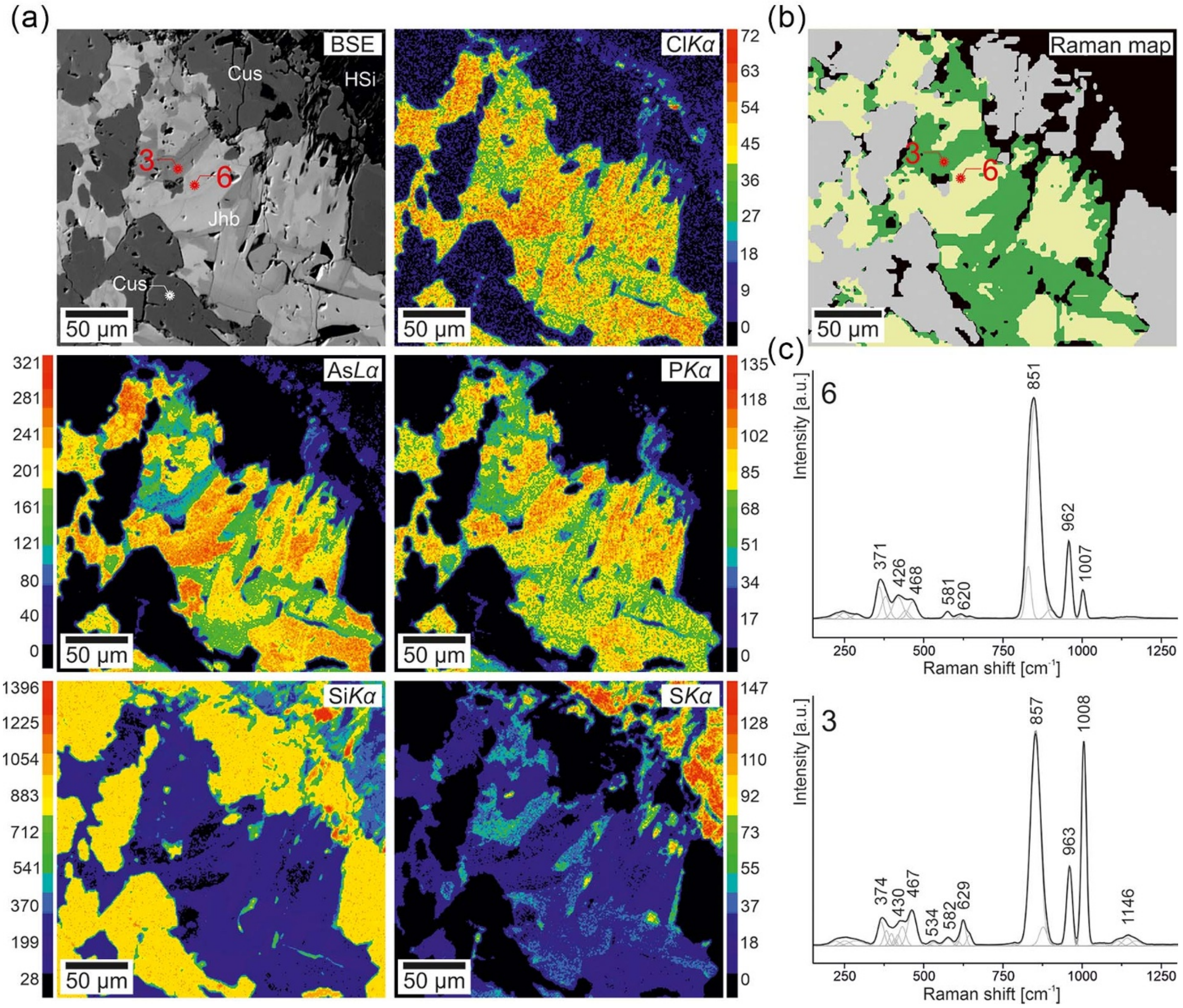

Figure 5. (a) BSE image and element-distribution mapping of the hydroxylellestadite–johnbaumite aggregate in the cuspidine vein. (b) *K*-means cluster analysis of the hydroxylellestadite–johnbaumite aggregate shown in (a); (c) Raman spectra of hydroxylellestadite (3) and johnbaumite (6) from the cuspidine veins marked in the BSE image in (a). The numbers in the spectrum correspond to the chemical composition in Table 1, point analyses #6 and #3, respectively. Abbreviations: Csp – cuspidine; Hel – hydroxylellestadite; Jbm – johnbaumite; and Hsi – unidentified hydrosilicates.

zones of the xenolith contain much less B- and As-bearing minerals.

