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HEAT SENSITIVE BLUE QUARTZ – THE UNUSUAL OCCURRENCE OF ALBEȘTI, ROMANIA

Adrian-Iulian PANTIA[1,2] & Andra-Elena FILIUȚĂ[1]

[1]Geological Institute of Romania, Caransebeș Street No. 1, Bucharest, Romania, padrian.iulian2020@gmail.com
[2]University of Bucharest, Faculty of Geology and Geophysics, Traian Vuia Street No.6, Bucharest, Romania

Abstract: The blue quartz of the Albești metagranite is an interesting and puzzling occurrence in the Romanian geological landscape, both in terms of rarity and available data. The body of literature on blue quartz attributes the color to the Rayleigh/Tyndall scattering of light by nanometer/submicron inclusions, commonly identified as ilmenite or rutile, and as a theoretical possibility, fluid inclusions. The Albești blue quartz undergoes a visible loss of color at temperatures as low as 300°C, and for this reason the most commonly cited light scattering inclusions cannot be the cause of the coloration. Furthermore, there are only a handful of occurrences known to exhibit such a thermal behavior, potentially placing the Romanian occurrence in a rather exclusive class of rock forming blue quartz. The data gathered by optical observations, heat treatment, powder diffraction, infrared spectroscopy, and scanning electron microscopy have shown that the blue color is produced by light scattering, the scattering particles are sensitive to heat, recrystallization can also affect the color, and that the color is likely metamorphic in origin. Despite the fact that the identity of the scattering particles is still unknown (although fluid inclusions, and molecular colloids are suggested as potential light scattering elements), there is strong indication that the color is metamorphic in origin and that it could be used as a marker for a specific set of metamorphic conditions. The results of the present study constitute a first significant step in the understanding of the Albești blue quartz and point in the direction of future research.

Key-words: blue quartz, Rayleigh scattering, bleaching, metamorphism, Albești metagranite.

1. INTRODUCTION

Blue quartz is arguably the least understood of the colored varieties of quartz, both in terms of the causes of the coloration and geological significance. The second half of the XIXth and the first half of the XXth century witnessed some interest in the blue coloration of natural quartz through the work of Jayaraman (1939), and Iddings (1904), but there are only a handful of modern studies, such as those performed by Wise (1981), Zolensky et al., (1988), and Seifert et al., (2011).

While some occurrences owe their color to blue mineral inclusions, the majority of blue quartzes are believed to be blue because of the Rayleigh scattering of light by nanometric particles (Zolensky et al., 1988). For simplicity, the later type of blue quartz will be referred to as "blue quartz proper", even though it too is allochromatic (in the sense that the color is caused by impurities, not by structural or chemical characteristics specific to quartz). Other potential causes include Ti^{3+} centers and O^{-}-Al^{3+} holes (Bershov et al., 1977), cationic impurities such as Eu^{2+} and Ce^{3+} (Kim et al., 2015), and microfractures (Wise, 1981).

"Blue quartz proper" is usually hosted by granitic rocks and their metamorphic equivalents, but it is also found in dacite, rhyolite, volcanic tuff, diorite, or tonalite.

The scattering of light is highly dependent on particle size. Therefore, any inclusion could scatter light, provided it has nanometric dimensions. The geologic literature on the subject most often identifies Ti bearing minerals, mostly rutile and ilmenite as the scattering particles, although tourmaline, magnetite, micas, apatite, and others have also been reported (Pantia & Filiuță, 2019), but molecular colloids enabled by structural defects caused by temperature and/or radiation, as in the case of Blue-John-type fluorite (Bill & Calas, 1978) could also be taken into account as potential light scattering particles in the case of blue quartz.

Blue quartz proper is mostly associated with amphibolite and granulite facies conditions, and the occurrence pattern plots within continental scale tectonic features where such conditions were present (Pantia & Filiuță, 2019).

In conclusion, most authors would agree that blue quartz owes its color to the Rayleigh scattering of light by mineral inclusions (ilmenite or rutile most of the times) only a few tens of nanometers across. There are, however, some blue quartz occurrences which seem to deviate from the standard model and raise the question of what the "standard model" for blue quartz actually is. To date, the number of investigated occurrences is insufficient for establishing which type of blue quartz is the norm. The Albești blue quartz is an example of such an occurrence. Neither the cause of the coloration nor its geological significance have been specifically investigated. This variety of blue quartz lacks blue colored inclusions, and shows optical properties which can be associated with light scattering. By these two criteria, it would qualify as "blue quartz proper". However, it progressively loses its color when heated. Pantia & Filiuță (2019) have reported this anomalous behavior of the Albești blue quartz, without commenting of the causes or providing specific data regarding manifestation of Rayleigh scattering or heat sensitivity. The Albești occurrence is not alone in this respect, since loss of color has also been reported in the case of the blue quartz from the charnockites of Mysore, India (Jayaraman, 1939), Ollo de Sapo gneiss, Spain (Montero et al. 2009), and observed in the Pietrosu Bistriței porphyroid gneiss, Milbank granite and Cosăuți granite. Seifert et al., (2011) have linked the loss of color to strain, because the crystalloblastic growth of the nano-inclusions can render them incompatible with the Rayleigh scattering of light, but a correlation between temperature and loss of color in blue quartz is yet to be provided.

The purpose of this exploratory study, the first of its kind in Romania, and part of only a handful worldwide, is to gain insight into some issues regarding the Albești blue quartz: whether the color is caused by the scattering or light; whether the color is lost or merely concealed during heating; whether the quartz was blue when it first formed or became blue as an effect of its geologic history; and the potential nature and identity of the light scattering inclusions. To answer these questions, the Albești blue quartz was compared to the Llano occurrence. The Alpine Uricani metamorphic quartz (quartzite) was used, on occasion, as a baseline by virtue of its purity.

1.1. Rayleigh and Tyndall scattering

Rayleigh scattering, the most commonly cited cause for the blue color in quartz, is the elastic (i.e. without the modification of the wavelength) scattering of light waves by nanometric particles (typically 1/10 of the vacuum wavelength of the incident light) inside a transparent medium. The scattering particles can be solid inclusions, molecules, and even pores. The phenomenon is based on the polarizability of the particles inside a medium: lights electric field induces an oscillation of the particles electric field, turning it into a radiating dipole. The intensity of the scattering is proportional to λ^{-4}, and therefore shorter wavelengths will be scattered more successfully, while longer ones will be transmitted. When produced by Rayleigh scattering, the blue color in quartz is only visible in reflected light.

