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Typomorphic features of amazonitic K-feldspar from the Keivy granitic pegmatite (Kola Peninsula, Russia)

Mikhail Ostrooumov¹ and Arun Banerjee²

Abstract

This work characterizes the typomorphic features, i.e. crystal chemical and spectroscopic parameters, of different amazonite generations from Precambrian granitic pegmatite (Western Keivy, Kola Peninsula, Russia). The crystals of various generations and colors (blue, greenish-blue and green) were investigated using X-ray fluorescence and X-ray diffraction, UV-VIS-NIR, infrared spectrometry, electronic paramagnetic resonance (EPR), UV-fluorescence, heating and irradiation experiments. From the peripheral zones to the central part of the pegmatite, amazonite changes its composition systematically in terms of some major (e.g., K₂O) and trace components (e.g., Rb, Cs, Pb, H₂O) can be seen to increase in the amazonite samples. The later generations of amazonite contain the maximum concentrations of U (23 ppm) and Th (67 ppm). The amazonites are characterized by a high degree of Al/Si order. All the parameters obtained from X-ray diffraction (Δr , $\Delta t > 0.9$) as well as optical microscopy ($2V > 80^\circ$) show that the studied amazonites belonged to the maximum ordered microcline. The nature of the amazonite color is explained by the presence of hole-electron centers of Pb and Al and structural centers of ^{IV}Fe³⁺ that cause the corresponding absorption bands of 380 nm (Al – O⁻ – Al; Fe³⁺), 625 nm (Pb⁺) and 740 nm (O⁻ – Pb) in the UV-VIS-NIR spectra. The EPR spectra show that the signals of Pb centers disappear at the same time as the absorption of characteristic bands after heating: hole Pb centers at approximately 280 °C, and electron Pb centers at 450–500 °C. The colors of all the treated samples were intensified by irradiation because of the formation of Pb and Al hole centers. After X-ray irradiation the intensities of the bands at 740 nm and 380 nm increased. The most typical features of the amazonitic K-feldspar in the Precambrian pegmatite are seen in the UV-VIS-NIR and EPR spectra and are related to the form of electron-hole paramagnetic centers. The crystal chemical and spectrometric parameters of amazonite may be important for the exploration of diverse deposits of rare metals and REE mineralizations and their economic evaluation.

Keywords: typomorphic features, amazonitic K-feldspar, Precambrian pegmatite.

1. Introduction

Amazonite (amazonstone) is one of the minerals, which has attracted the attention of mineralogists for generations. Among the scientists that have investigated amazonite are many famous geologists and mineralogists, including A. des Cloiseaux, Nikolay Kokcharov, Vladimir Vernadsky, Victor Goldschmidt, Aleksandr Fersman. It is curious that half a century ago, amazonite was considered to be a very rare mineralogical variety of the potassium feldspar species. According to recent data (Ostrooumov, 1991), amazonite has been found on every continent (except Antarctica).

The rich blue-green colors of amazonite have been the object of investigation by mineralogists and geologists, which began over 200 years ago

(Ostrooumov, 1982a). Among many hypotheses attempting to explain the cause of this specific color, none takes into account all of the crystal chemical peculiarities of amazonitic K-feldspar. The hypothesis of a relation between the color of amazonite and the incorporation of Pb is today the most widely recognized (Marfunin and Berschov, 1970; Hofmeister and Rossman, 1985; Ostrooumov et al., 1989). On the other hand, the color has been linked to the incorporation of Fe and molecular H₂O, and the degree of Al/Si order in the feldspar structure (Ostrooumov, 1991). These factors do not exclude one another but rather complement each other. It is clear that the color of amazonite is affected by a number of parameters, which reflect the great variation in the chemical and structural peculiarities of this variety of potassium feldspar.

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During the last few decades, geologists and mineralogists have discussed the use of amazonite in the exploration for deposits of rare metals and REE, and there are different (both positive and negative) opinions regarding this problem. From our point of view, the correct response to all of this discussion is to be found in the detailed characterization of the geological setting of the amazonite, as well as in the proper investigation of its chemical composition, structural features and properties with respect to each genetic type of granite. According to our data, the distinctive features of the chemical composition, structure and properties of amazonite depend on the conditions of its geological, petrological and geochemical origin (Ostrooumov, 1989, 1991). For this kind of study, the mineralogists of the Russian scientific school have proposed the term "typomorphic features" of minerals (Typomorphism of Minerals, 1989).

At present, more than one hundred large amazonite deposits have been located, and there are many lesser-known deposits. The deposits of this mineral were formed in various genetic types of granites, including different pegmatites, aplites, hydrothermal veins, and in sub-volcanic rocks. All are characterized by their unique geological setting. The geological age of these amazonite formations varies from Pre-Cambrian (1800–2000 Ma) to Mesozoic (60–70 Ma). Pegmatites of Paleocene age (approximately 40 Ma) containing amazonite, however, occur in the Eastern Alps

(Makart and Preisinger, 1965). The amazonite-bearing pegmatites linked to the formation of alkaline granites are the oldest (Precambrian) and occur in the deepest crustal levels, whereas the Mesozoic F–Li granites are younger and at shallower levels. Ostrooumov (1989) has shown that the oldest amazonites are clearly distinguishable by a more intense and richer color and only occur in Precambrian pegmatites.

The purpose of this work is to characterize the typomorphic features, i.e. the crystal chemical and spectroscopic parameters of different amazonite generations, formed in association with the rare-metal and REE mineralizations in a Precambrian pegmatite of Western Keivy (Kola Peninsula, Russia).

2. Geological Setting

In the late 1920s, a large vein of alkaline magmatism was opened in the central part of the Kola Peninsula, Russia (Fig. 1a), and a genetic connection was postulated between the massif of alkaline granites and the fields of amazonite pegmatites (Batieva, 1976; Ostrooumov, 1989). The biggest field is West Keivy, where two large alkaline plutons can be distinguished, one in the North and one in the South (Fig. 1b). Albite–microcline pegmatites are situated in the nearest part of the contact aureole, whereas amazonite pegmatites are situated farther from the alkaline massif.