Cahnite

Cahnite was found in the outer altered zone (III) of the xenolith, which is composed mainly of minerals of the thaumasite–ettringite series, fluorite, tobermorite, calcite, Ca–Al hydrosilicates and bultfonteinite and less common cuspidine, perovskite, lakargiite and svabite. It forms irregular crystals up to 200 μm across (Figs 3d and 7a, b). The empirical formula of cahnite from the Upper Chegem Caldera is $Ca_{2.00}B_{1.00}(As_{0.82}S_{0.06}Si_{0.06}P_{0.04}V_{0.02})_{\Sigma 1.00}O_4[(OH)_{3.95}F_{0.05}]_{\Sigma 4.00}$ (Table 2), which is close to the ideal formula, $Ca_2B(AsO_4)(OH)_4$ and to formulae reported previously (Palache and Bauer, 1927; Shiraga *et al.*, 2002). Some minor differences are reflected in insignificant impurities of S, Si, P and V substituting As at the As–O tetrahedron and the negligible presence of F substituting hydroxyl groups.

To confirm the presence of boron and determine the area of its distribution in the grains the ToF-SIMS maps were obtained on the selected grain of cahnite. This analysis confirmed the presence of boron; two peaks at m/z = 11 Da and m/z = 10 Da were assigned to ^{10}B and ^{11}B isotopes (not shown). Figure 7 shows the distribution maps of $^{11}B^+$, Ca^+ and Mg^+ reconstructed from the mass spectra resulting from the Fast Imaging Mode of the spectrometer operation. The ion distributions vary, and mineral phase boundaries are clearly visible. Boron has a homogeneous distribution in the area of the grains studied.

The Raman and IR spectra obtained are in agreement with previously published data (Ross, 1972; Shiraga *et al.*, 2002). The main bands in the Raman and IR spectrum of cahnite (Fig. 8) are related to vibrations of borate and arsenate groups. The Raman spectrum of cahnite is primarily determined by the one intense band centred at 844 cm^{-1}, which is assigned to the AsO_4 ν_1 group vibrations and other weaker ones originating from ν_3 (791 cm^{-1}), ν_2 (280 cm^{-1}) and ν_4 (443 cm^{-1}) (Ross, 1972). Arsenic in tetrahedral coordination was confirmed in the IR spectrum by the bands associated