Tyndall scattering (also known as Willis-Tyndall scattering) occurs when light passes through a colloid, and requires scattering particles with dimensions comparable to the wavelength of visible light, which is a tenfold increase in size from what is required for Rayleigh scattering. The intensity of the scattering is proportional to λ^{-4} as well, with the same implications.

At the end of arguably the best study on the topic, which set the general tone in which blue quartz occurrences are approached, Zolensky et al., (1988) have concluded that the blue quartz of the Llano rhyolite (Texas, USA) owes its color to the Rayleigh scattering of light caused by rounded ilmenite plate-like inclusions cca. 60 nm across. The results of their study may hold true for some occurrences, but cannot be applied to heat sensitive blue quartz. As long as the transparency of the medium and/or particle size does not change, Rayleigh scattering should still occur in heated quartz grains, provided that the color was indeed produced in this manner.

1.2. The Albești metagranite

The Albești metagranite, one of the most unusual and controversial granite occurrences in the South Carpathians, according to Negulescu (2013), is located in the upper part of the Iezer Complex, Leaota Metamorphic Suite, South Carpathians, Romania, where it forms stratigraphically concordant lenses. The Albești metagranite samples used in the current study have been collected from the Valea Caselor River, aprox. 4 km from its confluence with the Dâmbovița River, Dragoslavele Village, Argeș County, Romania.

According to Negulescu et al., (2018), it originated by crustal anatexis in a syn/late-collisional setting, but magmatic origins and emplacement along tectonically wakened planes have also been proposed (Negulescu, 2013).

The Albești metagranite was affected by a 600°C and 10 kbar moderate metamorphic event (Negulescu & Săbău, 2015) which plots in the high pressure area of the amphibolite facies.

Various ages have been reported for the Albești granite: 300.9±11.1 Ma (Târgului River), 318.9±12 Ma (Tâncava River) (Udubașa et al., 1985), 472.7±7.3 Ma (Balintoni et al., 2009), 481.16±10.83 Ma (SHRIMP) (Negulescu, 2013). The ages obtained by Udubașa et al., 1985 most likely reflect the Variscan metamorphism which overprinted the metagranite, while the later age represents the age of emplacement.

The blue quartz grains, roughly >5 mm across on average, show a slightly milky appearance, and an apparent color zoning even in unpolished hand samples (Pantia & Filiuță, 2019). The granite is generally isotropic, but gneissic and even schistose textures are locally present. The abundance of the blue quartz grains decreases with increasing metagranite textural anisotropy, and there are also outcrops free of blue quartz. This trend has also been reported in the Ollo de Sapo gneiss, where the blue quartz is present only in areas of low metamorphic grade (Montero et al., 2009). Seifert et al., (2011) presented the correlation between strain and loss of color as a general rule.

1.3. The Llano rhyolite blue quartz

The Precambrian Llano rhyolite porphyry (llanite) is a hypabyssal intrusion hosted by the Llano Uplift, Texas and is dated at 1106±6 Ma (Rb/Sr) (DeLong & Long, 1976). Subsequent to its crystallization, the llanite underwent a very low grade metamorphic event (subgreenschist) (Zolensky et al., 1988).

The quartz has a deep blue color, the contour is hypidiomorphic-idiomorphic, and chatoyancy is readily noticeable, as is the core to edge color zoning.

As mentioned in the Introduction, Zolensky et al., (1988) have determined that nano-meter size ilmenite plates scatter light, thus bestowing the blue coloration. The light scattering ilmenite itself is of magmatic origin, i.e. it was added to the quartz growth surfaces directly from the melt, and did not form as an exsolution product. According to the same authors, chatoyancy is produced by a second generation of ilmenite which was produced by exsolution, but its individual crystals are too large to scatter light and therefore do not contribute to the blue coloration. Furthermore, the color zoning observed within the individual grains is caused by the gradual increase in size of the ilmenite inclusions, from the core to the edge of the grains.

The llanite blue quartz is the standard against which the Albești metagranite blue quartz will be evaluated since it is the best documented occurrence in terms of light scattering inclusions. The llanite samples used were available courtesy of Mark A. Helper, PhD, University of Texas.

2. ANALYTICAL METHODS

The measurements were carried out using instruments and software available at the Geological Institute of Romania:

The optical observations were performed on grains, raw and polished samples, and thin sample slices in transmitted and reflected light, on black and white background, using a binocular microscope. The thin sections were analyzed using a petrographic microscope.

X-Ray powder diffraction (XRD) was performed using a Bruker D8 Advance diffractometer with Theta/2Theta configuration, and Cu anode. The measurements were performed with an increment of 0.01° and 2s/step, within a 2θ range of 4-90°, using 0.6 mm divergent and anti-scatter slits, a 0.1 mm receiver slit, and Ni monochromator, at 40 kV and 40 mA. The lattice constants were calculated using the Indexing and Least-Squares Powder Diffraction Program (Appleman and Evans, 1973).

FT-IR was carried out on a Bruker Tensor 27 spectrometer, within the 7500-210 cm^{-1} range, with a minimum spectral resolution of 1 cm^{-1}. The measurements were performed on 150 mg pellets made of KBr mixed in with 2 mg or 7.5 mg of sample powder.

The micro Raman investigations were performed on polished samples using the 532 nm laser of a Renishaw inVia spectrometer, with a 1800 l/mm grating, 50x objective, 2 s exposure time and 20 accumulations within a spectral range of 67.48 to 1836.93 cm^{-1}.

The hand samples and polished sample sections were heated in a Nabertherm Controller P320 oven to 1000°C for 24h to observe any changes which may occur in terms of color. The grains and powders were heated to 1000°C in both Ar and room atmosphere, with an increment of 1°K/min over a time interval of 16 h. using a Netzsch STA 449 C Jupiter simultaneous thermal analyzer.

Preliminary SEM investigations were performed on Cr covered polished samples, using a Tabletop Hitachi TM 3030, with a 10x-30000x magnifying power and EDS capability, and Au covered polished samples using a Zeiss Merlin Gemini 2, with a 40x-10^6x magnifying power, WDS, EDS and EBSD capability, and 1 nm resolution.

3. RESULTS

3.1. Optical observations

The study of the polished sections, grains, and hand samples shows a readily visible apparent color zoning, sometimes manifested as a clear, colorless grain core surrounded by a blue color band, with milky appearance and lacking chatoyancy, but mostly as an inner colored zone surrounded by a clear, colorless area (Fig. 1 A). The opalescent appearance reported by Pantia & Filiuță (2019) could be the result of increased Na content, as pointed out by Chernov & Khadzhi (1968) in reference to artificial quartz, and not necessarily of an opal-like structure.

