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CHARACTERIZATION OF HYDROTHERMAL GREEN QUARTZ PRODUCED BY GAMMA RADIATION

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ABSTRACT

A specific variety of quartz showing a green color in nature or induced artificially by radiation gamma (^{60}Co) is quite rare. Only two occurrences are known today, where this type of quartz can be found: Canada, at the Thunder Bay Amethyst Mine, Ontario and Brazil, at widely scattered geode occurrences along a 600 km stretch from Quaraí at Brazils southern most tip to Uberlandia in Minas Gerais. These two occurrences have been formed by strong hydrothermal activities.That way much quartz crystals showed a very fast growth history facilitating the formation of growth defects (twinning, small angle tilting, mosaic growth, striations) and the uptake of water in form of micro inclusions, molecular water, silanol (Si-OH) and OH. In the present work the material analyzed is from hydrothermal regimes found in intrusions of basaltic rocks located in the Rio Grande do Sul state. To characterize these materials, colored green by gamma rays, analyses by ICP, electron microscopy, water loss techniques and UV-VIS or NIR-FTIR spectroscopic measurements have been made. Silanol complexes are formed, which by radiation due to gamma rays form the color center NBOHC (Non-bonding Oxygen Hole Center), showing absorption between 590 to 620 nm, responsible for the green color. The water content with up to 3200 ppm by weight exceeds the amount of charge balancing cations (Fe, Al, Li). There is no correlation between water content and cations as in other color varieties.

1. INTRODUCTION

In recent years the world has registered a large interest by the gems and jewellery industry in minerals treated by irradiation processes carried out in electron accelerators and gamma radiation. These irradiation methods are forms of processing that accelerates the process of coloring gemstones. By natural radiation, emitted by radioactive elements such as uranium, thorium and potassium minerals, it would take thousands of years in nature to produce the same effect. In this respect it is worthwhile to mention that irradiation by gamma rays will not leave radioactive traces in the treated mineral [1]. One of the minerals which aroused most interest in these treatments is quartz, a very widespread mineral with a range of colors from violet, brown, pink, yellow to green.

A specific variety of quartz with green color, whether natural or induced by radiation is very rare. This is a mechanism of formation of color completely different of those well known and widely discussed in the literature. Schultz-Güttler et al. [2] [3], Henn & Schultz-Güttler [4] and Clerice [5] presented some studies on irradiated green quartz from regions of Rio Grande do Sul. Chemical analysis and UV-VIS and NIR spectroscopy showed, in an initial study, that the molecular water and the hydroxyl anion present in the structure of crystalline quartz, can be the main factor responsible for the green color.

Schultz-Güttler [6] and Henn & Schultz-Güttler [4] did some considerations regarding the definitions of Prasiolite and Green quartz. The name green quartz is applied to the quartz from the basaltic rocks of the Paraná basin, especially in southern Brazil, Uruguay and West of Minas Gerais (Uberlândia) that acquires the green color after treatment with gamma radiation. The name prasiolita or green amethyst is given historically to amethyst (green) obtained through the process of heating the purple amethyst extracted in Brazil, exclusively in the region of Montezuma,

Only two occurrences of green quartz of hydrothermal origin are known located in the region of the Paraná basin, in Brazil and in Thunder Bay Mine in Canada recently described by Hebert & Rossman [7]. These two occurrences were formed under strong hydrothermal activity, the one of Thunder Bay is due to tectonism and of the Paraná basin is related to the activities of meteoric water and hydro-thermal events of the Guarani aquifer. These hydrothermal quartz crystals have a history of very fast growth, allowing the formation of abundant growth defects such as twinnings, mosaic formation with small inclined angles and striations that facilitate the absorption of water in the form of molecular water, silanol (Si-OH) [8], hydroxyl (OH) and as micro inclusions. This type of quartz can be considered as "hydrated quartz" (wet quartz) similar to synthetic quartz.