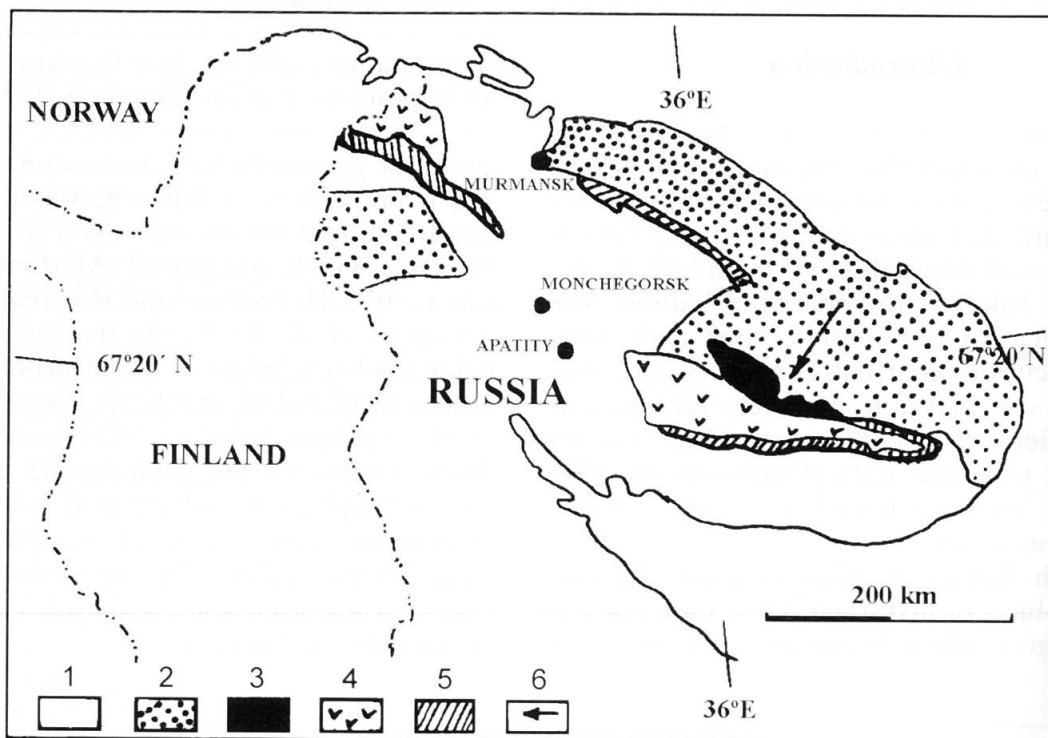


Fig. 1a Map of the Kola Peninsula in Russia showing the location of Keivy pegmatite field: Archean (1—undifferentiated, mainly Archean, 2—Granite, Gneiss); Proterozoic (3—alkaline granites; 4—volcanics, 5—sediments; 6—Keivy pegmatite field).

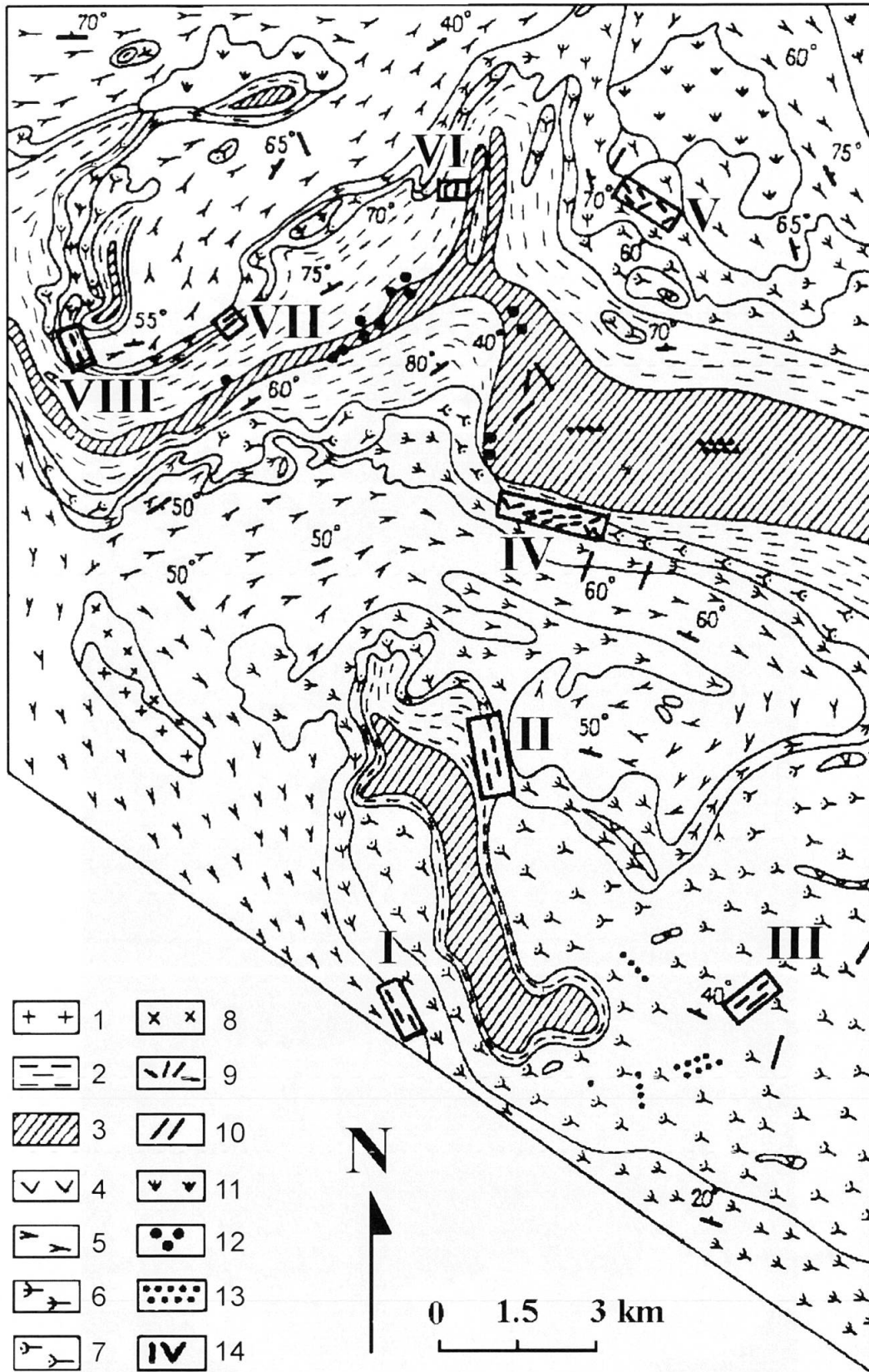


Fig. 1b Geological map showing the granitic pegmatites and alkaline granites of West Keivy, Kola Peninsula, Russia. Modified from by Batiyeva (1976). Symbols: 1— Archean granites; 2-8 — Proterozoic: 2— gneissic complex, 3— schist complex, 4— amphibolites, 5— alkaline granites, 6— alkaline granite-gneiss, 7— metasomatite gneiss, 8— alkaline syenite, syenites, 9— REE albite-microcline and albite-amazonite pegmatites, 10— diabase dikes, 11— Quaternary deposits, 12— muscovite pegmatites, 13— quartz veins, 14— pegmatite fields: I-III— fields of differentiated amazonite pegmatites; IV-VIII— fields of non-differentiated amazonite pegmatites. The Ploskaya pegmatite body was found in field III.

