# Studies of colored varieties of Brazilian quartz produced by gamma radiation*

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**Abstract.** Quartz occurs in Brazil mainly in two geological environments, called pegmatitic and hydrothermal. The quartz of hydrothermal origin occurs mainly in geodes in the basaltic rocks of the Parana Basin and the quartz formed in fracture systems of the Espinhaço Range. Quartz of pegmatitic origin forms often the core of pegmatites. The detailed mechanism of color center formation of these two types of quartz will be investigated by spectroscopic and chemical analysis. Until yet, it can be shown that due to chemical differences of the nature of mineral forming fluids, the two types behave differently. All quartz contains mainly traces of iron, aluminum, lithium and some amounts of water. The quartz of hydrothermal origin incorporated much structurally bound water, and despite some similarities with the chemical composition of pegmatitic quartz, this high water content is the reason for the formation of silanol radicals, giving green color to the quartz. The main difference in chemical composition of pegmatitic quartz is the presence of higher amounts of Al and Li, responsible for the brownish and yellowish colors formed by irradiation.

**Key words:** gemstone treatment • quartz color enhancements • color centers • quartz gamma irradiation

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## Introduction

The use of radiation and subsequent heat treatment to alter the colors of minerals is today a widespread method to increase the amount of gem material by using commercially less valuable qualities [12].

During the last decades, the use of $^{60}$Co radiation has shown very good results of color modification to quartz. Silica, in the stable form of $\alpha$-quartz, a widespread mineral of the earth crust, has two natural gem varieties, amethyst with its violet and citrine with its yellowish brown shades of color. Recently, other varieties appeared in large amounts on the market like 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 safirite or blueberry quartz, color varieties which are very rare or even unknown from natural occurrences.

Commercial irradiation units for gemstone treatments exist worldwide and it is very likely that most of these color varieties of quartz are produced by some type of radiation. The present work aims at exploring the use of gamma radiation to induce color mainly in two types of quartz, one of pegmatite and one of hydrothermal origin.

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Quartz, or more precisely α-quartz, the modification of $SiO_2$ stable in normal conditions until about 573°C, is a tectosilicate with three dimensional arrangements of polymerized tetrahedrons of $SiO_4$. It can build right handed or left handed crystal forms due to the steric sense of its crystal class. Under most growth conditions, some twin intergrowth between these two forms will occur, giving rise to growth defects.

The small ionic size of silicon does not permit substitution by many elements except mainly trivalent iron, alumina, phosphorous and germanium. Quartz is, therefore, a quite pure mineral and, as shown by Iwasaki *et al*. [9] and Guzzo [5], may contain impurities classified as included material (mineral matter or fluid inclusions) and as structural units. Those structural impurities, mainly responsible for the color centers, may be substitutional or interstitial. As shown by the authors above, these are: $Fe^{3+}$, $Al^{3+}$, $OH^-$ and $H_2O$ molecules as substitutional and $Na^+$, $Li^+$ and $H_3O^+$ as interstitial units located in the channels of the structure. The substitution of tetravalent Si by trivalent ions necessitates the presence of univalent cations to maintain charge balance. Details about some of the colors produced by the above-mentioned substitutions can be found in a paper by Rossman [17]. He confirms the role played by natural radiation activating color centers and producing the range of known color varieties of quartz found in a variety of rock types and formed in a wide range of geological conditions.

Quartz of gemological quality from Brazil and used for these treatments is found mainly in two contrasting geological occurrences, the hydrothermal deposits of quartz in the voids of the basaltic rocks of the Parana Basin, formed at very low temperature and the vein deposits of the Serra do Espinhaço Range, composed mainly of quartzite and showing low to medium range of temperature of formation, on the one hand and the pegmatite deposits of the Eastern Pegmatite Belt as shown by Chaves *et al*. [4] and tied strongly to granitic rocks and of igneous origin with relative high formation temperatures and pressures and slow growth on the other hand.

The hydrothermal quartz includes all the varieties of silica found in fractures and geodes of the basaltic and felsic volcanic rocks of the Parana Basin such as agates, amethyst, chalcedonies and the types which will show a green color after irradiation, as well as the silica varieties hosted by the vein systems of the quartzites of the Espinhaço Mountain Range. Famous are the quartz crystals and the smoky quartz from Minas Gerais as well as the amethyst from Montezuma, northern Minas Gerais, which turns green by heating and blue by irradiation [19].

