

COMPARATIVE ANALYSIS OF QUARTZ TREATED WITH GAMMA RADIATION ORIGINATED FROM THE HYDROTHERMAL GEODES OF THE PARANÁ BASIN (ARTIGAS-URUGUAY REGION), WITH QUARTZ GENERATED IN THE HYDROTHERMAL VEINS OF SERRA DO ESPINHAÇO (CURVELO-MG AND BREJINHO-BA REGIONS)

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ABSTRACT

In Brazil, hydrothermal quartz may be found in the geodes of the basaltic rocks of the Paraná Basin and in the vein systems of quartzites of the Serra do Espinhaço. The quartz of hydrothermal origin of the Paraná Basin contains a great amount of structurally bound water in the form of molecular water, silanol, hydroxyl and abundant growth defects that are responsible for the green color formed by irradiation. To register the influence of water in the formation of the green color in the quartz of the Paraná Basin, quartz samples from the following regions were analyzed: Artigas, located in the Paraná Basin, Curvelo and Brejinho located in Serra do Espinhaço. The quartz from Artigas, formed at low temperature, has high concentration of molecular water and silanol and a greater amount of Fe than Al. The quartz from Curvelo with Al, but, without water molecular and silanol was formed by intermediate temperature and the quartz from Brejinho has very little Al, Fe and a small silanol and molecular water content. To characterize these samples, ICP and NIR-FTIR spectroscopic measurements have been taken, together with water loss techniques and color stability, by UV treatment and heating. The analysis by FTIR spectrometry of Artigas quartz samples shows strong absorptions of H₂O and Si-OH, respectively, near the regions of 5300 cm⁻¹ and 4500 cm⁻¹. This content of molecular water and silanol in hydrothermal quartz of Artigas is responsible for the formation of NBOHC defects that produce, by gamma radiation, the green color.

1. INTRODUCTION

Several minerals, mainly quartz, are treated worldwide in many irradiation centers and they use this technique to activate the so-called “color centers” in minerals and produce higher valued gemstones. The presence of defects and faulty structures in the minerals, combined with the effect of the ionizing radiation, produces changes in the optical properties of these materials. These alterations are manifested as color.

In Brazil, hydrothermal quartz may be found in the Paraná Basin and in the Serra do Espinhaço Range. The hydrothermal quartz contains all the varieties of silica found in fractures and geodes of the basaltic rocks of the huge Parana Basin, including agates, amethyst, chalcedonies and the types which will show green color after irradiation, as well as the silica varieties hosted by the vein systems of the quartzites of the Espinhaço Mountain Range.

The formation of the green quartz found in nature or induced artificially by gamma radiation is very different from that widely discussed in the literature and responsible for the formation of the fumée, citrine and amethyst types of quartz, including the prasiolite (leak green quartz) formed by heating amethyst from Montezuma, Brazil. Schultz-Güttler [1] and Henn & Schultz-Güttler [2] did some considerations regarding the definitions of Prasiolite and Green quartz.

Two occurrences of green quartz of hydrothermal origin have been located in the region of the Paraná Basin, in Brazil and Uruguay, and in Thunder Bay Mine, in Canada, as described by Hebert & Rossman [3]. These two occurrences were formed under strong hydrothermal activity; the one of Thunder Bay is due to tectonism and that 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 twinning, mosaic formation with small inclined angles and striations [4,5,6], facilitating the absorption of water in the form of molecular water, silanol (Si-OH) [6], hydroxyl (OH) and as micro inclusions. This content of molecular water and silanol in hydrothermal quartz from the Artigas is responsible for the formation of NBOHC defects that produce, by gamma radiation, the green color [7].

The green quartz from hydrothermal origin may be found at widely scattered geode occurrences, along a 600 km stretch from Quaraí (Brazil) and Artigas (Uruguai) to Uberlandia in Minas Gerais. Some studies on irradiated green quartz, from some regions of Rio Grande do Sul, were presented by Henn & Schultz-Güttler [2], Schultz-Güttler et al. [8, 9] and Enokihara [10].