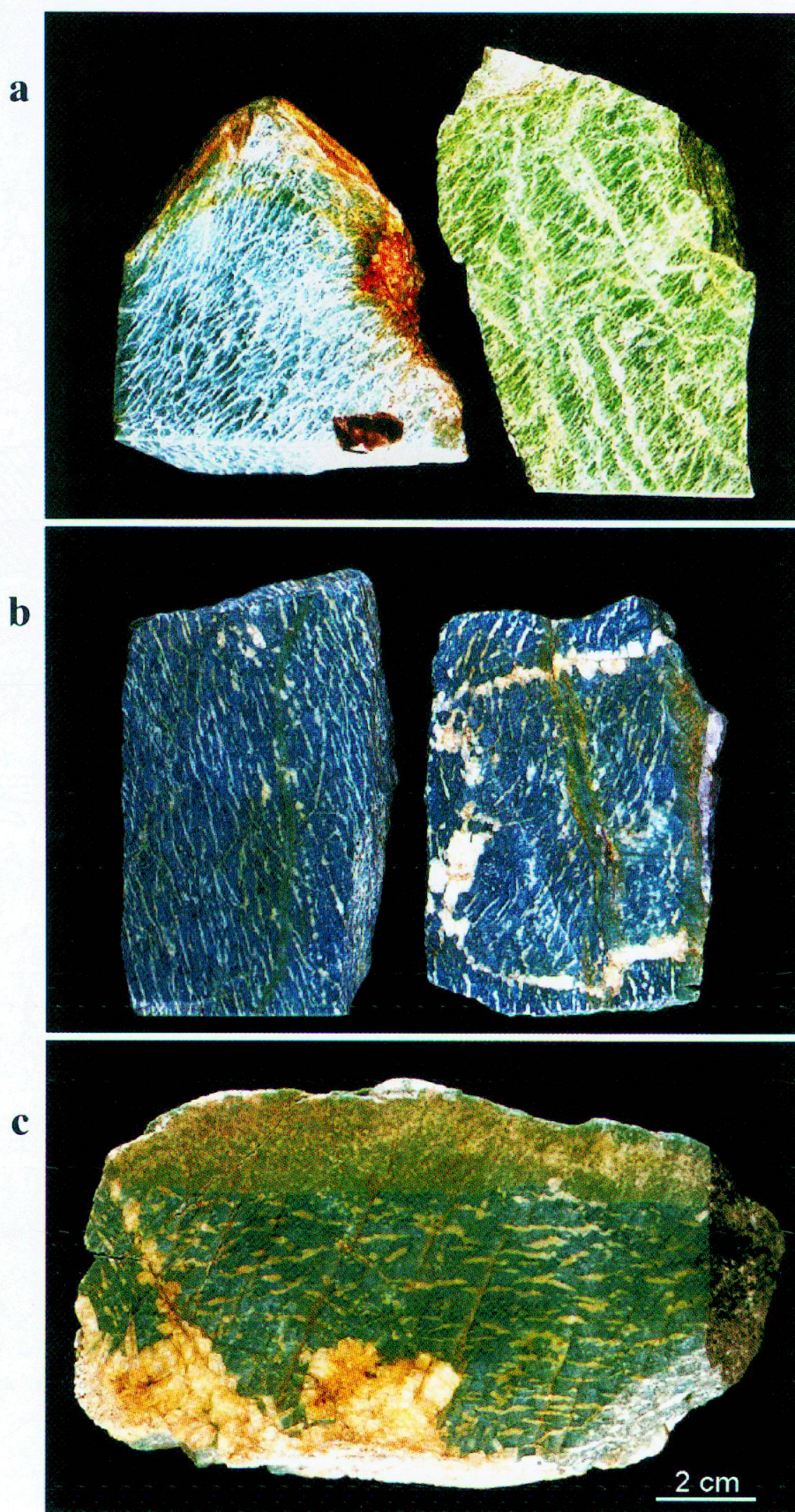


Fig. 2 Different generations of amazonite with cross-cutting relationships, revealing their relative age: (a) blue (generation I) and green (generation III) amazonite; (b) bluish-green amazonite (generation II) is younger than the blue amazonite of generation I; (c) green amazonite (generation II) cross-cuts the bluish-green amazonite of generation 2.

Batieva (1976) showed that the pegmatite formations are divided into two groups occurring in eight fields differentiated (I–III) and non-differentiated (IV–VIII).

Within these pegmatites, 75 mineral species have been identified, presenting almost all the crystal chemical classes (Voloshin and Pakhomovsky, 1986; Ostrooumov, 1989). The most common minerals are amazonite, microcline, albite, biotite, zinnwaldite, and quartz. The accessory minerals include Ta and Nb oxides as well as REE silicates and phosphates. In these pegmatites, various stages of formation have been established (Na-metasomatism or albitization, amazonite formation, and fluorite deposition), all of which are associated with various types of rare-metal and REE mineralizations (Table 1). For example, the Albitization II and Amazonite II stages are characterized by Nb–Ta mineralization, and the Fluorite II stage by REE mineralization.

Amazonitic K-feldspar showing different colors (blue, bluish green and green) has been discovered by Ostrooumov and Musina (1975) in the Ploskaya pegmatite body in West Keivy in the Kola Peninsula, Russia (Fig. 1b: field III). The Precambrian mica-gneiss is cross-cut by this pegmatite body.

This differentiated pegmatite body, was chosen in order to investigate the evolution of amazonite in terms of chemical composition, structure and color. In the Ploskaya pegmatite body all K-feldspars are amazonites, and they are associated with albite, quartz and micas (biotite, zinnwaldite). Typical accompanying minerals are plumbopyrochlore, plumbomicrolite, manganocolumbite, fergusonite, gadolinite, uraninite, thorite, zircon, cassiterite, fluorite and galena.

The pegmatite body is zoned, fairly large (~ 20 m thick, 200 m long), and consists of albite–oligoclase with quartz and amazonite. In the peripheral zone, the pegmatite is coarse-grained and contains a small amount of amazonite. Towards the interior, it is characterized by an extremely coarse-grained texture with generally blocky amazonite crystals, which are up to 2 m across and amounting to more than 90 vol%. The central zone consists mainly of a quartz nucleus and blocky K-feldspar amazonite. It is possible to distinguish on the basis of color three generations of amazonite between the peripheral and central zone: green amazonite is the nearest to the center, the lateral areas consist of blue amazonite, and bluish-green amazonite occurs in between. Our field observations (Fig. 2 a–c) show that the green amazonite (generation III) is younger than the bluish-green (generation II) or the blue varieties (generation I).

3. Sampling and Analytical Methods

The samples of amazonite with differing colors were all collected from the Ploskaya pegmatite body. The thickness of the samples was approximately 0.05 mm. The samples were ground and polished for further study.

To characterize the samples crystal chemically and spectrometrically the following analytical techniques were used at the National University of Mexico, the Universität Mainz in Germany, and at the University of Nantes in France. Chemical analyses were obtained by X-ray fluorescence (XRF). Major elements were determined on fused glass disks. These were prepared by mixing 0.8 g of “dry basis” sample powder with 7.2 g of $\text{Li}_2\text{B}_4\text{O}_7$ - LiBO_2 flux mixture (50:50 wt%). The non-wetting agent used was an LiBr solution in water (two drops with a concentration of 250 g/L). The mixture was poured into a crucible (95% Pt–5% Au), and heated to about 950 °C in a furnace with space for three crucibles for the simultaneous preparation of glass disks. Trace elements were analyzed in powder pellets prepared by mixing thoroughly 6 g of sample powder with wax-C (Hoechst) added as a binding agent. Major and trace elements were analyzed in a sequential spectrometer BRUKER SRS3000, with an end window Rh target. To date, we have analyzed 15 amazonite samples (5 samples of each of the three generations). For the detailed crystal chemical and spectroscopic investigation we have chosen the sample that is located in the center of each pegmatite zone (Tables 2, 3).

The structural parameters of the amazonite powder was identified by X-ray diffraction (XRD) using a Siemens D5000 diffractometer equipped with filtered $\text{CuK}\alpha$ radiation; scanning was set at $0.1^\circ 2\theta/\text{min}$ over the range 3 to $70^\circ 2\theta$. The Al/Si distribution in tetrahedral sites of amazonite feldspars (occupancy of Al in the $\text{T}_{1(\text{o})}$, $\text{T}_{1(\text{m})}$, $\text{T}_{2(\text{o})}$, and $\text{T}_{2(\text{m})}$ sites) was based in determination of the b and c unit-cell dimension as well as the angles α and γ .

This method uses the d-spacing of the $\bar{2}01$, 111, $\bar{1}\bar{1}1$, 130, $\bar{1}30$, 220, $\bar{2}02$, 131, $\bar{1}31$, $\bar{1}32$, 060, 400, and $\bar{2}04$ peaks (Stewart and Wright, 1974; Sosedko, 1976; Altaner and Kamentsev, 1995). The Al content in different T-sites was calculated according to the following equations:

$$\begin{aligned} \text{Al}_{\text{T}_{1(\text{o})}} &= \text{Al}_{\text{T}_{1}} + [\text{Al}_{\text{T}_{1(\text{o})}} - \text{Al}_{\text{T}_{1(\text{m})}}]/2 \\ \text{Al}_{\text{T}_{1(\text{m})}} &= \text{Al}_{\text{T}_{1}} - \text{Al}_{\text{T}_{1(\text{o})}} \\ \text{Al}_{\text{T}_{2(\text{o})}} &\approx \text{Al}_{\text{T}_{2(\text{m})}} \end{aligned}$$

Two samples of homogeneously colored material of each of the three above-mentioned color varieties were chosen for the spectroscopic study

Table 1 Stages and types of mineralization in Precambrian pegmatites.