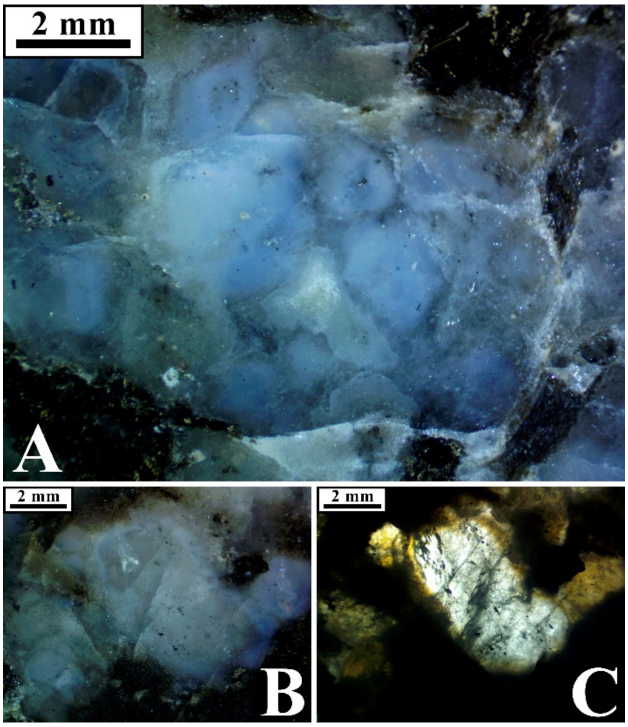

Figure 1. Polished samples of Albești blue quartz showing: A – characteristic color zoning; B – Albești blue quartz grain in reflected light; C – the Albești blue quartz grain from Fig. 1 B in transmitted light.

The morphology of the color zone is consistent with the overall shape of the quartz domains, a feature also seen in the llanite blue quartz. In the context of the Albești blue quartz, a quartz domain is a polycrystalline area with blue and colorless quartz which appear to delineate an initially larger single crystal grains. The morphology of the Llano blue quartz color zones closely resembles the subhedral shape of the grains because the light scattering inclusions were trapped during the growth of the grains themselves. This blue quartz variety shows chatoyancy, a feature owed to micron size ilmenite "ribbons" (Zolensky et al., 1988).

Much like the Llano blue quartz, the blue color of the Albești blue quartz is only visible in reflected light. In transmitted light, the grains turn yellow to yellowish brown. This chromatic behavior is only applicable to the blue zones (Fig. 1 B and C). The colorless areas do not experience any color change, regardless of light direction, a feature also shared by the regular clear quartz from Uricani, and reported by Jayaraman (1939), as well. The difference in color is indicative of light scattering, probably Rayleigh. Jayaraman (1939), described the blue quartz from the Champion Gneiss (State of Karnataka, India) as showing "turbidity", referring to a pale-yellow color observable in thin and thick sections, a term which might describe, in effect, the brownish-yellow zones (in transmitted light), which correspond to the blue zones in reflected light observed in the Albești and Llano occurrences. Furthermore, Jayaraman (1939) points to a correlation between "turbidity" and the presence and intensity of the blue color.

Under the petrographic microscope, the Llano quartz shows as single crystals encased in an aphanitic matrix, with no indication of recrystallization. In contrast, the quartz from Albești shows subgrain rotation recrystallization, despite having the appearance of single crystals in hand samples and when observed under the binocular microscope. The quartz grains from Albești also show strain shadows, a feature which was not observed in the llanite blue quartz.

Given the type of recrystallization, it is only natural that the recrystallized zones surround the core of the grain. This feature is reminiscent of the color distribution within the zoned quartz domains, and could be responsible for the colorless zones close to the edge of the grain.

Under parallel nicols, the polished sections with a thickness greater than that of the regular thin sections, show a light brown color which coincides with the blue areas observed in the samples from which the sections themselves were cut. Under crossed nicols, it becomes obvious that the light brown areas overlap with single crystal domains, while the colorless ones coincide with the recrystallized polycrystalline quartz (Fig. 2). Therefore, in the case of the Albești blue quartz, the color zoning is the effect of the spatial distribution of recrystallized quartz grains relative to the original single crystal. The colorless edges of the blue grains are in agreement with a subgrain rotation recrystallization pattern, while the colorless grain cores observed in some instances could be explained as recrystallized embayments. In summary, in the case of the Llano blue quartz, the color zoning manifests within single crystals, while at Albeşti it manifests as part of a polycrystalline quartz domain, shaped by the subgrain rotation recrystallization of a former single crystal.

If the blue and brownish colors are indeed linked, the absence of the latter in the recrystallized grains suggests that the blue color is either lost during recrystallization, or the conditions required for its generation were hindered by it. The correlation between recrystallization and loss of color has also been noted by Montero et al., (2009), and Seifert et al., (2011).

The Llano blue quartz is mostly euhedral to subhedral. The Albeşti blue quartz on the other hand is mostly anhedral, with rare instances of subhedral contours. (Fig. 1 A).

Biotite is the most significant identifiable inclusion in the Albeşti blue quartz, using both the binocular and petrographic microscope. When present, it mostly concentrates in the colorless recrystallized "core" (which is likely a recrystallized embayment in the original quartz grain, Figure 2) of the zoned quartz domains, surrounded by a blue zone (Fig. 1), and along grain boundaries, and fractures.

The blue areas of the grains are usually free of observable inclusions. Seifert et al., (2011) have reported that micas are the most abundant inclusions in blue quartz, and that they were trapped during the growth of the quartz crystals. In the case of the Albeşti blue quartz, these biotite inclusions appear to be related to colorless recrystallized domains rather than blue single crystals.

Rutile, the most popular explanation for the blue color in quartz, has not been identified in any of the thin sections investigated. The lack of microscopic rutile itself might be indicative of the peculiar character of the Albeşti occurrence.

The smallest inclusions observed in the Llano blue quartz are cca. 0.5 μm across and show a slight tendency towards preferential orientation.

Zolensky et al., (1988) measured the larger ilmenite inclusions, responsible for chatoyancy but with no part in the blue coloration of llanite quartz, at 100-200 nm. In the case of the Albeşti quartz, the smallest inclusions, as resolved by the petrographic microscope, have minimum dimensions of cca. 1μm, which are incompatible with Rayleigh scattering (50-60 nm on average), but get close to the high end of the Tyndall range (0.9-1 μm). However, as in the case of the secondary ilmenite inclusions from the llanite blue quartz (Zolensky et al., 1988), these inclusions play no part in the generation of the blue color.

