



# Gamma radiation of quartz from Entre Rios (SC) and Quaraí (RS)

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## ABSTRACT

The availability of gamma ray irradiators in Brazil increased the possibilities of the treatment of gemstones for color enhancement. One of the minerals with very high potential for these treatments is the quartz, a very widespread mineral with many colored commercial varieties. There is a specific variety of quartz in nature, showing a green color that may be produced artificially, by gamma radiation (<sup>60</sup>Co). In Brazil, the widely scattered geode occurrence from Quaraí, at Brazil southernmost location up to Uberlandia, in Minas Gerais, is one of these events. Quartz from these occurrences have been formed by strong hydrothermal activities. Hence, many quartz crystals showed a very fast growth occurrence, facilitating the formation of consequent defects and the uptake of water under the form of micro inclusions, molecular water, silanol (Si-OH) and OH. In the present work, the material analyzed is from hydrothermal regimes located near the towns Entre Rios and Quaraí. To characterize these materials, analyses have been made by ICP, NAA, electron microscopy, water loss techniques plus UV-VIS and NIR-FTIR spectroscopic measurements. Silanol complexes have been found by radiation, due

to gamma rays forming the color center NBOHC (Non-Bonding Oxygen Hole Center), showing absorption between 590 to 620 nm and leaving a transmission window at about 550nm, responsible for the green color. The spectroscopic water determination showed less molecular water (up to 2300 ppm, per weight), probably due to remaining silanol complexes. The water content, with up to 3200 ppm by weight, exceeds the amount of charge balancing cations (Fe, Al, Li).

**Keywords:** Quartz, gamma radiation, enhancement.

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## 1. INTRODUCTION

In the last decades, the use of quite strong  $^{60}\text{Co}$  gamma radiation has shown very good results of color modification for quartz. Silica, in its stable form of quartz, a widespread mineral, has mainly two gem varieties, amethyst and citrine, with their respective violet and yellowish brown shades of color. But, since a few years now, other quartz varieties appeared in the market, such as the “Green gold” or “Lima quartz”, the “Champagne” or “Beer” colored, the green colored variety called “Prasiolite” and the blue to blue-violet quartz called “Safirita or Blueberry Quartz” [1].

Quartz used for these treatments is mainly found in Brazil in two geological occurrences, the hydrothermal deposits of the basaltic rocks of the Paraná Basin and the veins in the quartzitic Serra do Espinhaço Range, besides the deposits of the long Pegmatitic Belt, tied strongly to granitic rocks and of igneous origin. 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, amethysts, chacedonies and the types which show a green color after irradiation, as well as silica varieties hosted by the vein systems of the quartzites of the Espinhaço Mountain Range.

The mechanism of the green quartz formation found in nature or induced artificially by gamma radiation is very different from the occurrences 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) shaped by heating amethyst from Montezuma, Brazil. Two events are known today, where this type of quartz may be found: in Canada, at the Thunder Bay Amethyst Mine [2], Ontario, a small district, and in Brazil, at widely scattered geode occurrences along a 600 km stretch

from Quaraí, at Brazil southernmost tip to Uberlandia, in the state of Minas Gerais. These two occurrences have been formed by strong hydrothermal activities, at Thunder Bay, due to tectonics and in Brazil by meteoric and hydrothermal waters of the Guarani aquifer. Some studies on irradiated green quartz from regions of Rio Grande do Sul were presented by Schultz-Güttler, et. Al. [3,4], Henn & Schultz-Güttler [5] and Clerice [6].

Quartz crystals formed by the processes mentioned above showed a very fast growth history facilitating the formation of growth defects (twinning, small angle tilting, mosaic growth, striations) [7] and the uptake of water in the form of micro inclusions, molecular water, silanol (Si-OH) [7] and hydroxyl (OH). There is no correlation between water content and cations as in other color varieties. Instead, silanol complexes are formed, and by gamma rays radiation form the colored center NBOHC (Non-Bonding Oxygen Hole Center), responsible for the green color [8].