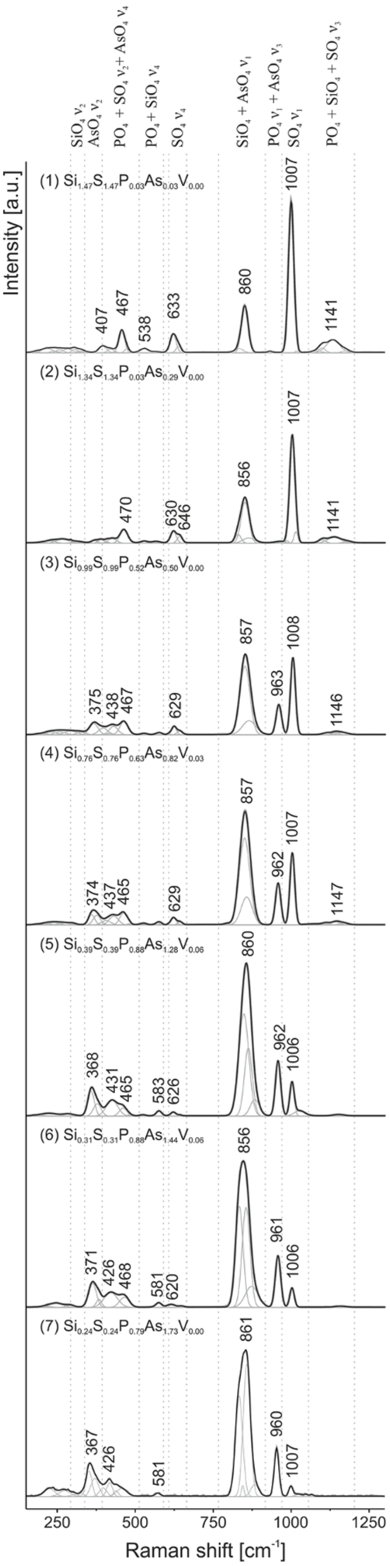

Figure 6. Raman spectra of the hydroxylellestadite–johnbaumite–svabite mineral series from xenolith no. 11, Upper Chegem Caldera, Kabardino-Balkaria, Russia.

with the AsO_4^{3-} ν_1 and ν_3 vibrations observed in the 750–900 cm^{-1} region (Baykal and Evren, 2006).

Confirming the presence of boron in the structure of cahnite and its structural coordination (tetrahedral, triangular, diboron, etc.) and assigning the vibration type to the B–O bond is challenging. Assuming the structural correctness of cahnite as reported by Prewitt and Buerger (1961), boron tetrahedrally coordinated by hydroxyl groups at each apex should exhibit both symmetric and asymmetric stretching vibrations of $B(OH)_4^-$ ν_1 (755 cm^{-1}) and ν_3 (947 cm^{-1}) as well as deformational bending modes ν_2 (374/394 cm^{-1}) and ν_4 (540 cm^{-1}) (Edwards *et al.*, 1955; Ross, 1972). There are only a few publications describing boron-phase minerals, making the interpretation and assignment of Raman bands problematic. Therefore, we have decided to correlate Raman spectroscopy data with infrared data to better understand the possible presence of boron in the structure of cahnite.

The interpretation of the IR spectrum proved to be somewhat more complicated due to the limited literature on boron-related phases, indicating that boron can also occur in non-protonated tetrahedral coordination, as evidenced by the symmetric stretching vibrations of the $[BO_4]$ group correlated to the band at 996 cm^{-1} (Balachander *et al.*, 2013). In addition, asymmetric stretching vibrations of hydroxylated tetrahedral boron coordination can be assigned to the band at 933 cm^{-1} (ν_3 $B(OH)_4$) (Ross, 1972). The infrared spectrum of cahnite also reveals the possible occurrence of boron in a triangular, spatially planar configuration, which contributes to the activation of two very intense bands at 1256 and 1303 cm^{-1} originating from the asymmetric and symmetric stretching vibrations of B–O bonds in the $[BO_3]$ units, respectively (Jun *et al.*, 1994; Balachander *et al.*, 2013; Shiraga *et al.*, 2002).

It is important to note that a polyborate anion, consisting of a BO_3 planar triangle and protonated or deprotonated BO_4 tetrahedra, may potentially exist. However, the vibrations within the BO_3 unit are Raman inactive. This theory could be confirmed by repeating single-crystal structural refinement, although this issue is not the subject of this article and will be developed in separate work.

Finally, the Raman and infrared bands observed between 3000–3500 cm^{-1} confirm the hypothesis about $B(OH)_4^-$ units. The Raman spectrum has shown a sharp, intense band at 3164 cm^{-1} and another low, intense band around 3400 cm^{-1}. The band at 3164 cm^{-1} in the Raman spectrum corresponds to a hydroxyl-related band reported by Shiraga *et al.* (2002) for the IR spectrum of cahnite. A similar value was observed in our IR spectrum (3170 cm^{-1}). According to Prewitt and Buerger (1961), this band is probably arranged in the hydrogen bonds (O_d–O_a = 2.795 Å), confirming the hypothesis of the presence of $B(OH)_4^-$. Another weak band around 3400 cm^{-1} is related to the sorbed hydroxyl groups or results from another internal interaction due to specific structural arrangements such as polyborate and arsenic units.