Various techniques of chemical analysis and spectroscopy were employed to characterize the samples of green quartz. To document the influence of water on the green color formation, analyses by FTIR spectroscopy were performed in quartz samples from the regions: Artigas (Uruguai), located in the geodos of the Paraná Basin, at Brejinho (BA) and Curvelo (MG), located in the veins of Serra do Espinhaço.

2. MATERIALS AND METHODS

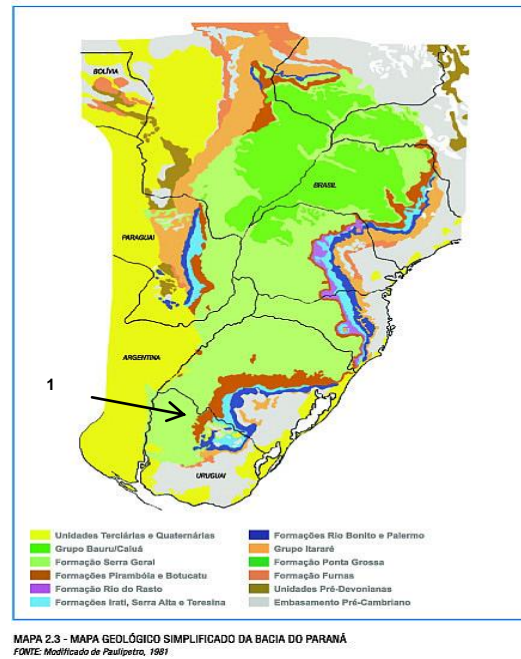
2.1. Materials

The samples used were hydrothermal origin macrocrystalline colorless quartz, with the shape of plates, chips, powder and faceted crystals. These samples are from the hydrothermal Paraná Basin and were collected in the locality of Artigas (Uruguai).

Samples of quartz, also, from hydrothermal deposits in the regions of Brejinho (BA) and Curvelo (MG.), were used as reference materials and for comparison purposes.

The quartz materials underwent initial surface cleaning steps in the laboratory of Radiation Technology Center – CETER of IPEN-CNEN/SP, and for some analyses, slices and powder samples were prepared. The slices were cut and polished at the laboratory of samples preparation, from the Institute of Geosciences of the University of São Paulo, with thicknesses from 2 to 5 mm.

The samples were collected in the region of Artigas (Uruguai), as shown in Fig.1.



1. Artigas

**Figure 1: Sampling regions of hydrothermal quartz from Artigas (Uruguai).
Adapted from ABAS [11].**

2.2. Irradiation procedures

The irradiation of colorless quartz samples were made in the ^{60}Co Multipurpose Irradiator installed at the Radiation Technology Center of IPEN-CNEN/SP [12]. It is a multipurpose compact type radiator, containing, currently, 64 pencils of ^{60}Co set in magazines. The quartz samples, enclosed in wired containers, were irradiated under water.

Maximum doses applied were up to 450 kGy. These doses were determined through the reading of dosimeters of polymethyl methacrylate (PMMA), Red Perspex 4034 type, and dosimeters of cellulose triacetate (CTA), with triphenyl phosphate.

2.3. Methods of characterization

Representative samples of quartz crystals were selected for chemical and spectroscopic characterization. For the chemical analysis, the techniques of Optical Emission Spectrometry, with Argon Plasma (ICP-OES), at the Chemical Laboratory from IPEN-CNEN/SP, have been used.

The near-infrared NIR and IR spectroscopy were made by using the FTLA 2000 – ABB Bomem spectrometer, at the Radiopharmacy Center of IPEN-CNEN/SP.

The determination of total H₂O concentration, present in quartz, was accomplished using the technique of Loss of Ignition Analysis.

To examine the defects of quartz samples growth, with regard to twinning, the polariscope and horizontal gemological research microscope, installed at the Gemological Laboratory of the Institute of Geosciences of the University of São Paulo, were used.

To analyze the loss of color as to time of exposure to ultraviolet radiation, an EQUILAM chamber, model EQUV that is installed in the Materials Technology Center of the IPEN-CNEN/SP, was used. It has 8 mercury fluorescent lamps of 40 Watts each, emitting ultraviolet radiation of 340 nm, in the UVA region. The samples were analyzed using the UV-VIS spectrophotometer Shimadzu LDPI, from the CETER-IPEN-CNEN/SP.