The pegmatitic quartz is found near large granitic batholiths scattered along a large belt covering the states of São Paulo, Rio de Janeiro, western Minas Gerais, Espirito Santo and Bahia. Silica varieties found in these igneous deposits are mainly rose quartz, smoky quartz, citrine and a few quartz types without apparent color, which produce the much sought after greenish yellow gemstones called green gold or lima quartz. Of these two are known today, located at São José da Safira and Itamarandiba, Minas Gerais. A third occurrence in the State of Para, Santana de Araguaia is under study.

As shown above, the material studied here is derived from natural occurrences and has been subjected to the most varied conditions of formation. As such, it is very difficult to define a standard sample of quartz and to make generalizations regarding the chemical and physical homogeneity of each crystal analyzed or subjected to irradiation. But despite this, the two chemical environments of formation, the hydrothermal and the pegmatite one will define by its specific chemical imprint mainly the colors obtained by treatment. The pegmatite quartz will show quite high amounts of lithium and alumina, producing yellowish to brownish colors, the hydrothermal quartz will show low amounts of lithium, but quite high concentrations of iron besides alumina producing the range of colors known from the famous geodes from Rio Grande do Sul.

These two environments of formation will define also the crystal perfection, a topic very often neglected by discussions about color center formation. As Laudise and Barnes [11] have shown, the perfection of synthetic quartz crystals and the uptake of water, hydroxyl and other impurities is directly proportional to the growth rate of the crystals, so one can assume that hydrothermal natural quartz will show more growth defects compared with pegmatite quartz. The latter, grown at a quite high temperature and pressure (400 to 500°C, about 1500 to 3000 bars pressure) and, therefore, with slower growth rate, will show much less growth imperfection, twinning and water content, a fact confirmed by Guzzo [5]. The following exposition is intended to show initial results of irradiation by gamma rays of commercial lots of quartz and procedures of characterization and colors produced. This paper is a full version of a presentation at the International Meeting on Radiation Processing – IMRP 2011 and intends to present some results of mineral irradiation done at the Radiation Technology Center (CTR) at IPEN-São Paulo, Brazil.

## Materials and methods

Some information will be given about the material, the irradiation procedures and the methods of characterization.

### Materials

The colorless quartz used in the present work, generally of irregular shape or fragments of crystals with weights from 2 to 50 g, comes from hydrothermal regimes created by the intrusions of basaltic rocks in the Parana Basin, Southern Brazil, and is derived from geodes or veins in rock fractures near the towns of Artiga and Quaraí at the border of Brazil and Uruguay. The material is collected by mineral dealers from local miners and sent in lots of 50 to 100 kg for routine irradiation at the CTR-IPEN. It is already trimmed by hammering and only transparent samples are present. The material shows much striations on the outer surfaces and indications of Brazil twins along the fractured parts. The pegmatite quartz samples, about 1 kg of material from each locality, was collected at São José da Safira, Itamarandiba and Curvelo, Minas Gerais and is known to produce yellowish colors by gamma irradiation. A sample of fused quartz, identified as GE 124, a very pure silica from the firm General Electric GE with a low hydroxyl content was included and this sample served as reference material to help to assign the peak positions of OH in the quartz samples.

### Irradiation procedures

The batches of colorless hydrothermal and pegmatite quartz were submitted to irradiation in a $^{60}$Co multipurpose irradiator at the Radiation Technology Center (CTR), IPEN-CNEN/SP [16]. The samples were inserted into irradiation devices built with a screen of fine mesh of stainless steel fixed at structures made of the same material. These were then lowered to the base of the source storage pool of the irradiator that contains 32 sources of $^{60}$Co producing a total of irradiation at about 150 000 Ci (August 2012).

The total dose of gamma radiation applied to these batches is variable. Maximum dose absorbed by the material was up to 650 kGy. The particular dose of each batch was calculated as a function of hours of irradiation to which the quartz was submitted, and the dose rate obtained through the reading of dosimeters Red Perpex 4034 used in all runs positioned inside of the devices.