The water content, with up to 3200 ppm by weight is higher than the concentration of the structural impurities such as Fe, Al and Li. In such hydrothermal quartz are formed complexes of silanol that when irradiated generate color centers NBOHC (Non-bonding Oxygen Hole Center) which presents absorption in the range of 590 nm at 620 nm forming a near 550 nm transmission window, responsible for the green color.

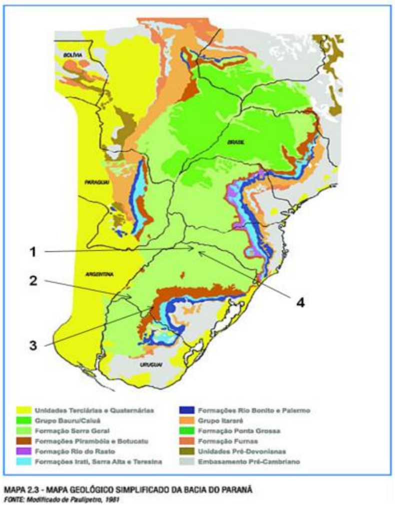
Various techniques of chemical analysis and spectroscopy were employed to characterize these samples of green quartz. To document the influence of water on formation of green color, analysis by FTIR infrared spectroscopy in quartz samples from 3 different groups of geological environments,(pegmatite quartz with Al and Li formed at high temperature from region of Santana do Araguaia, hydrothermal quartz with Al, but without water originated by intermediate temperature from the region of Curvelo and Amethyst with very little Al, Fe and small silanol content from Brejinho region are discussed in detail .

2. MATERIALS AND METHODS

2.1. Materials

This work used samples of macrocrystalline colorless quartz of hydrothermal origin in the form of plates, chips, powder and faceted crystals. These samples are from the hydrothermal deposits of the Paraná basin and were collected in the localities of Ametista do Sul (RS), Quaraí (RS), Santana do Livramento (RS) and Soledad (RS). They occur in geodes scattered in the basaltic rocks of the Serra Geral Formation that can reach an area exceeding 1,200,000 km^2. Fig. 1 shows the regions in which the samples were collected .

Samples of quartz from the region of Curvelo (MG), Brejinho (BA) and Santana do Araguaia (PA) as well as sample of fused silica and ultrapure GE 124 with low contents of silanol, produced by General Electric company were used as reference materials and for comparison purposes.



1. Ametista do Sul (RS)
2. Quaraí (RS)
3. Santana do Livramento (RS)
4. Soledade (RS)

Figure 1: Sampling regions of hydrothermal quartz from Paraná Basin. Adapted ABAS [9].

Before the samples are analyzed, all quartz material passed through initial surface cleaning steps in the laboratory of Radiation Technology Center – CTR of IPEN-CNEN/SP, and for some analysis, slices ore powder samples were prepared. The slices were cut and polished at the laboratory of preparation of samples from the Institute of Geosciences of the University of São Paulo and the Opto Electronics Company, from clear and transparent quartz crystals by cutting of samples perpendicular to the C axis of the crystal with thickness from 2 to 5 mm.

2.2. Irradiation procedures

Colorless quartz samples were subjected to irradiation in cobalt-60 multipurpose radiator, installed at the technology center of radiation of IPEN-CNEN/SP. It is a multipurpose compact type radiator (Fig. 2a) which contains currently fifty one ^{60}Co pencil (Fig. 2b) set in magazines that are distributed in four racks with a total dose of approximately 1.017 x 10^7 MBq (275,000 Ci) in May 2015. The quartz samples, contained in wired containers, are irradiated under water to maintain a low temperature.

The total doses applied to the samples ranged from 300 to 450 kGy. These doses were determined through the reading of dosimeters of polymethyl methacrylate (PMMA), of type Red Perspex 4034, furnished by the English company Harwell Dosimeters Limited and of dosimeters of cellulose triacetate (CTA) with triphenyl phosphate delivered by Fujifilm manufacturer.

(a)

(b)

Figure 2: Multipurpose Irradiator of the Radiation Techonology Center from IPEN-CNEN/SP: (a) control room and (b) botton of the pool with ^{60}Co sealed sources.