## 2. MATERIALS AND METHODS

The quartz crystals used in the present work, generally of euhedral shape or fragments of crystals, come from hydrothermal regimes created by the intrusions of basaltic rocks in the Parana Basin, Southern Brazil, and are derived from geodes or veins in rock fractures. The samples were collected in the regions of Entre Rios, eastern part of Santa Catarina state (SC) and Quaraí, south east of Rio Grande do Sul state (RS).

### 2.1. Irradiation procedures

The batches of quartz were submitted to irradiation in the  $^{60}\text{Co}$  Multipurpose Irradiator, at the Radiation Technology Center (CTR), IPEN-CNEN/SP. The samples were inserted into the irradiation devices built with a screen of fine mesh of stainless steel, fixed at structures made of the same material. They were, then, lowered to the base of the source storage pool of the irradiator, which contains 51 sources of  $^{60}\text{Co}$ .

The total dose of gamma radiation applied to these batches is variable. Maximum doses applied were up to 450 kGy and dose rate 20 kGy/h. The particular dose of each batch was calculated as

function of hours of irradiation to which the quartz was submitted and the dose rate obtained through the reading of the dosimeters "Red Perpex 4034" and of the dosimeters of cellulose triacetate (CTA), with triphenyl phosphate used in all runs positioned inside the devices.

## **2.2. Methods of characterization**

Some representative quartz crystals have been selected for preliminary chemical and spectroscopic characterization. The chemical composition has been analyzed by standard methods of ICP-Mass-Spectroscopy (Elan-6100DRC, Perkin Elmer) at the Chemical Laboratory of the Geosciences Institute - USP, by ICP-AES and NAA, at the NNA-Laboratory of IPEN-CNEN/SP. Ultraviolet-Visible and Near Infrared (UV/VIS-NIR) spectroscopy, from 200 to 3000 nm, was carried out by the use of CARYSCAN 500 spectrometer, at the Ionic Crystal Laboratory of the Physics Department, USP and FTIR Perkin Elmer Universal ATR equipment, with Sampling Accessory Spectrum 100, has been used to acquire the spectra of powdered material.

The determination of the concentration of total H<sub>2</sub>O present in the quartz was made using the technique of Loss of Ignition analysis. Scanning electron microscopy MEV, located at IPEN, has been used for information about the texture and topography of the samples, mainly regarding twinning Brazil Law and the analyses of striations .

To examine the defects of growth or "Realbau" of quartz samples , with regard to twinning, the polariscope and the horizontal gemological research microscope , installed in the Gemological Laboratory of the Institute of Geosciences of the University of São Paulo, were used. The minimum dose necessary to obtain the green colour has been found by tests of saturation point in clear and transparent quartz samples by varying the doses. The samples were analyzed using the UV-VIS spectrophotometer Shimadzu LDPI of the CTR-IPEN laboratory.

To study the stability of color to ultraviolet radiation exposure, a process of accelerated exposure using an accelerated aging Chamber has been devised. This camera is EQUILAM, model EQUV and it is installed in the Center of Science and Technology of Materials of IPEN-CNEN/SP. It has 8 mercury fluorescent lamps of 40 Watts each, which emit ultraviolet radiation in the UVA region of 340 nm.

### 3. RESULTS AND DISCUSSION

#### 3.1. Chemical analysis

NAA and ICP-OES chemical analyses in quartz samples of hydrothermal origin, from Quaraí and Entre Rios, are listed in Tables 1 and 2 and show a predominance of Fe, Al, Na, K and Ca impurities.