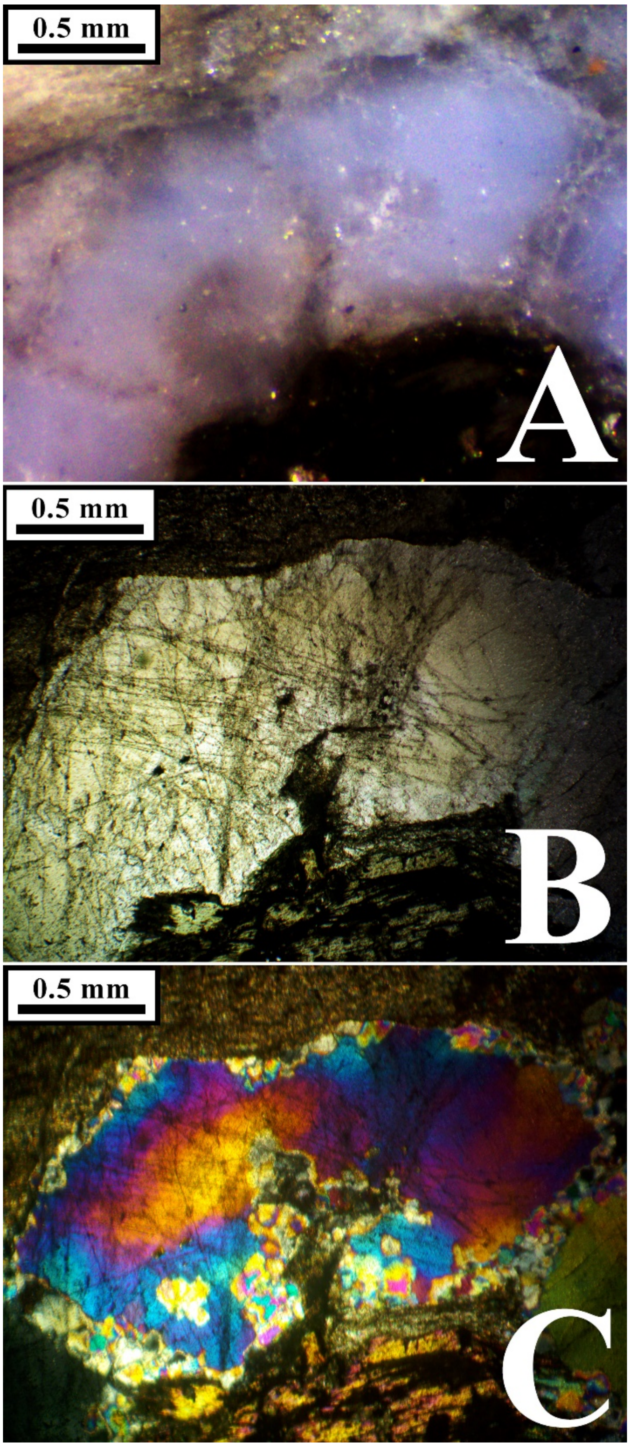

Figure 2 – Images of a zoned blue quartz grain under the binocular microscope (A), and parallel (B) and crossed (C) nicols, showing the correlation between the blue color, the faint brownish color, and the single crystal character of the grain. The anomalous colors under crossed nicols are caused by the thickness of the polished section.

3.2. Heat treatment

Albeşti metagranite, Llano rhyolite, and Uricani quartz hand samples and polished sections have been heated to 100, 300, 500, 600, 700, and 800°C for 24 h, and optically analyzed for color changes and cracks. Grains and powders were also heated to 1000°C over the course of 16 hours. The results are presented below.

The llanite blue quartz and the Uricani quartzite showed no optical change at any stage of the heating, whether in terms of color, transparency, or mechanical stress. The Llano and Uricani samples remained optically unchanged even when heated to 1000°C. Therefore, the focus will shift towards transformation of the Albești blue quartz (Fig. 3).

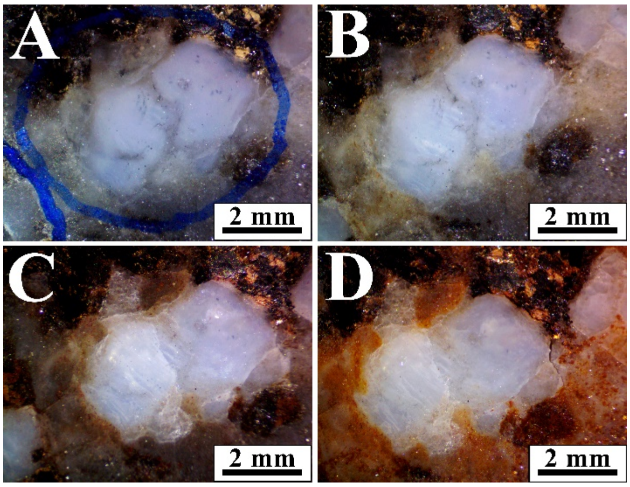

Figure 3. Albești blue quartz grains: A – room temperature; B – heated to 300°C; C – heated to 600°C; D – heated to 800°C.

At 100°C the blue color is still clearly visible, but loses some intensity. The colorless areas of the grains preserve their transparency. There is no indication of mechanical stress caused by temperature.

At 300°C most of the areas which were blue turned whitish, with only isolated patches of light blue still distinguishable. The transparency of the colorless areas is not affected and no stress features have developed (a constant throughout the entire heating process). On the other hand, the blue areas get slightly clearer, allowing for the observation of additional mineral inclusions and fractures. This trend is observed, with increasing degree, up to 800°C.

At 500°C there is not much change in terms of bleaching, but locally, the grains become slightly rusty in appearance.

At 600°C the blue color is no longer visible.

At 800°C, cracks become especially visible in the colorless areas.

While the complete loss of color is the norm, isolated instances of grains which still preserve some of the color, even after being subjected to temperatures or 800°C, have been recorded. Heating the same grains for longer (72 h) resulted in the loss of color.

The loss of the blue color in transmitted light during heating is also accompanied by a progressive loss of the brownish-yellow color in transmitted light, a trait shared with the blue quartz of the Champion Gneiss (Jayaraman, 1939).

It has been observed that the outer colorless areas of the grains become grainier, almost sugar like, with increasing temperature, while the blue areas preserve their mechanical integrity. This could be the result of volume increase caused by the α-β transition of the recrystallized grains; in effect, a macroscopic expression of the recrystallized domains observed under the microscope and further confirmation of the incompatibility between the recrystallized areas and blue color.

In agreement with the results presented above, the Albești blue quartz grains and powders, regardless of the atmosphere used (room or Ar), turn slightly rusty when heated. The Llano and Uricani samples preserve their pre-heating color. The thermogravimetric instrument used to heat the grains and powders did not show any correlation between bleaching and weight loss. Whether the correlation does not exist or it is an issue of instrument sensitivity is still unclear.