2.3. Methods of characterization

Representative samples of green quartz crystals were selected for chemical and spectroscopic characterization . For the chemical analysis techniques were used such as mass spectrometry (ICP-MS) performed in the laboratory of chemistry of the IG-USP and optical emission spectrometry with argon plasma (ICP-OES) performed in the laboratory of IPEN. The near-infrared spectroscopy (NIR) and IR were also carried out in the laboratories of IPEN. The determination of the concentration of total H_2O present in quartz was made using the technique of Loss of Ignition analysis. Scanning electron microscopy MEV located at IPEN were performed for information about the texture and topography of the samples mainly regarding Brazil Law twinning and the striations analyses.

3. RESULTS AND DISCUSSION

3.1. Irradiation

Most hydrothermal quartz samples from localities of Quaraí, Ametista do Sul, Soledade and Santana do Livramento after being subjected to radiation acquired a greenish tinge which may vary from a light green to deep green and some displaying a grayish green tone. It has been observed in the tests that approximately 70% to 80% of the irradiated samples of the Quaraí with doses of approximately 300 kGy display green tint gray and about 10% to 30% remained colorless as shown in Fig. 3.

Figure 3: Quartz samples from Quaraí region, irradiated at 300 kGy.

3.2. Chemical composition

The results of chemical analysis carried out by ICP-OES indicate that the chemistry of quartz samples of hydrothermal origin is dominated mainly by impurities of Fe (80-138 ppm), Al (148-336 ppm), Na (109-237 ppm), K (81-131 ppm) and Ca (~50 ppm), and OH and H_2O, determined by in Fire Loss Analysis (LOI). The results of the samples analyzed are shown in Table 1. For comparison the analysis of a sample of synthetic quartz GE 124 is cited that presented the following data: Al (14 ppm), Fe (0.2 ppm), Na (0.7 ppm), Ti (1.1 ppm) and Li (0.6 ppm). This sample can be considered very pure. As has been shown by Ihinger et al. [10], the concentrations of trace elements and water vary as a function of certain growth sectors and directions. Similar relationships were shown by Lias et al. [11] and Brice [12] on samples of synthetic quartz. It was noted that the growth rate of crystals affects strongly the incorporation of trace elements.

Table 1: Optical emission spectrometry with argon plasma (ICP-OES)

Element (µg/g)	Locality			
	Ametista do Sul (RS)	Quaraí (RS)	Santana do Livramento (RS)	Soledade (RS)
Na	195 ± 6	109 ± 12	208 ± 9	237 ± 21
Al	287 ± 1	148 ± 2	336 ± 11	327 ± 2
K	104 ± 2	81 ± 2	131 ± 3	109 ± 2
Ca	50 ± 7	< 2,0	< 2,0	< 2,0
Fe	89 ± 14	80 ± 1	136 ± 8	138 ± 6
Cr	< 8,0	< 8,0	< 8,0	< 8,0
Mn	< 1,5	< 1,5	< 1,5	< 1,5
Zn	< 5,0	< 5,0	< 5,0	< 5,0
Ni	< 16,0	< 16,0	< 16,0	< 16,0
Cu	< 25,0	< 25,0	< 25,0	< 25,0
Ba	< 3,0	< 3,0	< 3,0	< 3,0
Mg	< 1,5	< 1,5	< 1,5	< 1,5

3.3. UV-VIS and FTIR Spectroscopy

Fig. 4 shows the spectra obtained by UV-VIS spectrometry of 5 samples of quartz, with the graduation of hues from intense green to light green, and of a sample of colorless quartz. As can be seen the spectra of samples of green quartz present an absorption band at 620- 630 nm, while the colorless quartz shows no peak.