Stages of mineralization	Types of mineralization
Na metasomatism or Albitization I Amazonite formation I (blue, generation I)	Monazite $Ce PO_4$ Thorite $ThSiO_4$ Zircon $ZrSiO_4$ Gadolinite $Y_2FeBe_2Si_2O_{10}$ Fergusonite $YNbO_4$ Manganocolumbite $MnNb_2O_6$
Fluorite deposition I	Monazite Bastnäsité $CeCO_3F$ Xenotime -(Y) Aeschynite $Y (Ti,Nb)_2 (O,OH)_6$ Euxenite $YTiNbO_6$
Na-metasomatism or Albitization II Amazonite formation II (bluish-green and green, generations II and III)	Plumbopyrochlore $(Pb,Y,U,Ca)_{2-x} Nb_2O_6 OH$ Plumbomicrolite $Pb (Ta_{1.5} Nb_{0.5}) O_6$
Fluorite deposition II	Xenotime-(Y) Bastnäsité Keiivite-(Y,Yb) Vyuntspakhkite-(Y) Hingganite-(Y,Yb)
Low-temperature hydrothermal process	Native Bi (Ostrooumov, 1981; Voloshin, Pakhomovsky, 1986) Galena PbS Wulfenite $PbMoO_4$

in the laboratory. The UV-VIS-NIR polarized absorption spectra of natural amazonites were recorded from 350 nm to 850 nm by a Lambda 3 UV-VIS Perkin-Elmer spectrophotometer equipped with an integrating sphere. The diameter of the analyzed area was approximately 5×10 mm. Deconvolution of the bands was achieved by the GRAMS software and by applying the FFT Self-Deconvolution technique.

Infrared spectrometry (IR) was performed in order to determine the vibrations of H_2O molecules, hydroxyl groups, ionic substitutions and local bonds in the structure. The IR spectra of natural amazonite were measured by an FTIR Nicolet 20 SXC spectrometer, scanning from 4000 to 400 cm^{-1} and using the KBr pellet method. The pellets were prepared by mixing approximately 3 mg of the sample with 300 mg KBr. The FTIR- reflectance spectra of the samples were obtained with an FTIR-Perkin-Elmer 1760 spectrophotometer equipped with an accessory for specular reflectance measurement.

Electronic Paramagnetic Resonance (EPR) spectra were taken at room temperature and 78 K using a Bruker ERD 200 spectrometer at about 9.3 GHz. The EPR spectra were measured for each single crystal of the two principal amazonite color-types (blue and green) and for samples that had first been heated and then irradiated. The

EPR samples had the approximate dimensions of $3 \times 5 \times 7$ mm.

The UV-fluorescence spectra of the samples were measured by a Fluorescence - Spex F 212 - spectrophotometer. In each case the excited wavelength was 290 nm.

Heat treatment of the samples was carried out in an electric furnace between 200–500 °C in air and with heating times of between 0.5 and 10 h. In order to correlate loss of the EPR signals and the amazonite absorption bands, systematic heating and irradiation experiments were carried out at the same condition as those of Ostrooumov et al. (1989) using three color-type amazonite crystals from each of the different generations. Heating occurred in steps of 10 °C, with a 15-minute heating time at each step.

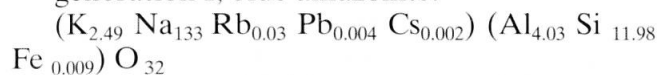
The samples were irradiated at room temperature with X-rays produced with a filament current of 30 mA and a Mo target at an acceleration potential of 80 kV. Typical radiation times were 30 minutes. One sample of each color served as a reference and was not treated, whereas the other samples underwent irradiation. The changes evidenced in the samples by heating and X-ray irradiation were investigated by EPR, UV-Fluorescence UV-VIS and FTIR transmission spectroscopy, and by comparing the spectra of the treated samples with those of the untreated samples.

4. Results

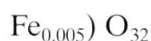
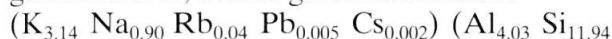
4.1. Chemical Composition

The chemical composition of amazonite changes within wide limits, but displays a distinct compositional evolution (Table 2). From generations I to III, the K₂O contents increase from 10.8 to 14.6 wt%, whereas the concentration of Na₂O decreases from 3.8 to 1.53 wt%. The range of the main components was 63–87 mol% orthoclase and 13–38 mol% albite. Several minor and trace elements were detected, including Pb, Rb, Cs, U and Th. The highest Pb concentration was found in the late green generation (up to 1.2 wt% PbO). The average concentrations of U (12.5 ppm) and Th (27.2 ppm) considerably surpass the average for these elements in other types of the microcline in pegmatites (Krivokoneva and Karaeva, 1989). The following crystal chemical results were obtained from different generations of amazonites:

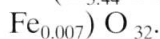
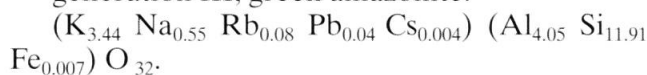
generation I, blue amazonite:



generation II, bluish-green amazonite:



generation III, green amazonite:



These data clearly show that the chemical composition of amazonite is different in the different generations and thus, zones within the pegmatite body. In summary, the concentrations of K₂O, Rb₂O, Cs₂O, PbO, Tl, Ga, Sr increase from the periphery to the central zone of the pegmatite, whereas the contents of Al₂O₃, Na₂O, Fe₂O₃ and Ba decrease. Moreover, the later generations of amazonite are enriched in U (23 ppm) and Th (67 ppm) compared to the earlier generations as well as to microcline without amazonite color (Tijomirova, 1973; Ostrooumov, 1989). The chemical trends described for amazonite are also reflected by the associated rare metal and REE minerals in the pegmatite (Table 1).

4.2. Structural characteristics

In the studied pegmatite body, the structural state of amazonites of different color is characterized by a high degree of Al/Si order in the structure. All the parameters obtained from X-ray diffrac-

Table 2 Chemical analyses of different generations of amazonite (oxides in wt%, elements in ppm).

Pegmatite Zone	Blue amazonite (generation I) ^a	Bluish-green amazonite (generation II) ^a	Green amazonite (generation III) ^a
	Peripheral	Intermediate	Central
SiO ₂	66.20	65.53	64.44
Al ₂ O ₃	18.9	18.8	18.6
Fe ₂ O ₃	0.07	0.06	0.04
K ₂ O	10.8	13.5	14.6
Na ₂ O	3.80	2.56	1.53
Rb ₂ O	0.23	0.34	0.69
Cs ₂ O	0.022	0.036	0.058
LOI	0.009	0.012	0.034
PbO	0.09	0.12	0.79
Or (mol%)	65.1	77.6	86.2
Ab (mol%)	34.8	22.3	13.7
U	4	12	23
Th	8	32	67
Tl	12	75	150
Ga	30	94	145
Ba	200	115	17
Sr	30	124	210
Colorimetric parameters			
l, nm ^b	491	500	522
P %	22	17	17
Y %	33.1	29.4	27.1

^a Individual analysis of the amazonite samples with characteristic typomorphic features located in the center of each pegmatite zone.