Datolite

The ToF-SIMS results revealed another boron-rich mineral in the mass of secondary minerals around cahnite, which, according to the EDS analyses, is a borosilicate with a Ca:Si ratio of 1:1. The ToF-SIMS distribution maps of boron indicate regions with significantly higher counts (greater intensity) compared to the cahnite phase, as demonstrated in Fig. 7c, d. The Raman spectrum obtained (Fig. 9) allowed this phase to be identified as datolite, $CaBSiO_4(OH)$. It forms small grains intergrown with low-temperature Ca-hydrosilicates (Fig. 7a, b).

The Raman spectrum of datolite from the Upper Chegem Caldera is almost identical to spectra for this mineral obtained from other localities (Frost *et al.*, 2013; Goryainov *et al.*, 2014;

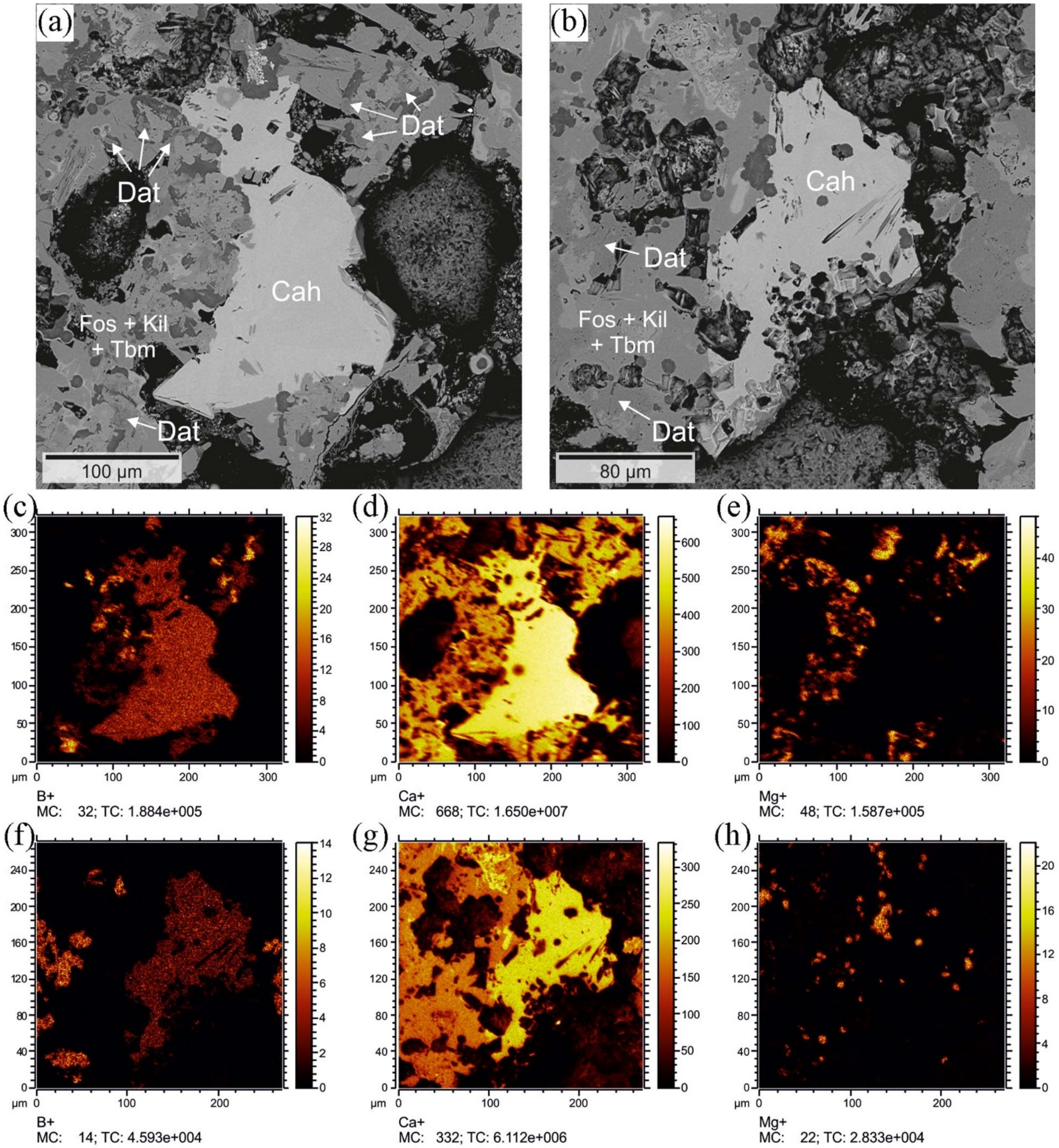

Figure 7. (a, b) BSE image of cahnite with datolite relic; (c, d, e) ToF-SIMS B, Ca and Mg images of cahnite grain and associated minerals in (a); (f, g, h) ToF-SIMS B, Ca and Mg images of cahnite grain and associated minerals in (b). Mineral abbreviations: Cah – cahnite; Dat – datolite; Fos – foshagite; Kil – killalaite; and Tbm – tobermorite.

Bailey *et al.*, 2019; Yoshida *et al.*, 2021). The main high intensity bands in the 600–1200 cm^{-1} range are associated with 'breathing' modes of four- and eight-membered rings (Goryainov *et al.*, 2014). Bands related to the symmetric and asymmetric B–O vibrations are assigned to bands at 918 and 983 cm^{-1}, respectively (Frost *et al.*, 2013; Bailey *et al.*, 2019). The bands associated with the symmetric and asymmetric modes of Si–O are assigned to bands at 1076 and 1174 cm^{-1} (Frost *et al.*, 2013; Bailey *et al.