For the tests of color stability by heating, a Black & Decker electric furnace with maximum temperature up to 350 °C and glass cover, allowing visual monitoring of the discoloration of the quartz samples, was used.

3. RESULTS AND DISCUSSION

3.1. Chemical analysis

Chemical analysis ICP-OES were carried out in quartz samples from hydrothermal origin of Artigas and are listed in Table 1, showing a predominance of Al, Fe, Na and K impurities.

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

<i>Element</i>	<i>Concentration ($\mu\text{g/g}$)</i>
Na	147 ± 2
Al	286 ± 19
K	114 ± 1
Ca	< 2.0
Fe	159 ± 8
Cr	< 8.0
Mn	< 1.5
Zn	< 5.0
Ni	< 16.0
Cu	< 25.0
Ba	< 3.0
Mg	< 1.5

The results of chemical analysis carried out by ICP-OES indicate that the chemistry of quartz samples of hydrothermal origin, from Artigas, are dominated mainly by impurities of Fe (159 ppm), Al (286 ppm), Na (147 ppm), K (114 ppm) and H₂O. The results of the samples analyzed are shown in Table 1. As it has been shown by Ihinger et al. [13], the concentrations of trace elements and water vary as a function of certain growth sectors and directions. It was noticed that the growth rate of crystals affects, strongly, the incorporation of trace elements.

3.2. FTIR Spectroscopy

The graph presented in Fig. 2 shows the FTIR spectra of transmittance of the samples from Artigas (ARS), Brejinho (BS) and Curvelo (CS) regions. The graph shows the distribution of H₂O contents in various molecular forms in the samples.

Artigas samples show strong absorptions of H₂O and Si-OH, respectively, near the regions of 5300 cm⁻¹ and 4500 cm⁻¹ [14]. These concentrations may be related to the presence of polysynthetic twinning of Brazil Law [15], facilitating the capture of water and OH groups. Brejinho samples show larger absorption near 3400 cm⁻¹, indicating slightly higher molecular water content. Samples of Curvelo are poor in H₂O and show peaks linked to Al, Li and OH.

With respect to silanol (Si-OH), analyzing the range of the wave numbers near 4500 cm⁻¹, samples from Curvelo did not show any transmission, indicating the total absence of silanol. Brejinho samples showed a small absorption of silanol (4500 cm⁻¹), far lower than Artigas samples.

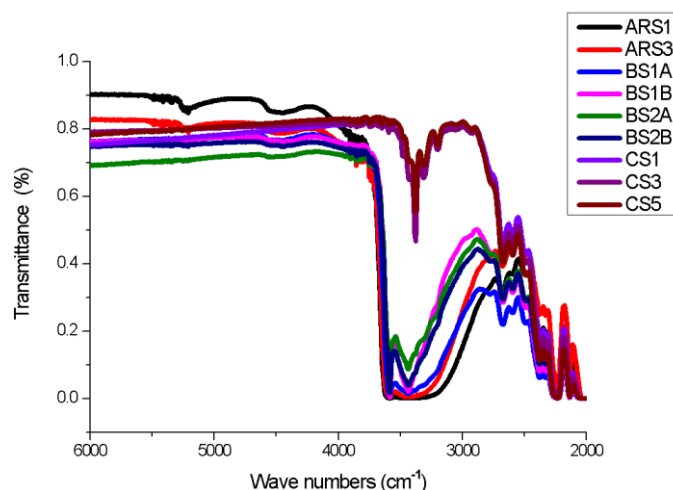


Figure 2: FTIR spectra of quartz samples from Artigas, Brejinho and Curvelo regions.

According to Lias et al. [16], the growth rate influences strongly on the incorporation of water and other impurities. In addition, some quartz sectors are better able to absorb impurities, as a function of temperature and speed of growth. This incorporation of water may take place in two different ways: as a molecule wholly fixed in the gaps, in the channels of the structure or in hydroxyl (OH) form. The analysis of infrared absorptions in the medium region, from 400 cm^{-1} to 4000 cm^{-1} , does not allow these two forms to be distinguished.