### Methods of characterization

Some representative quartz crystals, in their natural state as well as after irradiation and absorbed dose of 400 kGy, have been selected for preliminary chemical and spectroscopic characterization. The chemical composition has been analyzed by routine methods of ICP-mass spectroscopy, ICP-Ms, (Elan-6100DRC, Perkin Elmer) at the Chemical Laboratory of the Geosciences Institute, USP, by ICP-optical absorption spectroscopy (ICP-OAS) and by neutron activation analysis (NAA) at the NNA-Laboratory of the IPEN--CNEN/SP. Ultraviolet-visible and near infrared (UV/VIS-NIR) spectroscopy from 200 to 3000 nm was done by the use of a CARYSCAN 500 spectrometer at the Ionic Crystal Laboratory of the Physics Department, USP, and some measurements of photoluminescence (PL) at the Laboratory of the Chemical Department, USP, after standard treatment of the samples.

## Results and discussion

### Irradiation effects

The hydrothermal quartz, after irradiation showed generally a green color after the removal from the irradiator. The shades of green varied much from slight greenish to a greenish tone mixed with gray or olive, to a strong green or gray-green even in the same batch and under the same irradiation dose. Some batches showed about 10 to 20% colorless samples, indicating that there exists radiation resistant quartz coming from the same locality. Besides these shades, very few samples showed amethystine color, confirming the presence of iron in the samples, as already has been supposed by the appearance of Brazil twins [13].

It could be observed also that the color was not always evenly distributed, but that some parts of some samples stayed colorless or only slightly colored. Inspection of some of those samples showed that the green parts were always concentrated on the part with more fractures and striations. Observations of a large numbers of samples have shown that some did not acquire any color, others may have been partially colored, with the crystal tips of a deep green and the rest colorless, or sometimes at very high absorbed doses above 500 kGy, nearly all crystals had a greyish cast. There does not exist any systematic study correlating the chemistry of those crystals with the intensity of color produced. It may very well be that there exists more than one type of color center.

All the quartz samples from pegmatite were black and opaque after the applied radiation dose of 100 to 400 kGy. This indicates that an additional heat treatment is necessary to unravel the final expected color of samples of this origin in line with observations by Nunes [14].

### Chemical analysis

Preliminary chemical results have confirmed that the crystal chemistry of the hydrothermal quartz is mainly dominated by substitutional impurities of iron, alumina and hydroxyl or molecular water, in line with the data shown by Guzzo [5]. No correlation of amounts of iron or alumina with color could be noted till now. Therefore, only the range of trace elements content will be given. All quartz samples had Fe (32 to 249 ppm), Al (612 to 1648 ppm), Na (350 to 1070 ppm), Mg (105 to 286 ppm), Ti (33 to 174 ppm) and Li (1.4 to 18 ppm) and water (molecular and OH) contents at 1000°C, determined by standard gravimetric procedures, from 140 (colorless samples) to 1274 ppm by weight. The GE 124 sample has 14 ppm Al, 0.2 ppm Fe, 0.7 ppm Na, 1.1 ppm Ti and 0.6 Li and about 5 ppm OH, as given in the literature. It should be noted that the GE 124 glass sample is free of molecular water and that the water content of hydrothermal quartz is very high, much higher than the contents of synthetic quartz [2].

The few chemical analyses of pegmatitic quartz samples showed high alumina and Li contents, in line with the data given by Iwasaki *et al*. [9] and Guzzo [5]. Colors obtained by irradiation and subsequent heating of some material from Itamarandiba (Minas Gerais) are quite intense with yellow shades.

These colors are quite similar to those of material from São José da Safira, studied by Nunes [14] a variety of quartz called green gold. He showed that the yellow color is produced by Al for Si substitution and charge balance by Li. Again, no systematic study has been undertaken to correlate chemical composition to shade and depth of color.