*, 2019). The 691 cm^{-1} band has been attributed to the deformational vibrations of tetrahedral B–O bonds (Frost *et al.*, 2013; Bailey *et al.*, 2019). The low intensity bands below 600 cm^{-1} are associated with the external modes of tetrahedra, rings and chains of silicate minerals (Goryainov *et al.*, 2014). The band at 3504 cm^{-1} is related to stretching vibrations of OH groups in datolite (Frost *et al.*, 2013; Bailey *et al.*, 2019).

Discussion

The members of the apatite supergroup minerals discovered in xenolith no. 11 within the Upper Chegem Caldera provide a unique

Table 2. Chemical composition of cahnite, cuspidine and hydroxyledgrewite from xenolith no. 11.

	Cahnite $n = 6$			Cuspidine $n = 7$			Hydroxyledgrewite $n = 8$		
	Wt.%	Range	S.D.	Wt.%	Range	S.D.	Wt.%	Range	S.D.
SO_3	1.64	0.60–1.90	0.77	n.d.	–	–	n.d.	–	–
P_2O_5	0.93	0.70–1.60	0.52	n.d.	–	–	n.d.	–	–
V_2O_5	0.52	0.00–2.04	0.98	n.d.	–	–	n.d.	–	–
SiO_2	1.33	1.04–3.92	1.36	32.60	32.27–33.33	0.31	31.01	30.62–33.76	1.01
As_2O_5	32.44	29.39–34.13	2.70	n.d.	–	–	n.d.	–	–
B_2O_3*	12.05	–	–	n.d.	–	–	n.d.	–	–
CaO	38.63	38.48–39.14	0.33	60.82	59.89–61.00	0.43	65.10	62.47–66.14	1.22
Cl	n.d.	–	–	n.d.	–	–	0.05	0.03–0.06	0.01
F	0.32	0.15–0.44	0.13	10.33	10.16–11.77	0.18	1.18	0.39–1.37	0.32
H_2O*	12.27			n.d.	–	–	1.76		
–O=F+Cl	0.13			4.35			0.51		
	100.00			99.41			98.58		
	Calculated on 4 cations			Calculated on 6 cations			Calculated on 13 cations		
S	0.06			–			–		
P	0.04			–			–		
V	0.02			–			–		
Si	0.06			2.00			4.00		
As	0.82			–			–		
B	1.00			–			–		
Ca	2.00			4.00			9.00		
Cl	–			–			0.01		
F	0.05			2.00			0.48		
OH	3.95			–			1.51		

Note: * – calculated on the basis of charge balance; S.D. – standard deviation; n.d. – not detected.