^b Parameters in the International Commission of Illumination (ICI) color measuring system (λ - dominant wavelength; P - saturation; Y - lightness).

tion ($\Delta r_{131, \bar{1}31} > 0.95$, $0.9 < \Delta t < 1.0$), as well as the optical microscopy ($2V > 80^\circ$), showed that the studied amazonites belonged to the maximum ordered microcline (Ostrooumov, 1982b). In amazonite with well-ordered distribution of Al/Si over the four non-equivalent tetrahedral positions, nearly all Al atoms are located at $T_{1(o)}$ and nearly all Si atoms at $T_{1(m)}$, $T_{2(o)}$, and $T_{2(m)}$. According to the interpreted data, none of the diffractograms showed the mixture of triclinic and monoclinic modification (including varieties with higher concentrations of Rb and Cs). In other words, all of the amazonite generations contained only one triclinic K-dominant phase. At the same time, the green stage-III amazonite generation clearly has a lower degree of structural disorder. The values of $\Delta r_{131, \bar{1}31}$ and Δt for these generations are always smaller in comparison with the earlier generations I and II (Table 3). From these data we conclude that the high concentrations of rare alkaline elements and Pb lead to a decreasing degree of Al/Si disorder. A monoclinic phase is absent in the amazonite-perthite.

Table 3 shows the structural and unit-cell parameters of amazonite before (sample 241, blue; sample 293, green), after heat treatment (corresponding samples, but with white bleached color), and after irradiation (sample 241, pale blue; sample 293; grey white). The data demonstrate that there is no change in the structural state (degree of Al/Si order/disorder) of amazonite during heating up to 500 °C, but that heating is accompanied by the disappearance of the specific color. It should be noted that in other genetic types, amazonites can be found with a relatively high structural disorder (even in the monoclinic feldspars containing the characteristic green color).

We conclude that the main impurity elements that form the electron and hole centers of color are not related to the structure of the Si–Al framework, and that they are located in the empty parts of the lattice in the positions of alkaline cations. The low intensity of the amazonite color with a high degree of Al/Si disorder is, as a rule, found in the early generations of high temperature in certain granitic Mesozoic bodies, such as those from the area of Zabaikalie, Siberia, or pegmatitic deposits of younger age from the Alps (Ostrooumov, 1989). This clearly explains the relatively low concentrations of impure elements and the color centers.

4.3. UV-VIS Spectroscopy

The UV-VIS-NIR polarized absorption spectra of natural amazonites show at least two characteristic bands (Fig. 3). The first is in the short-wave domain with a maximum at ~380 nm in the nearest ultraviolet (UV) region. The second is a long-wavelength band in the visible region between 625 and 740 nm. The band in the visible range is more characteristic of amazonite. Because of this the current hypothesis regarding shades of amazonite color (from clear blue to intense greenish-blue and different shades of green) depends on the relation between the relative intensities of the ultraviolet and visible spectrum bands. In the absorption spectra all bands are strongly polarized in the b direction, perpendicular to (001), and weakly polarized in the a direction, perpendicular to (010).

In the literature, the presence of the visible band has been explained by the presence of electron-hole centers of Pb^+ or Pb^{3+} (Marfunin and Bershov, 1970; Hofmeister and Rossman, 1985),

Table 3 Structural and unit-cell parameters of amazonite.

Sample	Color	Structural state		Distribution in tetrahedral positions			Unit-cell parameters of amazonitic K-feldspar						
		Δr^a	Δt^b	$T_{1(o)}$	$T_{2(m)}$	$T_{2(o)} - T_{2(m)}$	a (Å)	b (Å)	c (Å)	V	α	β	γ
241	Blue	1.00	0.98	0.99	0.01	0.00	8.597	12.955	7.218	721.73	90.5	116.0	87.8
241 (heated)	White, Bleached	0.96	0.96	0.97	0.01	0.01	8.595	12.974	7.218	723.16	90.8	115.9	87.5
241 (irradiated)	Pale blue	0.96	0.99	0.96	0.02	0.01	8.593	12.971	7.218	723.09	90.7	116.0	87.6
293	Green	0.96	1.00	0.97	0.01	0.01	8.594	12.971	7.221	723.23	90.9	115.9	87.6
293 (heated)	White Bleached	0.94	0.98	0.96	0.02	0.01	8.600	12.971	7.219	723.83	90.7	116.0	87.6
293 (irradiated)	Grey white	0.96	0.96	0.99	0.01	0.00	8.602	12.966	7.218	722.59	90.5	116.0	87.8

^a $\Delta r_{131, \bar{1}31}$; the degree of Al/Si order according to Goldsmith and Laves (1954).

^b $\Delta t = T_1 - T_2$; the degree of monoclinic order according to Stewart and Wright (1974), Krivokoneva and Karaeva (1989), and Altaner and Kamentsev (1995).

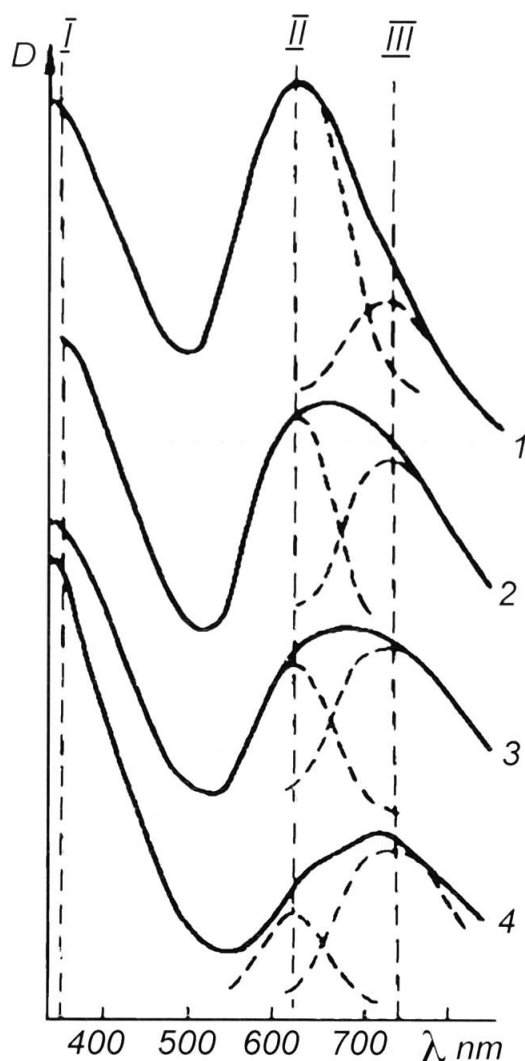


Fig. 3 UV-VIS-NIR spectra of the studied amazonite samples. Measured spectra shown by solid lines, deconvoluted spectra shown by dashed lines. Symbols: 1—blue; 2 and 3—bluish-green; 4—green amazonite variety.

or by the combination of various electron-hole centers and isomorphous impurities (Ostrooumov et al., 1989). At the same time, in the literature there was no interpretation of the nature of the band with the maximum in the nearest UV region.

The main absorption band in the visible range changes its position according to observed color and specific color shade of amazonite. By applying the FFT Self-Deconvolution technique (Griffiths and Pariente, 1986) we were able to resolve two principal peaks between 600 and 750 nm, which compose the main characteristic absorption band in the spectra of natural amazonite. We established that the apparent shift of this main band from 625 in blue amazonite to 740 nm in green amazonite is due to intensity redistribution between those spectral constituents. In Fig. 3 the deconvoluted spectra (dashed lines) are shown, which correspond to the raw spectra of different

amazonite generations. If we assume that this large asymmetric and intense absorption band could be a spectral area of some elemental components, we can show that two Lorentzians would be enough to correctly describe the experimental spectrum that was obtained. Analyzing in greater detail the spectra of different amazonite colors reveals that the main absorption band is characterized by a complex structure which, in reality, is a superposition of the two absorption bands at ~625 and ~740 nm (Fig. 3). The maximum displacement of this complex zone corresponds to a variation in the relative intensities of these two absorption components.