In previous works, especially by Kats [17], the OH bonds with trace elements such as Al and Fe are known, but not their specifications. These specifications may be studied only by absorption analysis in the near infrared between 4000 cm^{-1} to 8000 cm^{-1} . In such case, larger thickness samples were necessary in order to have a higher absorption, as the intensities of a higher order of absorption are weaker.

In Fig. 3, the transmittance spectra of these localities samples are shown, in the range of 6000 to 4000 cm^{-1} . It may be observed that the quartz plate from Curvelo shows, in this interval, a line without absorptions. The quartz plate from Brejinho shows absorptions between 4300 and 4600 cm^{-1} . Finally, Artigas quartz plate shows absorptions between $4300 - 4700\text{ cm}^{-1}$ and near 5200 cm^{-1} . The absorptions in the 4400 cm^{-1} range show ripples, indicating various absorption bands.

According to Aines et al. [18], the absorptions in the vicinity of 4400 cm^{-1} are related to T-OH, with T indicating tetrahedron. Hence, these absorptions may be Al-OH, as well as Si-OH (silanol). The absorption near 5200 cm^{-1} is related to molecular H_2O . Then, it may be concluded that the Curvelo sample contains little or no molecular water or silanol concentration. Brejinho sample contains little silanol concentration as well as little Brazil Law twinning and it has little or no amount of molecular water, while Artigas sample shows very well defined molecular water and silanol content.

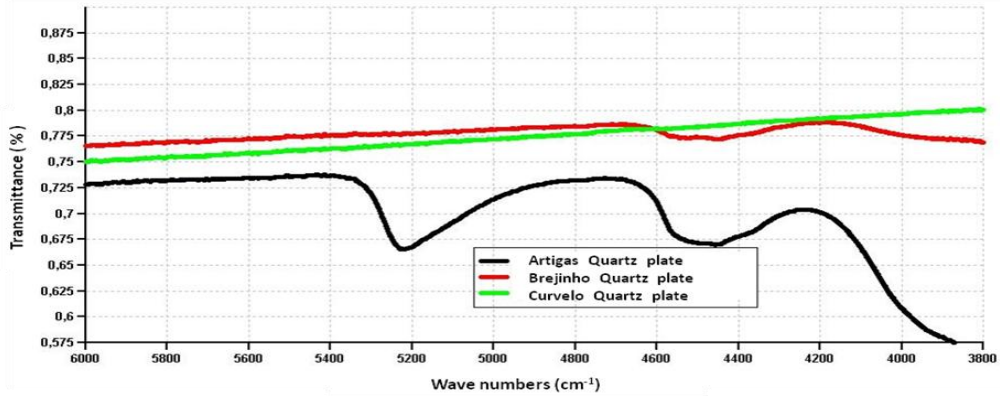


Figure 3: Spectrum in the near infrared range of quartz samples from Artigas, Brejinho and Curvelo regions, with various water specifications.

3.3. Analysis of growth defects by the use of the Polariscope and a Gemological Microscope.

The quartz samples of Artigas region from the geodes of the Paraná Basin (low pressure and temperature conditions) are heavily twinned. This analysis shows that samples of Brejinho and Curvelo regions originated from hydrothermal regimes of Serra do Espinhaço (intermediate pressure and temperature) and present few traces or no Brazil Law twinning.

Figs. 4 (a) and (b) show the samples of the locality of Quaraí/Artigas with perfect Brazil Law twinning involving the whole crystal. This twinning is called polysynthetic, with crystal composed of thousands of crystalline planes (thin slices), with nano-sized micrometric thickness, interconnected and interwoven with numerous planar defects and giving rise to oxygen without connection with other tetrahedra. This state is ideal for forming Silanol (Si-OH) and NBO (Non-Bridging Oxygen or Non-Bonding Oxygen), producing the NBOHC color centers, responsible for the green color [7].