During heating, quartz grains develop grain boundary micro-cracks, at temperatures in excess of 600°C, and internal micro-cracks at over 750°C (Hajpál & Török, 2004). These micro-cracks could scatter light and conceal the blue color or the quartz. Chernov & Khadzhi (1968) pointed out that heat treated quartz does develop microscopic cracks 5-100 μm wide and approximately 100 nm cavities, in areas with a high density of impurities, which can cause the scattering of light. In the case of the samples from Albești, the internal features of the grains are still visible after heating, so it is unlikely that sets of cracks cause sufficient optical disturbances to conceal the color, even more so at temperatures as low as 300-500°C. A certain degree of scattering is inevitable, but it is not the determining factor in the loss/apparent loss of color. It is worth reiterating that after being heated, the blue quartz from Llano underwent no observable changes in terms of color or transparency.

Chernov & Khadzhi (1968) also noted that when heated, the degree to which the quartz turns milky-white, to the point of completely opaque porcelain-like, is directly related to Na content. Maximum concentrations of 0.002-0.003 wt% Na do not affect the transparency of quartz subsequent to heating, whereas concentrations of at least a few tenths wt% Na turn the quartz completely opaque after heating to 600-700°C.

The blue quartz from the Pietrosu Bistriței porphyroid gneiss, Milbank granite and Cosăuți granite, referenced in the Introduction section, also lose color when heated, but the subject will be addressed in a future study.

3.3. XRD

The powder diffractions performed on quartz grains from the Albești metagranite and Llano rhyolite showed no relevant differences between the two. Based on the diffraction data, the a and c lattice parameters of the two blue quartz occurrences were calculated and compared to other varieties available in the RRUFF database (Table 1).

Table 1. The lattice parameters of various quartz types and occurrences. The asterisks in the Obs. column indicates measurements performed by the authors; R****** is the RRUFF database code for the quartz occurrences considered.

	Occurr. / Type	a (*Å*)	c (*Å*)	Obs.
1	Albești	4.914(1)	5.406(2)	*
2	Llano	4.915(2)	5.407(4)	*
3	Uricani	4.915(2)	5.405(4)	*
4	Regular quartz	4.922(1)	5.407(2)	R100134
5	Regular quartz	4.9134(2)	5.4042(4)	R040031
6	Amethyst	4.91449(6)	5.40619(7)	R060604
7	Pink quartz	4.9130(2)	5.4049(2)	R050125
8	Synthetic quartz	4.9211(9)	5.4094(7)	R110108
9	Synthetic amethyst	4.917(2)	5.409(2)	R110104

The comparison has shown that the lattice parameters of the various quartz occurrences can vary significantly, as a function of chemical impurities, lattice distortions, and even sample preparation, and that the two blue quartz occurrences considered are in no way outstanding with respect to the lattice constants.

The solid inclusions from inside the quartz grains did not show on the diffractograms, meaning that they represent less than 5 wt% of the measured quartz sample. No amorphous phases, which could potentially explain the milky/opalescent appearance of the Albești blue quartz, have been detected. Heating the same powders to 1000°C over a time span of 16h did not produce any significant changes in terms of XRD signal, except for an apparent increase in crystallinity, as inferred from the relative height of the 67-69° 2θ interval (Murata & Norman, 1976).

3.4. SEM

The EDS mapping of the Albești quartz domains which show clear color zoning did not reveal any differences between the blue and colorless grains with respect to the distribution of major elements. This does not necessarily mean that chemical variations do not exist, but rather that they are below the detection limit of the instrument.

The EDS mapping has not shown any zoning in the blue quartz single crystals from Llano neither, likely because of instrument limitations and the fact that the zoning is not owed to significant chemical variations, but to the variations in the size and spatial density of the ilmenite inclusions.

The SEM investigations were preliminary in scope and focused on the color zoning, since the small scale of the light scattering inclusions is far beyond the detection limit of the instruments (TEM techniques are required). However, mineral inclusions have been identified, although too large to scatter light: the rutile and ilmenite minerals hosted by the Albești blue quartz grains, have dimensions in excess of 800 nm. Iron oxides, pyrite, and chalcopyrite are also present along cracks in quartz. The smallest (aprox. 200 nm) quartz hosted inclusions have halite like chemical composition, and are arranged in a linear pattern likely related to fluid inclusions from healed fractures.

3.5. FT-IR

FT-IR measurements performed on Albești and Llano blue quartz, and Uricani regular quartz show the absorption peaks characteristic of quartz: 1078.8-1075.3 cm^{-1} corresponding to Si-O υ3 asymmetrical stretching vibrations, 798.14-777.83 cm^{-1} corresponding to Si-O υ1 symmetrical vibrations, 694.89-693.18 cm^{-1} absorption band corresponding to Si-O υ2 symmetrical bending vibrations, and 467.89-458.15 cm^{-1} corresponding to Si-O υ4 asymmetrical bending vibrations. For comparison, Saikia et al., (2008), cite the 1080-1175 cm^{-1}, 780-800 cm^{-1}, 695 cm^{-1} and 464 cm^{-1} bands as characteristic for quartz, while Müller et al., (2011) place the most intense peaks between 830 and 1250 cm^{-1} (asymmetric Si-O-Si stretching vibrations), followed by the ones in the 400-600 cm^{-1} interval (O-Si-O deformation/bending modes), and finally 670-830 cm^{-1} (symmetric Si-O-Si stretching vibrations).

The measurements have also shown that the investigated samples are free of hydrogen related defects, as indicated by the absence of the diagnostic 894 $cm^{-1}$and 916 cm^{-1} absorption bands (Stenina, 2004). On the other hand, only the room temperature Albești blue quartz samples show a definite absorption peak at centered around 3557 cm^{-1}, indicative of O-H bonds (despite the fact that all the samples were stored and processed in the same way). The 3557 cm^{-1} peak has only been observed in pellets consisting of 7.5 mg quartz and 142.5 mg of KBr. As in the case of XRD, the FT-IR data points to an increase of the crystallinity index after heating, as calculated from the ratio between the 1145 cm^{-1} peak and the highest peak of the FT-IR spectrum (Shoval et al., 1991), and the ratio between the intensity of the 778 cm^{-1} and 695 cm^{-1} peaks, expressed as transmission percentage (Razva et al., 2014).

3.6. Micro Raman

The micro Raman spectra showed no indication of transitional elements which could potentially generate the blue color in either the Albești or Llano blue quartz. The measurements produced clean quartz spectra, with Raman bands centered around 356, 264, 207, and 128 cm^{-1} (lattice modes), 465 cm^{-1} (symmetric stretching vibration), 807 cm-1 (Si – O – Si bending), and 1083 cm^{-1} (SiO_4 asymmetric stretching vibration) (Yadav & Singh, 2015).