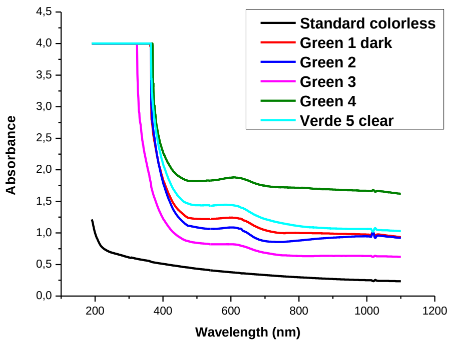


Figure 4: UV-VIS spectra of five quartz samples, with tonality varying from dark green to clear green, and of a colorless quartz sample.

These absorptions are related to the NBOHC defects and are very different from the color centers originated by the replacements by impurities of Fe Si and Li. NBOHC are defects in the crystal structures along dislocations without any direct connection with the tetrahedra of SiO_4 or may be present in the regions of bonds highly strained as for instance the twinning in step growth in spiral growth defects [13] [14]. Examining the green quartz crystals by higher magnification one can find fine striations parallel to romboedrical faces that are called Brazil

Law twinning [15], as shown in Fig. 5. These thin striae are indications of very fast crystal growth [4].

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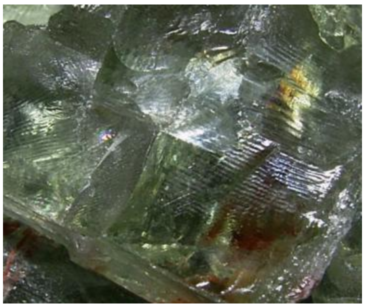


Figure 5: Brazil Law twinning in green quartz, with details of fine and parallel striations.

Fig. 6 shows the FTIR spectra of transmittance of several samples of the localities of Ametista do Sul (AMS) Brejinho (BS), Curvelo (CS) and Santana do Araguaia "green gold" (GG). The graph shows the distribution of the contents of H_2O in various molecular forms in the samples. Samples of Santana do Araguaia and Curvelo (at the top of Fig. 6) are poor in H_2O and show peaks linked to Al, Li and OH. Brejinho samples show larger absorption near 3,400 cm^{-1} indicating a slightly higher molecular water content. The Ametista do Sul specimens show very low transmittance verging on zero and are rich in H_2O. With respect to silanol (Si-OH), analyzing the range of the wave numbers near 4,500 cm^{-1}, one note that the samples of Santana do Araguaia and Curvelo show no transmission indicating the total absence of silanol. Brejinho samples show a small absorption of silanol (4500 cm^{-1}), far lower than the Ametista do Sul specimens.

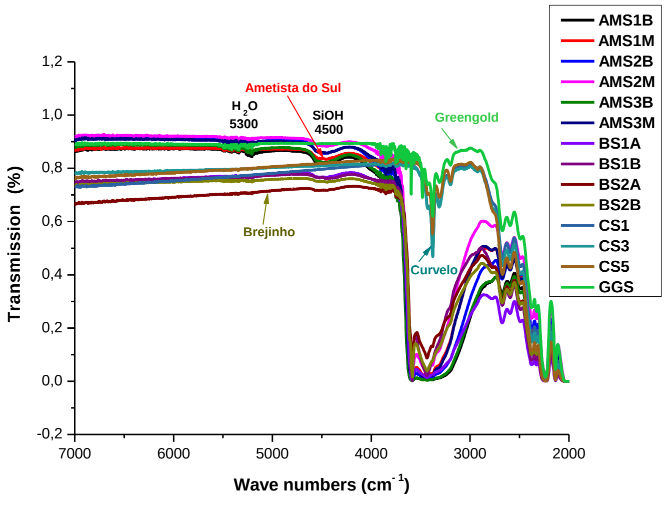


Figure 6: FTIR of transmission spectra of quartz samples in OH and H_2O molecular region.

Fig. 7 shows the FTIR spectra of seven sliced samples of a single crystal derived from hydrothermal quartz from the Ametista do Sul region , and of the plate of fused silica GE. It can be observed that the quartz plates and GE feature peaks corresponding to the hydroxyl

(OH) 7050 cm^{-1} (1450 nm), 4450 cm^{-1} (2250 nm) and 3700 cm^{-1} (2700 nm). However, only the hydrothermal quartz plates display the peak of molecular water at 5250 cm^{-1} (1900 nm).