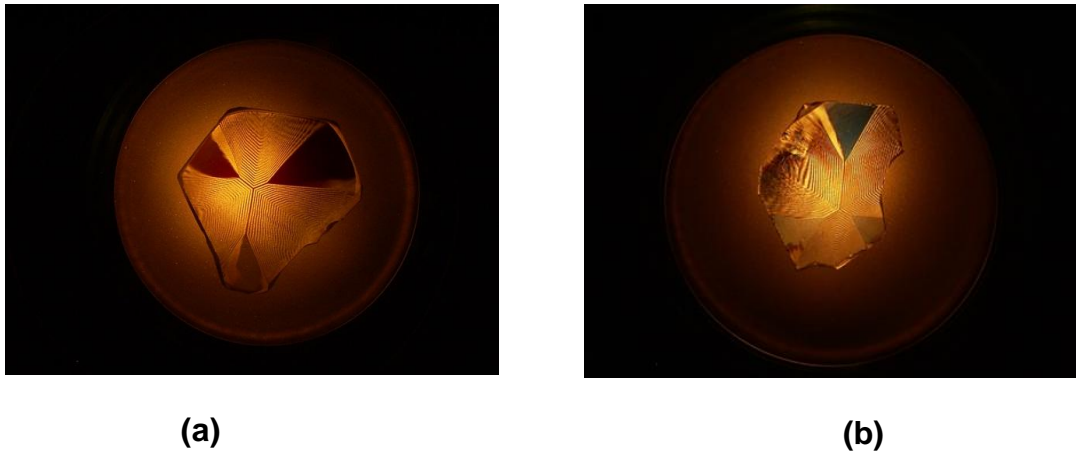


Figure 4: Images obtained in the polariscope of quartz plates from Quaraí/Artigas in the Paraná Basin (a) and (b) with Brazil Law twinning.

Fig. 5 shows the images of a hydrothermal quartz sample from Brejinho region (Serra do Espinhaço), where there is a decrease in Brazil Law twinning. This fact does not occur with the hydrothermal quartz sample from the Curvelo locality (Serra do Espinhaço) presented in Fig. 6, which does not show any Brazil Law twinning.

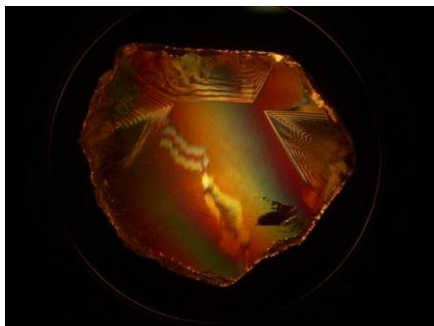


Figure 5: Image of a quartz plate from Brejinho region.

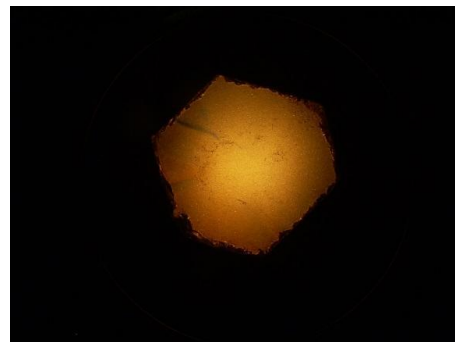


Figure 6: Image of a quartz plate from Curvelo region.

3.4. Loss of ignition (LOI) analysis

Loss of ignition analysis was performed to determine the concentration of total H₂O present in the samples of colorless and green color quartz from Artigas region, and to verify a possible correlation between the color and the concentration of water. The result presented in Table 2 shows a clear relationship between the amount of water and the consequential irradiation color.

Table 2: H₂O concentration (ppm) in quartz samples determined by Loss of ignition analysis (LOI) and the correlation with color

<i>Locality</i>	<i>Concentration (ppm)</i>		
	<i>Dark green</i>	<i>Clear green</i>	<i>Colorless</i>
Artigas	963	665	173

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

Table 3: H₂O quantity in percentage and ppm from Artigas region analyzed by Loss of ignition analysis (LOI)

<i>Locality</i>	<i>% H₂O</i>	<i>Concentration H₂O (ppm)</i>
Artigas	0.20	2000

The value presented in Table 3 is high. Therefore, with an amount of water far exceeding the contents of trace elements, as indicated previously, it is not possible to make similar correlations, as shown by Iwasaki et al. [19], between the water content and the sum of trace elements. The high concentration of water, whether in the form of OH or molecular water, compensates any lack of correlation with structural elements (substitutional and interstitial).