The color of the amazonite and its two principal different shades were determined, in the first place, by the existence of centers of colors which provoke two absorption bands in the region of 625 to 740 nm. We must point out that the second absorption band at ~740 nm is the main band in the visible spectrum of the green amazonite, whereas the band of approximately 625 nm always prevails in the spectrum of blue amazonite.

It is well known (Platonov et al., 1984; Ostrooumov et al., 1989) that the color of amazonite changes in the case of a specific X-ray irradiation treatment or by heating within the interval of 250–500 °C. After irradiation, the studied samples of different colors showed that the characteristic band at 740 nm has a greater intensity than the non-irradiated samples, as the 625 nm band decreases in intensity. As a consequence, the maximum band of the two components is displaced towards longer wavelengths. Heating to 270–280 °C over the time span of an hour provokes the disappearance of the 740 nm and changes the color to blue-grey. After this the color does not change if heating at these temperatures continues. In the case of heating of up to 450–500 °C for 1.5 to 2 hours, the blue color and the 625 nm band disappear.

The band with its maximum at approximately 380 nm is also characterized by a complex nature. In this zone, the bands have absorption characteristics of oxides and hydroxides of Fe, of hole centers of Al, and of structural centers of $^{IV}Fe^{3+}$. Chemical analysis and EPR spectra confirm the presence of all these elements in amazonites (Ostrooumov et al., 1989). This band is typical in the spectrum of many alkaline feldspars: microclines (yellow, pink and red), orthoclase (yellow), and natural and irradiated grey sanidines. It is probable, that the structural centers of Fe^{3+} may participate also in the formation of exchange-linked $Pb^{2+}-O-Fe^{3+}$ complexes causing a strong intensity increase of the transition ${}^6A_1 \rightarrow {}^4T_1$ in Fe^{3+} ions substituting Al at $T_1(0)$ positions.

The two bands, both in the visible red-orange region and in the near-UV region, contribute to the different colors of amazonite. We conclude that the color of the amazonite, and even more so its different shades, are determined by three centers of color, provoking various zones of absorption in the experimental spectrum of this variety of potassium feldspar.

4.4. EPR Spectrometry

Marfunin and Bershov (1970) first reported EPR spectra of amazonite taken at 9.3 Ghz and 78 K. An electron center ascribed to Pb^+ was observed only in amazonites. The spectrum consisted of a central line with two hyper-fine structure lines, which can be described with a spin Hamiltonian

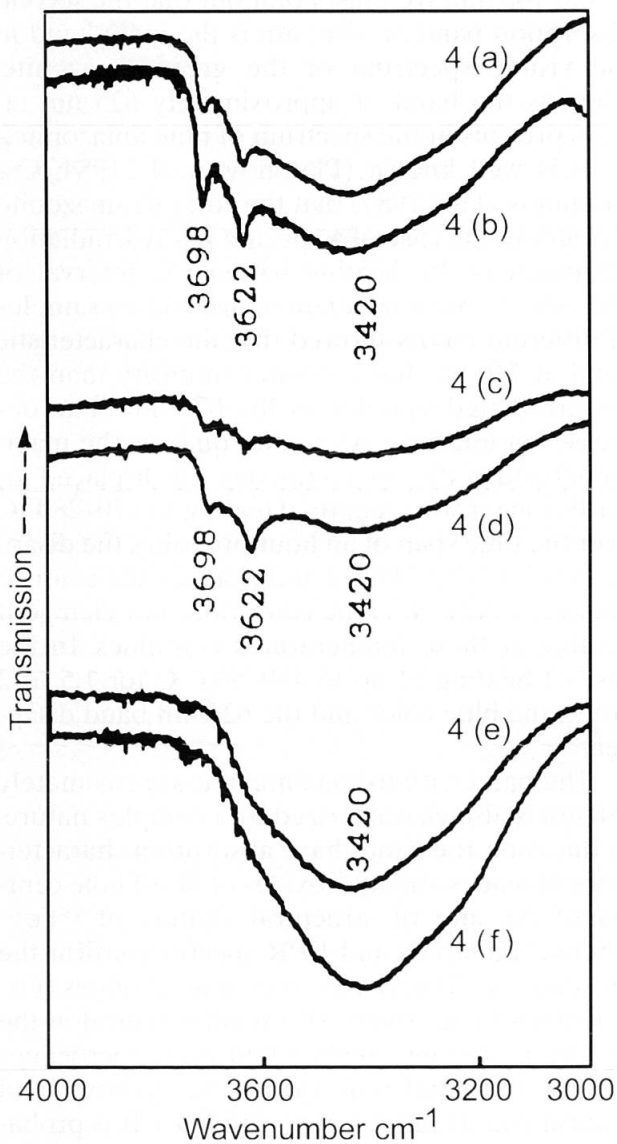


Fig. 4 IR-transmission spectra of amazonite showing changes of the OH-stretching vibrations before (b,d,f) and after (a,c,e) irradiation: (a), (b) = green amazonite; (c), (d) = bluish green amazonite; and (e), (f) = blue amazonite.

with orthorhombic symmetry and a g-factor of 1.390, 1.565 and 1.837. The amazonite was heated to 400–500 °C for several hours until it lost its characteristic color and Pb^+ spectrum. The EPR spectrum ascribed to Fe^{3+} was unchanged by heating. These authors concluded that the color of amazonite results from Pb^+ produced by the substitution of Pb^{2+} for K followed by the capture of an electron. The change of color and the formation of defect centers in different feldspars (including one amazonite) after X-ray irradiation have been investigated using EPR spectroscopy by Speit et al. (1982) and by Hofmeister and Rossman (1985). Recently, using EPR, two non-equivalent Pb ions in an amazonite-type microcline structure were indicated (Petrov et al., 1993). The problem is that in these publications there has been no explanation for the difference between EPR signal and the color of the two principal generations (blue and green) of amazonite.

EPR spectra of the amazonite varieties show some characteristic lines in the two zones between 5000–3500 Gauss and 3400–3200 Gauss. The same peaks appear systematically in the spectrum of the studied samples. The associated paramagnetic centers are shown in Table 4. Starting from principal values of the g-factor at the center I allowed to attribute the peaks to a Pb^+ electron center as described above. Center II was interpreted as a result of an $O^- - Pb$ hole type center by Marfunin and Bershov (1970), and Speit and Lehmann (1982). The axis of the g-tensor of these two centers is in parallel. The Center II disappeared in a heating process of up to 280 °C for 1–1.5 hours. Resonance attributed to a Pb^+ electron center was most common in the blue variety of amazonite (generation I), whereas an $O^- - Pb$ hole center is more typical for the green amazonite (generation III). The room temperature spectrum of natural bluish-green resulted from the combination of these two centers.

The EPR spectrum of all color varieties of amazonite consistently turned up an $Al - O^- - Al$ hole center ($g_z = 2.0043$, $g_y = 2.0070$, $g_x = 2.0555$), which is more concentrated in green amazonite. It is known that upon irradiation with X-rays, almost all feldspars showed this type of center. That is why the irradiated green amazonite shows EPR spectra with a higher concentration of Pb and Al hole centers in comparison to blue and non-irradiated varieties. In addition to this, particularly with the green sample, it was also observed, like previously by Speit and Lehmann (1982), that they attain a brownish hue (formation of the Al hole centers).