4. DISCUSSION AND CONCLUSIONS

The data gathered over the course of this study is not usually reported by authors who refer to or investigate blue quartz. Most papers mention light scattering rutile or ilmenite inclusions for their respective occurrence, with no reference to any study. On the other hand, the papers regarding the identity of the inclusions are very focused in scope and make no mention of thermal behavior, with the notable exception of Jayaraman (1939). Color zoning (whether apparent or not) and the milky/opalescent appearance, despite being reported for several occurrences, have not been investigated, except for the Llano blue quartz. Furthermore, a review of the literature on the subject of blue quartz reveals that the investigations usually jump from hand samples directly to thin section and electron microscopy. The apparent zoning in the Albești metagranite, for example, easily observable in polished samples, has not been reported until Pantia & Filiuță (2019), perhaps for the same reason.

The observations and measurements performed on the Albești blue quartz produced the following results:

I. Optical observations

- in hand and polished samples, the quartz domains show a color zoning with milky appearance and lacking chatoyancy;

- the color zoning of the quartz domains is owed to the spatial distribution of recrystallized and non-recrystallized grains;

- the blue color is only visible in reflected light. In transmitted light, the blue areas of the grains turn brownish-yellow;

- the pattern and morphology of the quartz grains is indicative of subgrain rotation recrystallization;

- the recrystallized zones coincide with colorless grains of the color zoned quartz domains;

- biotite is the most significant clearly identifiable inclusion and tends to concentrate in the colorless, recrystallized quartz. The blue areas are usually free of microscopic inclusions. Rutile has not been observed;

- the smallest inclusions observed are aprox. 0.9-1 μm across.

II. Heat treatment

- when the Albești blue quartz grains are heated, their color fades starting with temperatures as low as 100°C. The bleaching is accompanied by the loss of the complementary brownish-yellow color observed in transmitted light;

- as a result of heating, the colorless areas of the grains tend to develop a sugar like appearance, while the blue areas maintain their integrity; this is an effect of the grain boundaries caused by the subgrain rotation recrystallization.

III. XRD

- blue quartz does not significantly differ from other varieties of quartz in terms of lattice parameters;

- the inclusions present in quartz are less than 5 wt% and do not produce a discernable XRD signal.

IV. SEM

- rutile and ilmenite inclusions are too large (>800 nm) to produce Rayleigh scattering. The smallest (aprox. 200 nm) inclusions identified have halite like composition and are associated with secondary inclusions.

- the EDS mapping has not shown any differences between the blue and the colorless areas of the grains in terms of major elements.

V. FT-IR

- an O-H bond was identified at 3557 cm^{-1} only in unheated Albești blue quartz; no other deviations from the standard quartz spectrum have been identified in either the Llano or Uricani quartz, both heated and not heated.

VI. Micro Raman

- no trace of transitional elements was detected, a result consistent with the light scattering hypothesis.

The issues raised at the end of the Introduction section regarding the nature of the coloration, thermal behavior, timing of the coloration, and the potential identity of the light scattering inclusions, will be addressed below.

4.1. Is the color caused by the scattering of light?

The Albești blue quartz displays the diagnostic characteristic of light scattering environments. The grains are blue only in reflected light and brownish-yellow in transmitted light. The latter is unlikely to be caused by light being absorbed by impurities inside the grains, and independent of the blue color. Blue color zones coincide with the brownish-yellow ones, meaning that they are the result of the same volume of quartz when viewed at different angles relative to the light source. They are affected by heat simultaneously and proportionally (both colors fade gradually with increasing temperature), an expected outcome if the two colors have the same cause. Furthermore, the colorless areas of the grains remain so in transmitted light as well, suggesting that light absorbance is negligible in “clean” quartz, and no indication of transitional elements, which could produce the blue color, has been observed by micro Raman spectrometry. The observations point to the scattering of light, a coloring mechanism in agreement with the body of literature on blue quartz worldwide.

Also, the fact that EDS mapping has not shown chemical differences between adjacent blue and colorless quartz grains suggests that there are no quantitatively significant inclusions present. This is another reason to suggest that the color is not caused by micronic blue mineral inclusions. It follows that the color must be caused by factors with a quantitatively low chemical signature (undetectable by the method used) which could be an effect of the submicron / nanometer size of the particles (potentially compatible with light scattering).

4.2. Is the color lost or concealed during heating?

When heated, the Albești blue quartz turns white (bleaches). This transformation has only been observed in the colored zones. With the exception of some clearly visible fractures at temperatures in excess of 600°C, the colorless zones are unchanged. The optical observations have shown that after bleaching, the formerly blue areas of the quartz retain their transparency, as inclusions and textural features from inside the grains are still clearly visible. This level of transparency suggests that the grains remained largely unaffected by thermal expansion/contraction, and therefore it is safe to conclude that the color is lost and not concealed by light being scattered off fissure planes. Most of the mechanical transformations have been observed in the external colorless areas of the grains, in agreement with the pattern of the recrystallized zones, but irrelevant with respect to the loss of color.

Milky-white, and even opaque white appearances have been reported in the case of heated quartz, in relation to light scattering microscopic fractures and sub-microscopic cavities. These mechanical defects may play a role in the appearance of the Albești quartz subsequent to heating, but likely not a decisive one.

The exact mechanism by which heat affects the color is difficult to establish without first knowing the identity of the light scattering inclusions, because of the multiple potential effects of heat on quartz crystals.

4.3. Was the quartz formed blue or became blue?

The Llano blue quartz trapped the light scattering inclusions from the magma, as the crystals developed. Therefore, for all intents and purposes, this particular occurrence was formed blue. The color is stable even at 1000°C and arguably only a dynamic metamorphic event (which did not occur) could have destroyed it via the processes of crystalloblastesis suggested by Seifert et al., (2011).

The Albești metagranite, on the other hand, was emplaced 481 Ma ago and underwent a Variscan 600°C and 10 kbar metamorphic event aprox. 180 Ma later. Considering the fact that the color clearly fades at 300°C, and that there are Albești metagranite outcrops which are not consisted of blue quartz, two possibilities arise: (1) the quartz was formed blue, but the metamorphic overprint locally affected the color, or (2) the initial quartz was colorless, but locally turned blue as an effect of metamorphism. One of these two scenarios may also hold true for the gneiss/charnockite hosted blue quartz investigated by Jayaraman (1939).