The differences of concentrations observed in Tables 2 and 3, with analyses performed at IPEN and IG-USP, may be explained by the fact that different physical forms were used in two analyses. The values obtained and presented in the samples of Tables 2 and 3 were used in the form of small splinters, whereas in the analyses done at IG-USP, quartz powder samples were used.

3.5. Color stability by UV radiation

To study the stability of color to ultraviolet radiation exposure, irradiated green quartz samples from Artigas region were placed in an aging test chamber, with radiation-emitting ultraviolet lamps in the UVA region of 340 nm. In this assay, clear green, dark green and medium samples of quartz were exposed to UV radiation for 1440 hours, for approximately 60 days. After this period, a decrease in the intensity of the green color could be observed by the spectra obtained with UV-VIS spectroscopy analysis, shown in Fig. 7 (before UV treatment) and Fig. 8 (after UV treatment). Comparing with data shown above, in Table 4 the calculated absorbance coefficients α of these samples may be observed.

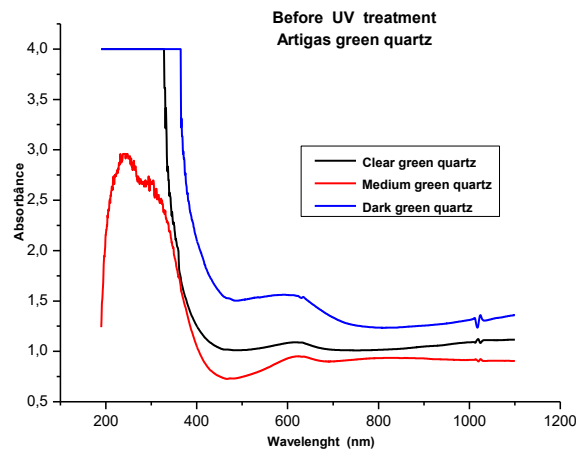


Figure 7: Qualitative absorbance spectra of Artigas green quartz before UV radiation treatment.

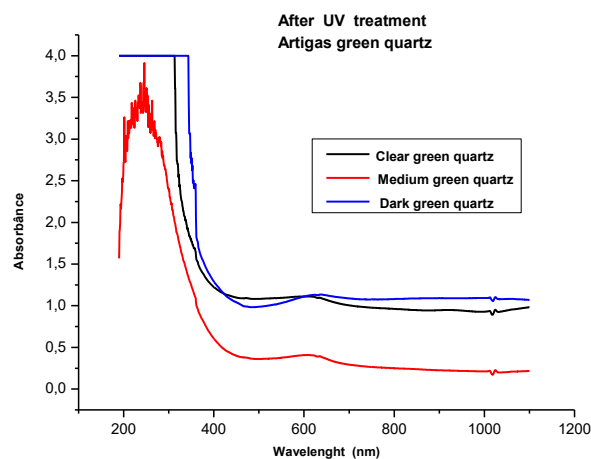


Figure 8: Qualitative absorbance spectra of Artigas green quartz after UV radiation treatment.

Table 4: Absorbance coefficient (α) of green quartz samples, before and after UV radiation treatment.

<i>Occurrences</i>	<i>Absorbance coefficient (α) (cm^{-1})</i>					
	<i>Before UV</i>			<i>After UV</i>		
	<i>Dark green</i>	<i>Medium green</i>	<i>Clear green</i>	<i>Dark green</i>	<i>Medium green</i>	<i>Clear green</i>
Artigas	0.21	0.14	0.11	0.13	0.09	0.09

It may be noticed in the spectra obtained after UV treatment, for 1440 hours, that the absorbance coefficients (cm^{-1}) from samples before exposure to UV radiation are relatively higher than the coefficients of the samples after exposure, indicating that there was loss of the green color intensity.