opportunity to study the effect of chemical composition in the Raman spectra, in particular, variations in the $SiO_4/SO_4–AsO_4$ ratio at the T site in the structure. Our study shows that even a small change in the occupancy of the tetragonal sites affects the shape of the Raman spectrum. Thus, it can be used as a preliminary non-destructive method to distinguish group members within the apatite supergroup. However, at present, a more precise assignment to a specific mineral species is not possible because of a lack of spectroscopic studies focusing on the effect of the occupancy of the X site in the structural channel on the shape of the spectrum, apart from a band appearing at 3568 cm^{-1} associated with the OH group vibrations. To be certain, further studies are needed on apatite supergroup minerals with equal occupancies within the T site but with different substitutions in the structural channels. Nonetheless, the data from this investigation have shown the occurrence of a solid-solution system between hydroxylellestadite, svabite and johnbaumite, which has not been described previously.

In view of the wide chemical diversity of the apatite supergroup minerals studied, it is necessary to consider the genesis of the mineral association presented in this paper. The first important issue is the source of arsenic and boron contained in the mineral paragenesis of calcium–silicate xenoliths from the Upper Chegem caldera. The research presented shows that the B and As contents in the minerals of xenolith no. 11 change with distance from the xenolith–ignimbrite contact. The highest contents of arsenic and boron were confirmed in the outermost, altered zone (III) adjacent to the ignimbrite. The central zone (I) of the xenolith is characterised by lower boron and arsenic contents (Fig. 3a, b; Table 1, #1–2).

Investigations of the mineral and isotopic composition of the ignimbrites from the Upper Chegem caldera and surrounding rocks show no evidence of pre-caldera volcanism (Gazis, 1995). The existence of extensive post-caldera hydrothermal alteration has been ruled out (Gazis, 1995). Instead it is postulated that boron and arsenic could either have been present in the protolith rocks prior to pyrometamorphic processes or were introduced into the system with the intrusion of rhyodacite lava. Boron is a readily leached element (Schmitt *et al.*, 2002) and is, therefore, generally removed from rocks during metamorphic processes (Palmer and Swihart, 1996). Considering this, and also the presence of boron in the outer zone of the xenolith, the presence of this element in the calcium protolith seems unlikely. On the other hand, ignimbrites are a proven carrier of boron and are commonly cited as a potential source of B for borate deposits (Alonso *et al.*, 1990; Floyd *et al.*, 1998). Woodford *et al.* (2001) also demonstrated that the formation of boron-rich skarn minerals is related to the magmatic source of this element. In addition to boron, volcanic rocks are common sources of arsenic (Murray *et al.*, 2023). In particular, rocks containing a significant amount of silica, such as rhyolites, dacites and ignimbrites, are characterised by a high arsenic content (Mazzuoli *et al.*, 2014; Murray *et al.*, 2023). It is worth noting, that arsenic is a volatile element and is a typical component of volcanic gases (Pekov *et al.*, 2018). Hence, it is possible to incorporate this element into metamorphic rocks with fluids associated with magma injection. In conclusion, it is reasonable to assume that ignimbrite was the source of boron and arsenic for the formed minerals within the Upper Chegem caldera xenoliths.

Another critical issue is the order of crystallisation of the apatite supergroup minerals. Given the occurrence of only one metamorphic episode associated with the rhyodacite intrusion, it can be assumed that all the minerals belonging to the apatite supergroup crystallised simultaneously. This theory is also supported by the co-occurrence of hydroxylellestadite and johnbaumite within