**Table 1:** Neutron Activation Analysis – NAA.

| Element<br>( $\mu\text{g/g}$ ) | Locality      |                  |
|--------------------------------|---------------|------------------|
|                                | Entre Rios    | Quaraí           |
| <b>Cr</b>                      | $5.5 \pm 0.9$ | $1.17 \pm 0.13$  |
| <b>Fe</b>                      | $124 \pm 18$  | $19.44 \pm 0.15$ |
| <b>K</b>                       | $39 \pm 2$    | $49 \pm 12$      |
| <b>Mn</b>                      | $0.7 \pm 0.1$ | $4.6 \pm 0.3$    |
| <b>Na</b>                      | $53 \pm 4$    | $80.2 \pm 3.1$   |
| <b>Zn</b>                      | nd            | $1.98 \pm 0.43$  |
| <b>As</b>                      | $16 \pm 3$    | $22 \pm 2$       |
| <b>Co</b>                      | $69 \pm 2$    | $487 \pm 4$      |
| <b>Ce</b>                      | $133 \pm 7$   | $65 \pm 11$      |
| <b>La</b>                      | $9 \pm 1$     | $32 \pm 9$       |
| <b>Sb</b>                      | $33 \pm 6$    | $92 \pm 7$       |
| <b>Sm</b>                      | $1.7 \pm 0.5$ | $2.7 \pm 0.3$    |
| <b>Sc</b>                      | $1.5 \pm 0.5$ | $0.68 \pm 0.03$  |
| <b>Th</b>                      | nd            | $486 \pm 11$     |

**Table 2:** Optical emission spectrometry with argon plasma (ICP-OES).

| <b>Element<br/>(<math>\mu\text{g/g}</math>)</b> | <b>Locality</b>   |               |
|---|-------------------|---------------|
|   | <b>Entre Rios</b> | <b>Quaraí</b> |
| <b>Na</b>                                       | $84 \pm 4$        | $109 \pm 12$  |
| <b>Al</b>                                       | $158 \pm 3$       | $148 \pm 2$   |
| <b>K</b>  | $77 \pm 3$        | $81 \pm 2$    |
| <b>Ca</b>                                       | $< 2.0$           | $< 2.0$       |
| <b>Fe</b>                                       | $211 \pm 12$      | $80 \pm 1$    |
| <b>Cr</b>                                       | $< 8.0$           | $< 8.0$       |
| <b>Mn</b>                                       | $< 1.5$           | $< 1.5$       |
| <b>Zn</b>                                       | $< 5.0$           | $< 5.0$       |
| <b>Ni</b>                                       | $< 16.0$          | $< 16.0$      |
| <b>Cu</b>                                       | $< 25.0$          | $< 25.0$      |
| <b>Ba</b>                                       | $< 3.0$           | $< 3.0$       |
| <b>Mg</b>                                       | $< 1.5$           | $< 1.5$       |

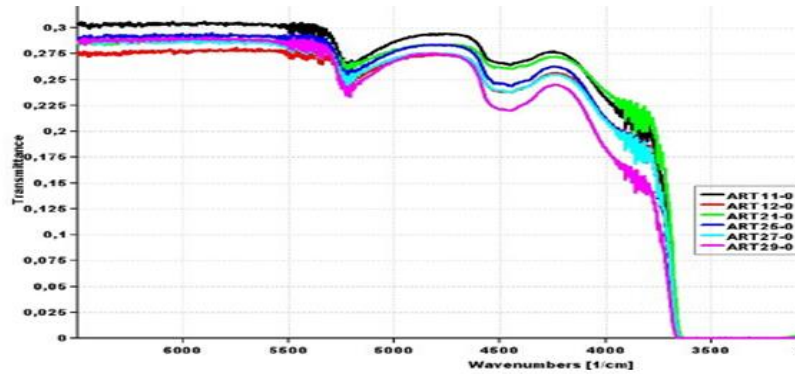
Comparing the content of elements determined by NAA and ICP-OES of samples with the same origin, differences in the results of the different techniques are observed. This fact is due to the use of diverse crystals, from the same locality, showing different chemistry of the crystals analysed.