3.6. Color stability by heating

The experiments of color loss due to heating performed in the samples of green quartz, from Artigas region, irradiated up to 300 kGy, are given in Table 5 and the corresponding graph, in Fig. 9.

Fig. 9 graph shows the times that the samples, divided into groups of 1 to 6, according to the shade of green, varying from dark to clear, led to lose color totally, at temperatures of 150 °C, 175 °C, 200 °C, 225 °C and 250 °C. The graph shows that the higher the intensity of the green color, the longer the heating time necessary for the discoloration will be.

Table 5: Time for total discoloration of the green quartz samples from the Artigas region.

<i>Temperature (°C)</i>	<i>Time for total discoloration (min)</i>					
	<i>Group 1</i>	<i>Group 2</i>	<i>Group 3</i>	<i>Group 4</i>	<i>Group 5</i>	<i>Group 6</i>
150	32	29	26	25	22	20
175	27	25	17	16	16	15
200	14	15	10	9	9	9
225	9	10	8	8	7	6
250	8	8	7	6	6	6

OBS .: Variation of the shade from dark green (Group 1) to clear green (Group 6).

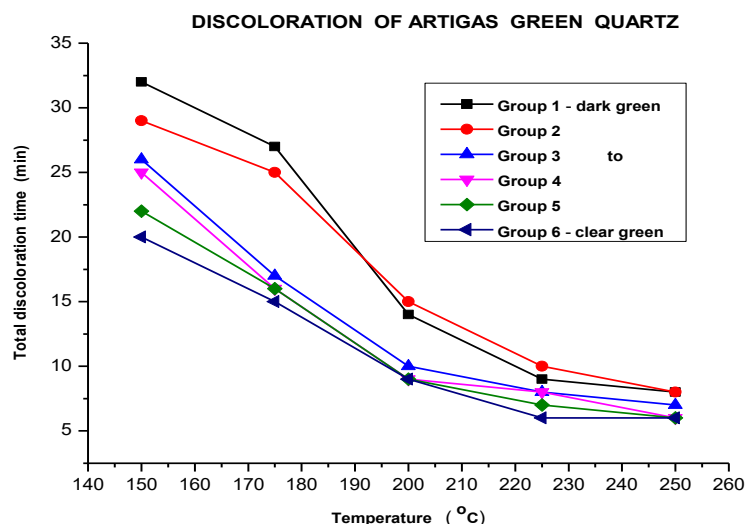


Figure 9: Variation of the discoloration time in relation to the heating temperature, in the Artigas green quartz samples.

4. CONCLUSIONS

The FTIR spectroscopy analyses performed on Artigas samples showed absorptions between 4300 cm^{-1} and 4700 cm^{-1} , connected to 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 it is responsible for the formation of defects called NBOHC that produce, by natural or artificial radiation, the green color in crystals from hydrothermal origin. This high concentration of silanol may be related with the presence of Brazil Law twinning in samples of hydrothermal quartz, as it may be observed in the images obtained by Polariscope and Gemological Microscope.

Brejinho samples show small absorption, between 4300 cm^{-1} and 4600 cm^{-1} , related to Si-OH. However, they present little or no molecular water. Some Brazil Law twinning have been confirmed by the "Realbau" analysis, in the Polariscope and Gemological Microscope.

Differently from geodes quartz from Paraná Basin, the veins quartz from Curvelo showed a line without the presence of absorptions in the regions of 4500 cm^{-1} and 5200 cm^{-1} , indicating absence of Si-OH and molecular H_2O . The analyses of samples with the polariscope and microscope did not show any Brazil Law twinning. The color obtained after irradiation and heating is gray (fumée).

Analyses and comparisons made it possible to differentiate and determine the formation of the Color Centre of NBOHC, with the color obtained by irradiation of hydrothermal quartz of the Paraná Basin, from Artigas region. Therefore, only quartz crystals with high concentration of molecular water and silanol have shown to be suitable to develop the green color by gamma radiation.

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