### UV-VIS-NIR spectroscopy

Figure 1 shows the combined spectroscopic results of three types of materials, the irradiated green quartz

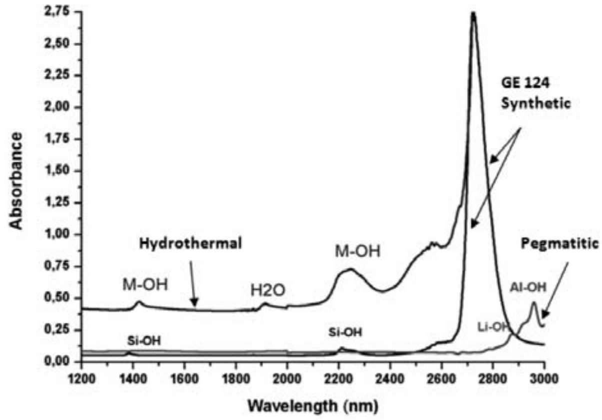


**Fig. 1.** Near infrared spectra of different quartz types including GE silica glass. The features at 1900 nm and 2300 nm indicate the presence of water and OH in the hydrothermal samples. The peaks at about 3300 nm indicate the presence of Li and alumina in the pegmatite derived quartz.

(hydrothermal), the pegmatitic quartz from Minas Gerais and, for comparison purposes, the spectrum of the industrial ultrapure fused silica GE 124, in the wavelength range from 1200 to 3000 nm. Comparing the three spectra, one notes some similarity between the GE 124 and the hydrothermal sample with respect to OH absorption. Additionally, the presence of molecular water at about 1900 nm is obvious. The pegmatite sample, however, is different. The latter shows Al and Li related features near 3000 nm [6] which are absent in the spectra of the other samples and a lack of features in the range from 1200 to 2500 nm, indicating the absence of molecular water and hydroxyl.

One notes the very high M-OH peak at about 2300 nm. In this, as well as in the 1400 nm region are mainly the first overtones of the Silanol groups (Si-OH) [22]. From this it appears that the hydrothermal quartz from southern Brazil is quite different and much more hydrous than the pegmatitic quartz from Minas Gerais. Indicated in Fig. 1 is also the peak of molecular water at about 1900 nm [3].

Spectra taken in the UV/Visible region (Fig. 2) show likewise differences in the absorption behavior of the differently formed quartz crystals. The crystals from pegmatitic origin show much less absorption at wavelengths smaller than 300 nm, whereas the hydrothermal quartz strongly absorbs above this range. This feature is useful for type determination of unknown samples.

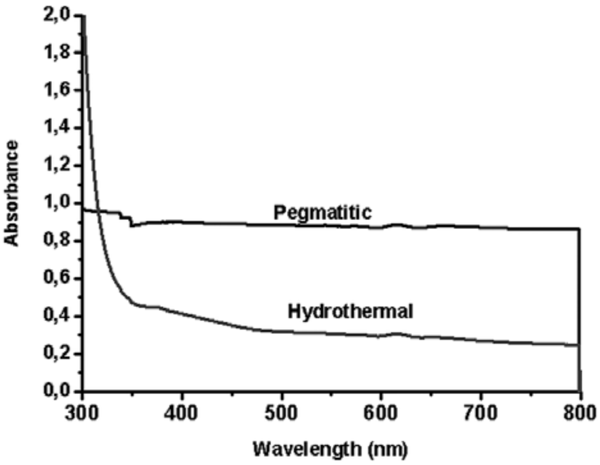


**Fig. 2.** UV/VIS spectra of pegmatitic and hydrothermal quartz. One notes the strong absorption of the hydrothermal sample at about 300 nm.

This high water and OH content of the hydrothermal quartz from southern Brazil is unique and only synthetic quartz [2], sol-gel derived silica samples [3] or microcrystalline quartz show similar features. From the spectroscopic evidences it appears that the high water content overrides the influences of Fe and Al contained in the samples. This means that the normal color centers related to iron and alumina are masked by the presence of high amounts of molecular water and OH as shown by Aines and Rossmann [1] and Iwasaki and Iwasaki [8].