A comparison of the concentration ranges of trace elements, demonstrated in Tables 1 and 2, with data of quartz samples from various localities of Brazil and presented in the work of Iwasaki, et. Al. [9], shows that the chemical composition of samples of all these regions is very similar. Also, the variations shown are typical features of both, the geological environment of formation together with local conditions, and the time span of each crystal growth.

### 3.2. FTIR Spectroscopy

The graph shown in Figure 1, obtained by FTIR spectrometry of quartz samples from Quaraí/Artigas, shows strong absorptions of H<sub>2</sub>O and Si-OH, respectively, near the regions of 5300 cm<sup>-1</sup> and 4500 cm<sup>-1</sup>, according to Fukuda, et. Al. [10]. These concentrations may be related to the presence of polysynthetic twinning of Brazil Law [11], facilitating the capture of OH groups and water.

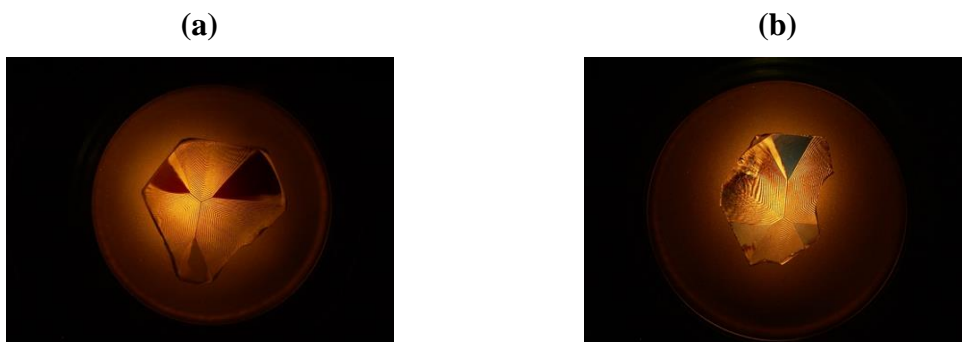
**Figure 1:** FTIR spectra of samples in the area of molecular  $H_2O$ , at around  $5300\text{ cm}^{-1}$  and SiOH at around  $4500\text{ cm}^{-1}$ .



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

Quartz crystals of the Quaraí region were analyzed with polarized light and growth defects in the samples found. The 24 polished slices were the same ones used in FTIR infrared spectroscopy. This analysis shows that the samples from hydrothermal regions feature Brazil Law twinning, as shown by Figures 2 (a) and (b).

**Figure 2:** Images obtained in the polariscope in quartz plates of the Quaraí (a) and (b), with Brazil Law twinning.



This is a twinning called polysynthetic whereby the crystal is composed of thousands of crystalline planes (thin slices) with nano-sized micrometric thickness, interconnected and interwoven with numerous planar defects, 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), resulting in the NBOHC color centers, responsible for the green color [8].

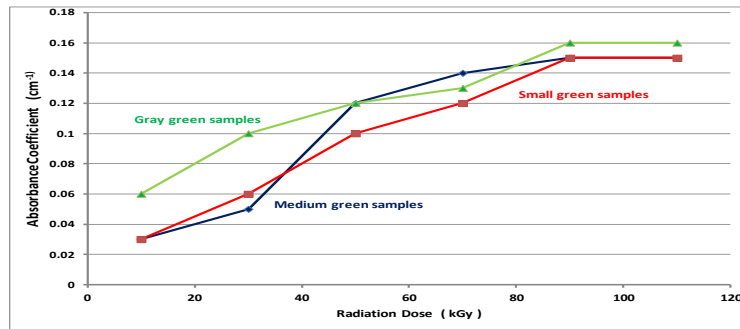
### 3.4. Measurements of radiation dose for color saturation

These measurements were made, preliminary, to detect the limit of radiation dose. In the first series, small chips of 1 cm thick were selected. In the second, all chips from the region of Quaraí have been selected. These samples were irradiated with doses of 10, 30, 50, 70, 90 and 110 kGy, and greenish color with light gray tint has been obtained. Another group of quartz samples was irradiated with the same doses and produced green quartz with a strong grey color component.