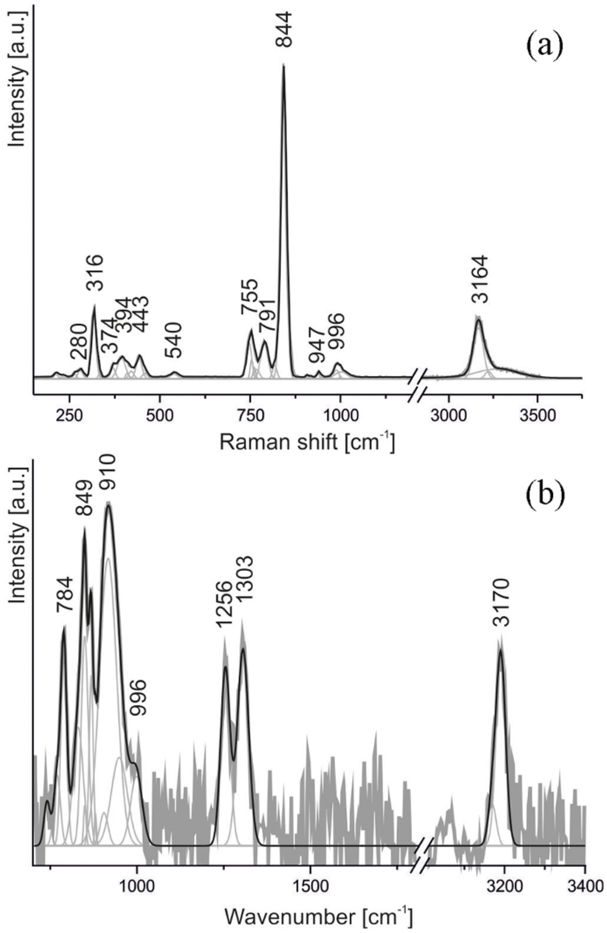

Figure 8. The Raman (a) and infra-red (b) spectra of cahnite obtained *in situ* in the sample from the Upper Chegem Caldera xenolith, Kabardino-Balkaria, Russia.

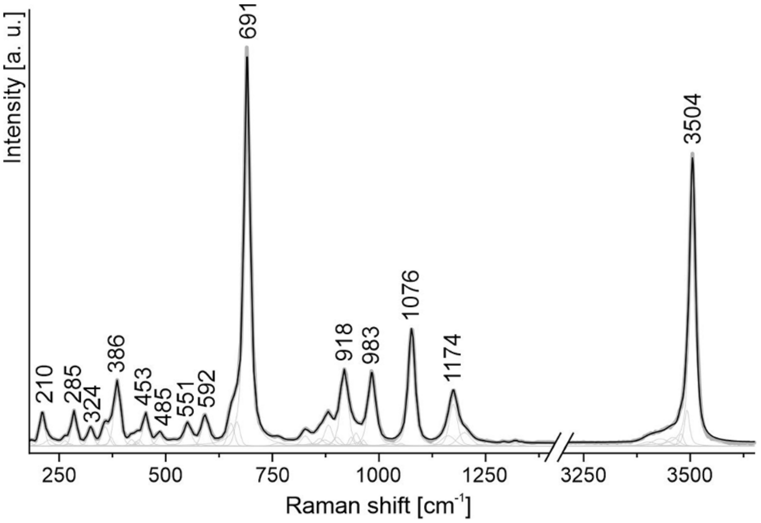

Figure 9. Raman spectrum of datolite from xenolith no. 11, Upper Chegem Caldera, Kabardino-Balkaria, Russia.

the cuspidine veins. These crystallise as aggregates composed of independent individuals with different chemical compositions. If johnbaumite was related to the alteration of hydroxylellestadite, crystals with zoning associated with different levels of arsenic in the structure would be formed. However, we are presented with mostly homogeneous crystals in terms of chemical composition. The presence of cahnite in the mineral association is also noteworthy. Shiraga *et al.* (2002) suggest that cahnite is a secondary mineral formed by hydrothermal alteration of johnbaumite. Given the co-occurrence of cahnite and svabite in the xenolith from the Upper Chegem Caldera, we can exclude the possibility that this mineral formed as a secondary phase that developed after the apatite supergroup minerals in this case. Alternatively Helvaci (2015) reports that cahnite forms as a secondary mineral after the low-temperature mineral colemanite, due to diagenetic alteration and that other B-bearing minerals can also be precursors of cahnite. In our investigation the occurrence of datolite relics in the vicinity of cahnite suggests that datolite was the parent mineral for cahnite. The explanation for the genesis of datolite is more problematic, as it can occur in a wide range of geological environments (Goryainov *et al.*, 2014).

Supplementary material. The supplementary material for this article can be found at https://doi.org/10.1180/mgm.2024.87.

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