The colors of all of the treated samples were intensified by irradiation. However it is important to note that after X-ray irradiation, not only were

the intensities of the bands at 740 nm and 380 nm seen to increase, but the intensity of the band at 625 nm decreases. With the heating of the green amazonite sample to 280 °C, the band at 740 nm and the EPR signals of the Center II disappear, to be replaced by the lines of Center I. Heating for several hours at 280 °C does not cause this center to disappear. The EPR signals of center I and the absorption band at 625 nm disappear after heating to 450–500 °C. Thus, the EPR signal behavior of these centers (I and II) after heating and irradiation can be well correlated with the behavior of the amazonite absorption bands at 625 and 740 nm (Table 4). These data do not agree with the results obtained by a theoretical study of the absorption spectra of Pb^{+} and Pb^{3+} in the K^{+} site of microcline (Petrov et al., 1993; Julg, 1998).

4.5. FTIR-Absorption and Reflectance Spectrometry

The IR transmission spectra in Figures 4a to 4f show the changes of the OH-vibrations in the amazonite samples before and after irradiation. As may be observed, all of the samples contained structural H_2O . The green and the bluish green amazonites show two distinct absorption bands at 3698 and 3622 cm^{-1} due to OH-stretching vibration, and one absorption band at 3420 cm^{-1} , which indicates the presence of H-bonded OH. The spectra of the blue amazonite, on the other hand, lacks absorption bands at 3698 and 3622 cm^{-1} , but displays a band at 3420 cm^{-1} , indicating that it contains only H-bonded OH.

Accordingly, the OH-stretching vibrations of amazonite also change due to irradiation. As shown in Figures 4a to 4f, the intensities of the absorption bands related to the OH-stretching vibrations mentioned above decreased considerably with X-ray irradiation of amazonite. Figure 4 shows that the intensity of most of the bands decreases in variable amounts due to irradiation.

4.6. UV-Fluorescence Spectroscopy

The UV-emission spectra of the green and the bluish green untreated amazonites are quite similar, but they differ considerably from that of the blue amazonites (Fig. 5). Each of the samples shows three UV-emission maxima at or about 465 nm, 678 nm and 741 nm.

Comparison of the UV-fluorescence spectra of the untreated samples with those of the treated ones reveals changes of fluorescence caused by irradiation. As mentioned above, the UV-emission spectra of the green and bluish green untreated amazonites are similar. Accordingly, their emissions spectra after the X-radiation are also similar, i.e. the main change is observed between 360 nm and 469 nm. Ostrooumov et al. (1989) reported that these bands correspond to the concentration of $Si - O^{-} - Si$ and $Al - O^{-} - Al$ hole centers, the concentration of which increases after irradiation.

It should be noted that in contrast to the green and bluish green samples, the change caused by irradiation in the case of the blue amazonite occurs mainly at 680 nm and 741 nm; i.e., the intensities of these two bands are increased, whereas the region between 362 nm and 460 nm remains more or less unchanged. The bands at approximately 700 nm are characterized by the typical spectrum of $^{IV}Fe^{3+}$, in which early blue generation-I amazonites with a maximum concentration of Fe (Table 2) are included.

5. Discussion

Using UV-VIS-NIR and EPR measurements of systematically heated and irradiated Precambrian amazonite single crystals we attributed the amazonite absorption bands at 625 nm (band II) and at 740 nm (band III) to the formation of Pb^{+} electron and $Pb-O^{-}$ hole paramagnetic centers, respectively. We attributed absorption band I, centered at about 380 nm, to finely dispersed oxides

Table 4 EPR data for the Pb centers in amazonite.

Center	g_z	g_y	g_x	Interpretation	
I	1.390	1.565	1.837	Pb^{+} electron center	The EPR signals of Pb^{+} and the absorption band at 625 nm disappear after heating to 450–500 °C.
II	1.989	2.0247	2.0579	$O^{-} - Pb$ hole center	The band at 740 nm and the EPR signals of $O^{-} - Pb$ hole center disappear in a heating process of up to 280 °C for 1–1.5 hours.

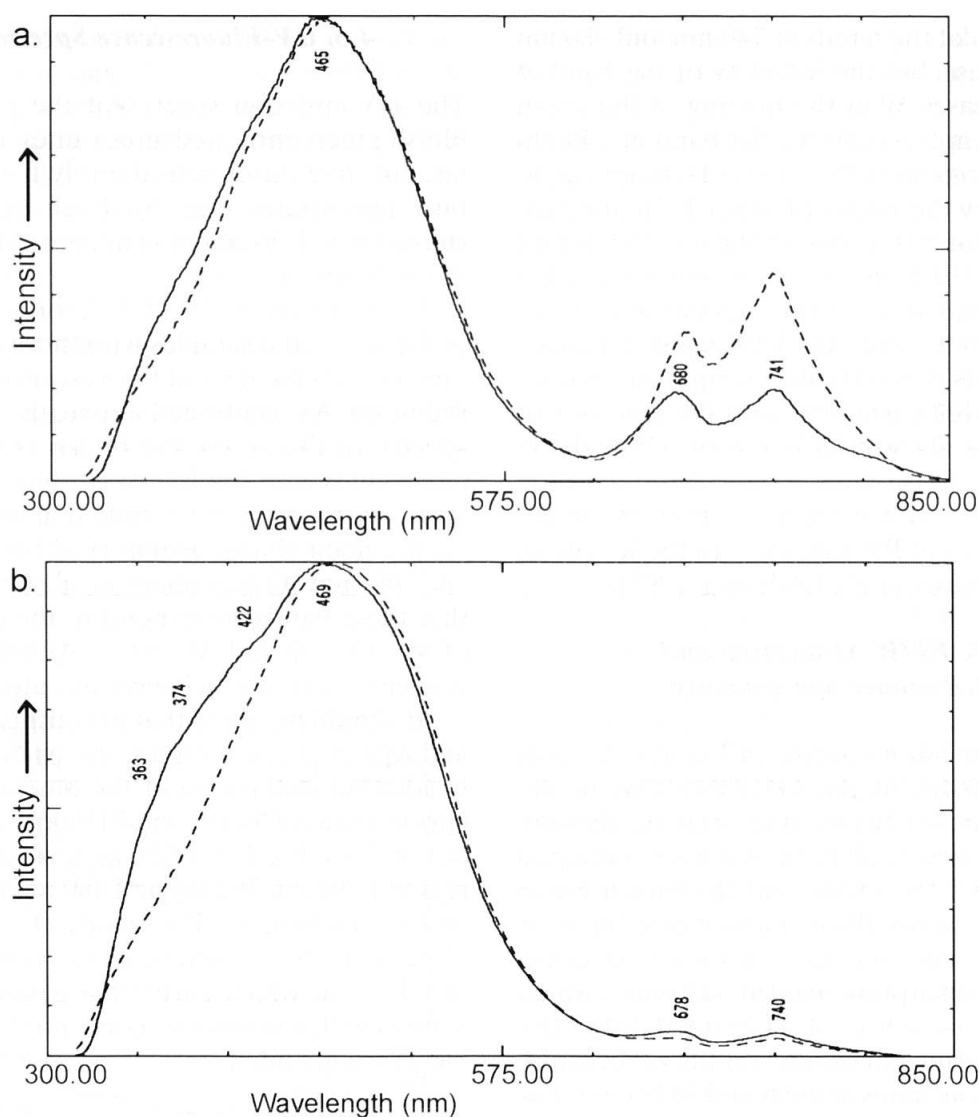


Fig. 5 UV-emission spectra of blue (top) and green (bottom) amazonite before (solid lines) and after (dashed lines) X-ray irradiation.

and hydroxides of Fe ($\text{Fe}_2\text{O}_3 - \text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$), hole center $\text{Al} - \text{O}^- - \text{Al}$ and structural center ${}^{IV}\text{Fe}^{3+}$.