Recrystallization appears to either affect the color, or inhibit its formation. The fracturing of the outer colorless areas of the grains during heating is arguably an effect of the recrystallized, polygranular nature of the colorless zones, and lends weight to the observation that the recrystallized quartz grains are colorless, and to the hypothesis that recrystallization is not compatible with the blue color in quartz.

In the case of the Albești blue quartz it is likely that temperature itself, rather than recrystallization, is the determining factor in the loss of color. The early onset of bleaching (300°C) is incompatible with significant structural changes in quartz.

If the color zoning is, as observed, the effect of the spatial relationship between recrystallized and single crystal quartz domain, the origin of the color is likely linked to some, as of yet unidentified, metamorphic process, which perhaps occurred during a low temperature retrograde stage. The temperatures involved in subgrain rotation recrystallization are incompatible with the blue color. Logic dictates that color formed in the wake of recrystallization. Therefore, the now blue Albești quartz was formed as regular quartz, underwent several metamorphic events, and during the retrograde stage of the latest, it locally tuned blue (if this timeline is accepted, the requirement for a very specific PT set of conditions must be considered, given that not all of the Albești granite outcrops have blue quartz). A magmatic origin cannot account for the selective loss of color in the recrystallized grains, and for the simultaneous preservation of the color in the single crystals, in spite of the temperatures which caused the recrystallization in the first place; a metamorphic process allows for recrystallization and temperature sensitive color generation at different stages of the geologic evolution.

4.4. The potential nature and identity of the light scattering inclusions

Because of their small size, the identity of the light scattering inclusions is especially difficult to establish. Even the conclusions of the study performed by Zolensky et al., (1988), a milestone in the study of blue quartz, are challenged by Kim et al., (2015), who suggested Eu^{2+} and Ce^{3+} activator ions as a cause for the coloration of the Llano blue quartz.

The common methods of mineralogical investigation can only observe the effects of the inclusions and narrow down their potential identity, but the inclusions themselves are outside of the detection range of most instruments. The data gathered over the course of this study is more suited for eliminating potential causes of the coloration, than for pinpointing the actual ones. TEM and EPR investigation techniques are required.

Because light is produced by scattering, it is a safe assumption that the inclusions are nanometric in scale. The loss of color at low temperatures, in the absence of significant changes in quartz, points to the fact that the inclusions are affected by heat in such a way that they can no longer scatter light. An increase in size brought about by polymorphic phase transitions, or the complete disappearance of the inclusions would affect the color. However, the vast majority of the inclusions cited by the geological literature are stable at temperatures well in excess of 300°C. The Llano occurrence is a good illustration of light scattering ilmenite unaffected by heat, which continues to generate blue color even after being subjected to 1000°C for 24 h.

In the case of the Albești blue quartz, based on the thermal behavior, the light scattering inclusions could be fluid in nature, or low temperature molecular colloids. The FT-IR measurements have shown that only the unheated Albești blue quartz generated a signal attributable to O-H bonds. Heating can cause the fluid inclusions to decrepitate and leave the quartz grains, but in the case of the Albești blue quartz, they would have to decrepitate and diffuse (or escape along an intricate network of submicroscopic fractures) at a very high rate. Molecular colloids can scatter light by virtue of their small size. Jayaraman (1939) suggested that molecular colloids resulted from a Ti excess could cause the blue color in the heat sensitive Champion Gneiss quartz, and Lee & Chung (1998) identified colloidal Co-Si-OH nanoclusters, only a few tenths of nanometers across, as the cause of the blue color in synthetic quartz. Molecular colloids/nanoclusters can be easily accommodated by structural defects resulted from metamorphism, and could be affected by heat, depending on their composition. More specialized means of investigation are required to settle the issue of the scattering inclusions.

4.5. Why is the Albești blue quartz unusual?

The Albești type of blue quartz is new to the blue quartz landscape, but definitely not unique. As is the case with blue quartz proper, as defined by Zolensky at al., (1988), the Albești blue quartz owes its color to the scattering of light. However, this is where the similarities end. The light scattering inclusions cited in literature cannot account for the thermal sensitivity of the blue color found in the rock forming quartz of the Albești metagranite, Champion Gneiss, Pietrosu Bistriței porphyroid gneiss, Milbank granite, or Cosăuți granite. Prior to this study, only Jayaraman (1939) has reported heat sensitive blue quartz, and this puts the Albești occurrence in a rather exclusive category. However, the rarity of these quartzes may be misleading, since there is simply not enough information on the subject to assess whether heat sensitive blue quartz is more common than inferred from the literature.

When compared to the blue quartz from Llano, the Albești blue quartz does not show an actual color zoning, in the sense that it does not occur as single crystals presenting both blue and colorless zones (as in the case of the Llano occurrence). The apparent zoning from Albești is owed to the spatial distribution of the recrystallized grains with respect to the initial single crystal. This is yet another difference between the Llano and Albești occurrences, and is indicative of different mechanisms for producing the light scattering inclusions (the origin of the color is fundamentally the same).

Although not in stark contrast with the Llano rhyolite or other blue quartz occurrences where the blue color is produced by light scattering particles, the Albești blue quartz (and other heat sensitive occurrences) deviates from the "blue quartz proper" model, and could be placed in a new category of heat sensitive blue quartz. It appears that the Albești type of blue quartz has a metamorphic rather than a magmatic origin, and this in turn could have different implications concerning the geological significance.

The Llano type of blue quartz represents the stable end of the blue quartz spectrum. It provides information regarding the geochemical particularities of the magmas from which it crystallized, but provides little clues concerning the post-crystallization geological history. On the other hand, the Albești type of blue quartz, because of its sensitivity to temperature in terms of either loss or generation of color, could provide information regarding the PT conditions and the spatial extent of the metamorphic events which overprinted its host rocks.

Despite having been investigated for more than 100 years, blue quartz is still virtually unknown. A comprehensive inventory of the occurrences does not exist, the causes for the coloration are unclear, and the geological significance of the different types of blue quartz has not been established. Occurrences like the one from Albești, which appear to defy the conventional model, may bring the issue of blue quartz worldwide into focus and stimulate further research by showing that the question of the blue color in quartz is far from settled.

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REFFERENCES

Appleman, D.E., & Evans, H.T., Jr., 1973, 1973. *Indexing and least-squares refinement of powder diffraction data*. U.S. Geol. Surv., Comput. Contrib. 20 (NTIS Doc. PB-216).

Balintoni, I., Balica, C., Ducea M.N., Chen, F., Hann, H.P. & Șabliovschi V., 2009. *Late Cambrian-Early Ordovician Gondwanan terranes in the Romanian Carpathians: A zircon U-Pb provenance study*. Gondwana Research, Vol. 16(1), pp. 119-133.