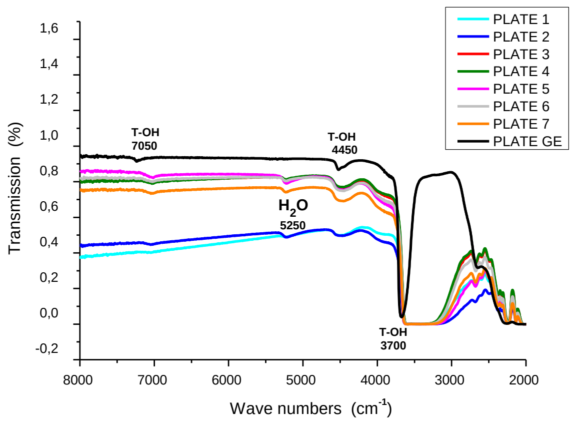


Figure 7: FTIR spectra of sliced plates from the same crystal and the GE fused silica plate.

3.4. Loss of ignition (LOI) results

Loss of ignition analysis was conducted to determine the total water content present in the samples of colorless and green color quartz , and to check a possible correlation of color with the concentration of water. Several analyses were carried out and the water values found in all samples of Quaraí, Santana de Livramento, Ametista do Sul and Soledade ranged from 56 to 2133 ppm by weight as presented in Table 2. This result shows a great dispersion of values between the samples. However, there was a clear relationship between the amount of water and the resulting color of irradiation.

Table 2: H_2O concentration (ppm) in quartz samples determined by Loss of ignition analysis (LOI) and correlation with color

Locality	*Dark green*	*Clear green*	*Colorless*
Quaraí	970	397	Not detected
Ametista do Sul	1697	1284	182
Santana do Livramento	2133	738	326
Soledade	147	103	56

Analyzing the water values presented in Table 2, one notes that the variation of these values accompanies well the intensity of the green color. The fact that the same shades of colour contains different amounts of water determined by the LOI, may indicate that a part of water can still be retained in the samples in form of Si-OH. To obtain more data on the amount of water LOI analyses of more samples of several localities were performed in the laboratory of chemistry of the Institute of Geosciences of USP, shown in Table 3. The content is given as a percentage and concentration (ppm) of water.

Table 3: H_2O quantity in percentage and ppm from various regions analyzed by Loss of ignition analysis (LOI)

Locality	*% H_2O*	*Concentration H_2O (ppm)*
Ametista do Sul (RS)	0,32	3200
Santana do Livramento (RS)	0,33	3300
Soledade (RS)	0,32	3200

All values presented in Table 3 are high. So, with an amount of water exceeding very much the contents of trace elements as indicated previously, it is not possible to make similar correlations as shown by Iwasaki et al. [16] between the water content and the sum of trace elements. The high concentration of water, whether in the form of OH or molecular, water makes up for any lack of correlation with structural elements (substitucional and interstitial). The differences of concentrations observed in Tables 2 and 3, whose analyses were performed on the IPEN and IG-USP can be explained by the fact that different physical forms were used in two analysis. The values obtained and presented in Tables 2 and 3 samples were used in the form of small splinters and the analysis done in IG-USP were used quartz powder samples.

3.5. Scanning Electron Microscopy (MEV)

Analyses were performed by MEV on samples of quartz of Quaraí region as shown in Fig. 8 which show superficially Brazil Law twinning. Fig. 9 (a) and (b) shows images of the distribution of Al and Fe in the region of Brazil Law twinning. It can be observed that there is a greater amount of Al than Fe and that both the Al as well as the Fe are concentrated on the right of the twinning lamellae. Observing the distribution of backscattered electrons shown by the elements Fe and Al one notes a parallel orientation to the stretch marks indicating that the elements embedded in quartz follow the relief of twinning. Fig. 10 shows the distribution of other elements such as P, Na, and K (a) Ge and Mn, Mg and Cu (b), on the part of the twinning. The Na and K are considered compensating elements.