Figure 3 shows the graph of absorbance ( $\text{cm}^{-1}$ ) at around 620 nm, as a function of radiation dose (kGy), for samples of the same thickness. It is observed the increase of absorbance value and, consequently, of some green tone at a more or less constant rate, but, slowing down above 90 kGy irradiation. The same result was obtained from a group of green quartz with radiation doses reaching 2000 kGy. Once again, the values of absorbance above 90 kGy radiation dose showed no increase. It appears that there is a specific concentration of water and hydroxyl and that the formation of color centers is limited. Irradiation with higher doses do not produce more intense colors.



**Figure 3:** Absorbance at 620 nm ( $\text{cm}^{-1}$ ), as a function of radiation dose (kGy) for small and medium samples of green and gray green quartz, from Quaraí region.



### 3.5. Color stability by UV radiation

To analyze the loss of color with time of exposure to ultraviolet radiation, irradiated green quartz samples of the Quaraí region were placed in an aging test chamber, with radiation-emitting UV lamps in the UVA region of 340 nm. In this assay, the clear green, medium green and dark green quartz samples were exposed to UV radiation by 1440 hours, by approximately 60 days. After this period, a decrease in the intensity of the green color may be observed, as shown in Figure 4. Table 3 shows the calculated absorbance coefficients ( $\alpha$ ) of these samples, indicating a decrease in color.

**Figure 4:** Clear, medium and dark green quartz Quaraí, (a) before and (b) after UV treatment.



**Table 3:** Absorbance coefficient ( $\alpha$ ) of green quartz samples, before and after UV radiation treatment.

| Locality | Absorbance coefficient ( $\alpha$ )<br>( $\text{cm}^{-1}$ ) |              |             |            |              |             |
|----------|---|--------------|-------------|------------|--------------|-------------|
|          | Before UV   |              |             | After UV   |              |             |
|          | Dark green  | Medium green | Clear green | Dark green | Medium green | Clear green |
| Quaraí   | 0.13  | 0.11         | 0.10        | 0.08       | 0.10         | 0.08        |

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

#### 4. CONCLUSIONS

It could be shown that natural quartz develops, by gamma irradiation, a color center which produces green colors in the samples. The reasons for this are linked to hydrothermal environments in which a very fast growth of crystals occurs, with multiple defects formation (Brazil Law twinning) facilitating the incorporation of high concentrations of hydroxyl and water and, thus, forming silanol (Si-OH). These high concentrations of molecular water and silanol may be seen in spectra by FTIR spectrometry carried out on samples from Quaraí and Entre Rios, by strong absorptions close to  $5300 \text{ cm}^{-1}$  and  $4500 \text{ cm}^{-1}$ . Analyses with the polariscope and gemological microscope on samples of quartz from the Quaraí area show high amounts of near-perfect Brazil Law twinning, which involves the whole crystal.

The tests performed with Quaraí samples for determining the radiation limit of dose for green color saturation showed, approximately, 90 kGy as the dose at which the green color saturation occurs. This fact indicates that in quartz crystals there is a specific concentration of molecular water and

hydroxyl and the formation of a color center is limited by this fact. The radiation with higher doses will not produce more intense colors.

The tests performed to study the stability of the colour by exposure to ultraviolet radiation in the UVA region (60 days) showed that the samples absorbance coefficients before exposure to UV radiation are relatively larger than the coefficients after treatment, indicating that there was, approximately, 10 to 50 % of loss of the green color intensity. This fact has to be considered by using these green quartz samples as gemstones in the trade. The intensity of the green color obtained by the same dose depends on the amount of silanol (Si-OH) and hydroxyl (OH) incorporated in the quartz crystals.

## 5. ACKNOWLEDGMENTS

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