Bill, H. & Calas, G., 1978. *Color centers, associated rare-earth ions and the origin of coloration in natural fluorites*. Phys. Chem. Minerals, vol. 3, pp. 117-131.

Bershov, L.V., Krylova, M.D. & Speranskiy, A.V., 1977. *$O^{-}Al^{3+}$ holes and Ti^{3+} electron centers in quartz as indicators of temperature of regional metamorphism*. International Geology Review, vol. 19(6), pp. 741-744.

Chernov, A.A. & Khadzhi, V.E., 1968**.** *Trapping of colloidal inclusions in the growth of quartz crystals.* Journal of Crystal Growth, vol. 3(4), pp. 641-646.

DeLong, S.E. & Long, L.E., 1976. *Petrology and Rb-Sr age of Precambrian rhyolitic dikes, Llano County, Texas*. Geol. Soc. Amer., v. 87, pp. 275-280.

Hajpál, M. & Török, Á., 2004. *Mineralogical and color changes of quartz sandstones by heat*. Environmental Geology, vol. 46, pp. 311-322.

Iddings, J.P., 1904. *Quartz-Feldspar-Porphyry (Granophyro Liparose-Alaskose) from Llano, Texas*. The Journal of Geology, vol. 12(3), pp. 225-231.

Jayaraman, N., 1939. *The cause of color of the blue quartzes of the charnockites of South India and the Champion gneiss and other related rocks of Mysore*. Proceeding of the Indian Academy of Sciences – Section A., vol. 9(3), pp. 265-285.

Kim, D., Jin, Y.-H., Jeon, K.-W., Kim, S., Kim, S.-J., Han, O. H., Seo, D.-K. & Park, J.-C., 2015. *Blue-silica by Eu^{2+}-activator occupied in interstitial sites*. RSC Advances, vol. 5, pp. 74790-74801.

Lee, Y.K. & Chung, S.J., 1998. *The dependence of cobalt concentration on the growth temperature in synthetic blue quartz.* Journal of Crystal Growth, vol. 196, pp. 151-155.

Montero, P., Talavera, C., Bea, F., Lodeiro, F.G. & Whitehouse, M.J., 2009. *Zircon geochronology of the Ollo de Sapo Formation and the age of the Cambro-Ordovician rifting in Iberia*. The Journal of Geology, vol. 117(2), pp. 174-191.

Müller, C.M., Molinelli, A., Karlowatz, M., Aleksandrov, T.O & Mizaikoff, B., 2011. *Infrared Attenuated Total Reflection Spectroscopy of Quartz and Silica Micro- and Nanoparticulate Films.*J. Phys. Cehm. C, vol. 116, pp. 37-43.

Murata, K.J. & Norman, M.B., 1976. *An index of crystallinity for quartz.* American Journal of Science, Vol. 276, pp. 1120-1130.

Negulescu, E., 2013. *Semnificația mineralelor și a asociațiilor minerale în determnarea istoriei metamorfice a cristalinului Masivului Leaota*. Iași, 100 p, ISBN 978-973-702-988-1.

Negulescu, E.. & Săbău, G., 2015. *Fluid-mediated alteration of eclogite lenses in subduction complexes: a case from the Leaota Massif (South*

Carpathians). In: **Zellmer G.F., Edmonds M., Straub S.M.** (eds). *The Role of Volatiles in the Genesis, Evolution and Eruption of Arc Magmas*. Geological Society Special Publication 410. The Geological Society of London, 2015, p. 292, ISSN 0305-8719.

Negulescu, E., Săbău, G. & Massonne, H. –J., 2018. *Growth of chloritoid and garnet along a nearly isothermal burial path to 70 km depth: an example from the Bughea Metamorphic Complex, Laorta Massif, South Carpathians*. Mineralogy and Petrology, Vol. 112(4), pp. 535-553.

Pantia, A.I & Filiuță, A.E., 2019. *Blue quartz around the globe*. Oltenia. Studii și comunicări. Științele Naturii. Tom. 35, No. 2/2019, pp. 207-213.

Razva, O., Anufrienkova, A., Korovkin, M., Ananieva, L. & Abramova, R., 2014. *Calculation of quartzite crystallinity index by infrared absorption spectrum*. IOP Conference Series: Earth Environmental Science 21.

Saikia, B.J., Parthasarathy, G. & Sarmah, N.C., 2008. *Fourier transform infrared spectroscopic estimation of crystallinity in SiO_2 based rocks*. Bull. Mater. Sci. vol. 31(5), pp. 775-779.

Seifert, W., Rhede, D., Thomas, R, Förster, H.-J., Lucassen, F., Dulski, P. & Wirth, R., 2011. *Distinctive properties of rock-forming blue quartz: inferences from a multi-analytical study of submicron mineral inclusions*. Mineralogical Magazine, vol. 75(4), pp. 2519-2534.

Shoval, S., Ginott, Y. & Nathan, Y., 1991. *A new method for measuring the crystallinity index of quartz by infrared spectroscopy*. Mineralogical Magazine, vol.5, pp. 579-582.

Stenina, N.G., 2004. *Water-related defects in quartz*. Bulletin of Geosciences, vol. 79 (4), pp. 251-268.

Udubașa, G., Gheuca, I., Balaban, A., Nedelcu, L., Dinică, I., Robu, N., Horvath, A., Robu, L., Lupulescu, A., Tatu, M., Anghel, S., Scurtu, S., Gheorghiță, I., Roșca, V., Rădulescu, Fl., Izvoreanu, I., Gaftoi, F., Zămârcă, A., Bratosin, I., Șerbănescu, A., Popescu, F. & Serban, E., 1985. *Studiul geologic și geofizic al Carpaților Meridionali cu privire specială asupra perspectivelor economice și orientării activității de prospecțiune și explorare. Munții Leaota și Munții Făgăraș de NE*. Report, Geological Institute of Romania Archive. In **Negulescu E.,** 2013. *Semnificația mineralelor și a asociațiilor minerale în determnarea istoriei metamorfice a cristalinului Masivului Leaota*. Iași, 100 p, ISBN 978-973-702-988-1.

Wise, M.A., 1981. *Blue quartz in Virginia*. Virginia Minerals, vol. 27(2), pp. 9-16.

Yadav, A.K. & Singh, P., 2015**.** *A review of structure of oxide glasses by Raman spectroscopy*. RSC Adv., vol. 5, pp. 67583-67609

Zolensky, M.E., Sylverster, P.J. & Paces, J.B., 1988. *Origin and significance of blue coloration in quartz from Llano rhyolite (llanite), north-central Llano County, Texas*. American Mineralogist, vol. 73, pp. 313-323.

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