As stated above, the different colors of amazonite are caused mainly by Pb electron and hole centers which are produced by the reaction of radiation-induced Pb^{2+} with the radiation-induced products of dissociation of the structurally bound H_2O (Hofmeister and Rossman, 1985).

The change of color of minerals caused by irradiation is, in most cases, due to the formation of one or more color centers. In some minerals, this phenomenon may be accompanied by a change of valence of an element, which is in accord with the following reaction (Ostrooumov et al., 1989): Amazonite (Pb^{2+}) \rightarrow irradiation with X-ray or γ -rays \rightarrow Pb^+ electron center or $\text{O}^- - \text{Pb}$ hole center.

In addition, structurally bound H_2O , stimulated by irradiation, as shown in the FTIR-transmission investigations, may also take part in this reaction. Ionizing radiation, either X-rays or γ -rays, dissociates H_2O molecules, forming H° - and OH° -radicals as the primary products of radiolysis. At

the beginning of the amazonite formation process, the OH° radically transformed the Pb^{2+} present in amazonite to Pb^+ . The H_2O is further regenerated through the reaction of the OH° radical with a hole center ($\text{O}^- - \text{Pb}$) and the subsequent recombination of OH^+ and OH^- (Aines and Rossman, 1986). It is very probable that ${}^{IV}\text{Fe}^{3+}$ also participates in this reaction as well as in the formation of exchange-linked $\text{Pb}^+ - \text{O} - \text{Fe}^{3+}$ complexes.

As shown in Figures 4a to 4f, the intensities of the absorption bands related to the OH-stretching vibrations mentioned above decreased considerably on X-ray irradiation due to the formation of crystal defects. Such crystal defects are also formed in other minerals, such as topaz, as a result of X-ray irradiation. It has been shown by Aines and Rossman (1986) that in the case of topaz, the OH-stretching vibrations change with irradiation, which, according to Platonov et al. (1984), is related to the crystal defects produced by irradiation. Marfunin and Bershov (1970) proposed that the changes in OH-stretching vibrations of the

amazonite samples are caused by similar crystal defects as Pb^{2+} is ionized to Pb^+ .

A further effect of X-ray irradiation is the production of radiation damage, which causes metamictization of the irradiated mineral. As a result of the radiation-induced damage to the structure of the mineral, irregularities in bond-lengths and bond-angles are found to occur. The metamictization due to radiation damage can be investigated by IR reflectance spectra, as Woodhead et al. (1991) demonstrated with zircon. Upon observing the IR reflectance spectra of the amazonite before and after irradiation, a metamictization due to X-ray irradiation and similar to that occurring in zircon is also produced in amazonite.

The typomorphic features of Precambrian amazonites observed in the UV-VIS-NIR and EPR specific spectra are related to the presence of isomorphic Pb impurities (electron-hole paramagnetic centers). These centers are not found in the feldspars of other chemical or structural nature. The spectrometric studies allowed us to conclude that in the coloration of these amazonites, different paramagnetic (Pb and Al) centers participate. The contribution of these centers is different in the early and late generations of amazonites. The spectroscopic data confirm the difference between the blue and green amazonites wherein the two bands of absorption, maximized in the visible regions, are related to the electron (625 nm) and hole (740 nm) centers of Pb. The band with its maximum in the near-UV region (380 nm) is also characterized by its complex nature, which is related to structural as well as non-structural Fe impurities (finely dispersed oxides and hydroxides of Fe), and the hole Al centers (Table 5).

Ostrooumov et al. (1989) reported an increasing content of radioactive elements (U, Th, Rb) in amazonite in relation to the paragenesis of amazonite with U and Th minerals. The electron-hole centers were formed in the amazonites in the Precambrian pegmatites wherein high concentrations of radioactive elements were found. The X-rays associated with radioactive decay could have caused formation of structural electron or hole

defects, which later transformed in the centers of color in the crystals of the amazonite.

Amazonites are always characterized by the presence of radioactive elements. This fact confirms the supposed participation of the radioactive elements in the formation of the centers of color in the crystals of the Precambrian amazonites. We must stress the fact that as early varieties of the microclines were found in other pegmatitic deposits of West Keivy along with the amazonite, we could observe only the hole Al and the structural Fe centers, which produced the appearance of the complex band with its maximum in the near-UV region.

6. Conclusions

The crystals of different amazonite generations from the Precambrian granitic pegmatite in Western Keivy are characterized by specific typomorphic features: (1) there is a chemical evolution of the amazonite from the peripheral zones to the center of the pegmatite body, characterized by increasing amounts of K_2O , Rb_2O , Cs_2O , PbO , Tl , Ga , Be , Sr , U and Th , and by decreasing amounts of Al_2O_3 , Na_2O , Fe_2O_3 and Ba ; (2) the amazonites are characterized by a high degree of Al/Si order in the structure. All the parameters obtained from X-ray diffraction as well as optical microscopy show that the studied amazonites belong to the maximum ordered microcline. Only in this structure can stable color centers be formed; and (3) optical absorption and EPR studies show that the characteristic blue-green color of amazonite is caused mainly by formation of hole-electrons centers of Pb and Al and the structural centers of $^{IV}Fe^{3+}$ that cause the corresponding absorption bands.

Finally, it is important to recognize the possibilities that amazonite offers as a prospection index for some types of rare-metals deposits (Ta, Nb), REE mineralizations and some gemmological minerals (topaz, beryl). The contradictions in the current evaluations of these possibilities are the result of insufficient studies of the geological setting, crystal chemical and spectrometric parameters of amazonite. According to the notation

Table 5 Color centers in the Precambrian amazonites.

Absorption Band	Color centers
Band II (625 nm)	Pb + electron center [or exchange-linked $Pb^+-(O,OH)-Fe^{3+}$ complexes]
Band III (740 nm)	Hole center O ⁻ - Pb
Band I (380 nm)	Finely dispersed oxides and hydroxides of Fe ($Fe_2O_3-Fe_2O_3 \cdot nH_2O$); hole center Al - O ⁻ - Al; structural center $^{IV}Fe^{3+}$

of Ostrooumov (1991) the different geological, petrological and geochemical setting of the amazonite crystals establish the distinctive features of its crystal chemical and spectrometric parameters. From our point of view, it is necessary to reconsider the importance of amazonite from a geological and mineral viewpoint. Amazonite, as a rule, appears in the final phases of formation in different genetic types of granitic and pegmatitic rocks and therefore represents a clear index of the manifestation of the later and superposition processes in the various types of deposits related to specific mineralization. For this reason, it is believed that deposits of amazonite delimit the areas of expansion of granitic rocks containing rare-metal and REE mineralizations.

Our data show that in the Precambrian pegmatites of Western Keivy, the blue generation-I amazonite ($\lambda=491\text{--}497$ nm, $P=15\text{--}20\%$, $Y=25\text{--}35\%$) is associated with manganocolumbite, fergusonite and gadolinite. Associated with the bluish green and green amazonite of generations II and III ($\lambda=510\text{--}540$ nm, $P=20\text{--}25\%$, $Y=20\text{--}30\%$) we typically find plumbopyrochlore, plumbomicrolite and galena. In these pegmatites, the REE mineralizations associate with the fluorite deposition (Table 1). The pegmatite bodies without any rare-metals and REE mineralizations are characterized only by the presence of pale green amazonites ($\lambda=550\text{--}560$ nm, $P=10\%$, $Y=40\text{--}45\%$). Therefore, in order to evaluate the various rare-metal and REE deposits correctly, in many cases it is still necessary to get detailed information on the typomorphic features for different amazonite generations.

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