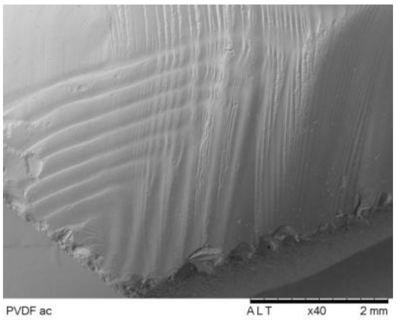
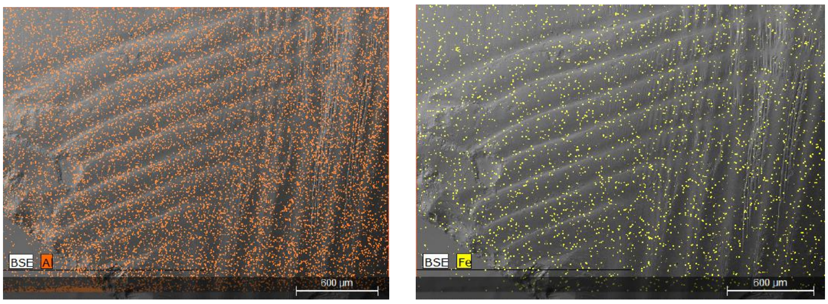
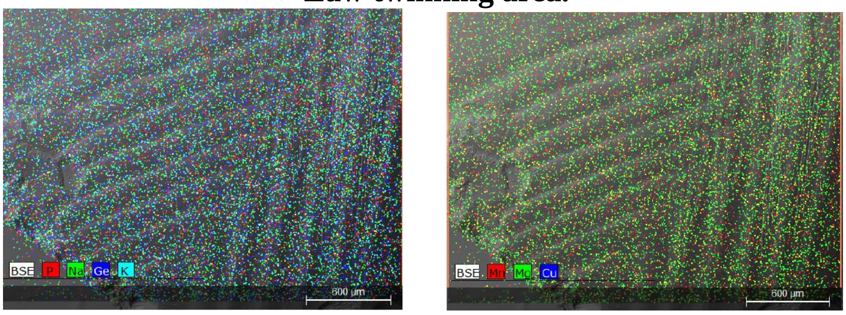


Figure 8: Image from quartz surface obtained by MEV shows Brazil Law twinning.



(a) (b)

Figure 9: Image detail of Al (a) and Fe (b) distribution in green quartz, in the Brazil Law twinning area.



(a) (b)

Figure 10: Image detail of P, Na, Ge and K (a); and Mn, Mg and Cu (b) distribution in green quartz, in the Brazil Law twinning area.

4. CONCLUSIONS

The infrared FTIR spectroscopy analyses carried out on samples of the Ametista do Sul, Santana do Livramento and Quaraí, showed absorptions between 4300 cm^{-1} and 4700 cm^{-1}, connected to the Si-OH. A strong absorption near 5200 cm^{-1}, is related to molecular water. This content of molecular water and hydroxyl in hydrothermal quartz is unique and is responsible for the formation of defects called NBOHC that produce, by natural or artificial radiation, the green color in crystals of hydrothermal origin. This high concentration of silanol can be related with the presence of Brazil Law twinning in samples of hydrothermal quartz, as can be observed in the images obtained by Scanning Electron Microscopy MEV from samples from Ametista do Sul.

The high concentrations of water can be proven by the analysis of Loss of ignition (LOI) performed on samples of hydrothermal quartz of the Paraná basin from various locations mainly in the regions of Ametista do Sul (3200 ppm), Santana do Livramento (3300 ppm) and Soledade (3200 ppm).

Analyses and comparisons allowed to differentiate and determine the formation of the Color Centre of NBOHC with the color obtaine by irradiation of hydrothermal quartz of geodes from the Paraná basin. Thus, only quartz crystals with high concentration of molecular water and silanol are suitable to develop green color by gamma radiation.

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