Figure 3 shows the UV-VIS-NIR spectrum of irradiated green quartz, showing different intensities of absorbance along different crystal axes. In this case spectra have been taken parallel and at right angle to the optic axis to explore the possibilities of pleochroism of the OH absorption. It should be stressed that unpolarized light has been used, acquiring these spectra. In the visible range the spectrum shows an absorption, peak at 592 nm with a linear absorption coefficient of 0.2 $cm^{-1}$. It is this absorption which produces the green color by defining a transmittance window at about 500 nm, there is the green region of the light spectrum. The position is very different from all peaks known for amethyst or citrine [15, 21] or even for the green variety called Prasiolite and produced by bivalent iron, absorbing at 720 nm [20]. Its position varies slightly from 590 to 620 nm for different samples which may indicate different precursors being activated by the irradiation. Besides, the absorption coefficient is dose and, at the same dose, sample dependent. Less radiation produces less absorption and, consequently, a less saturated green, but less water also produces less darkening as given in Table 1. Since neither iron nor alumina absorbs in this range, but only non-bridging oxygen bond hole center (NBOHC), it is very likely that irradiation interferes with structural or molecular water [1] or that there exist strained bonds much like those which produce the absorption at 630 nm at silica fibers [10] and produce the green light emanating from drawn fibers. The

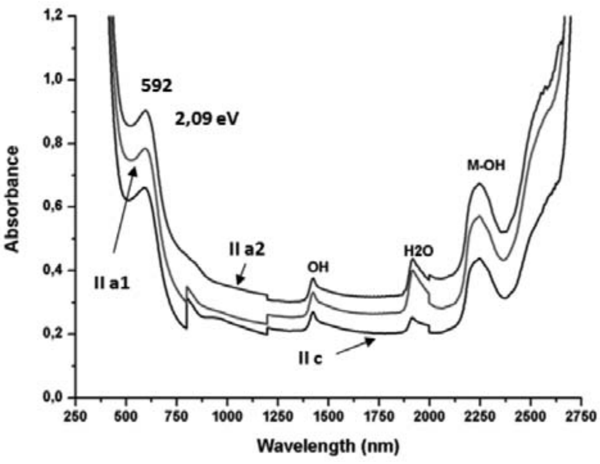


**Fig. 3.** UV-VIS-NIR spectrum of a green, irradiated quartz from southern Brazil. The whole range of wavelength to show the water-, OH- and NBOHC-related absorptions is shown. Sample thickness was 2 cm, irradiation dose was 236 kGy, non-polarized light was used.

**Table 1.** Correlation of water content, color and linear absorption coefficient of green quartz, irradiation dose of all samples 326 kGy, thickness 1 cm

| Sample | Color | Water content (ppm) | Linear absorption coefficient, $\alpha$ |
|---|---|---|---|
| Artigas 25 | Light green | 141 | $0.05\ cm^{-1}$ |
| Artigas 28 | Middle green | 234 | $0.09\ cm^{-1}$ |
| Artigas 30 | Intense green | 787 | $0.13\ cm^{-1}$ |

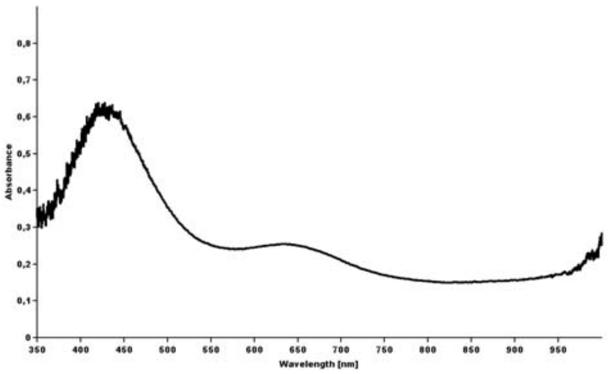


**Fig. 4.** VIS transmission spectra of green gold quartz, a typical sample of quartz from pegmatite origin. One notes the broad band at about 470 nm.

discussion about the role played by hydrogen in silica is still ongoing and much research will clarify the details [18]. Until now, only one occurrence of quartz with this special color has been described in the literature by Hebert and Rossman [7] showing spectra similar to the ones shown above, but without considerations about the possible color center.

The VIS-NIR spectra of quartz of pegmatite origin producing the chartreuse yellow, called green gold in Fig. 4 shows a typical absorption by alumina. It may well be that this color is produced by an interplay of Al and Fe substitutions in quartz. Further investigations will throw light on this question.

## Conclusions

Spectroscopic methods have been used to characterize different types of quartz. It could be shown that there exist various types of the colorless form of quartz, each one with its own chemistry. Since the formation conditions may change rapidly at each locality of growth, it is not possible to speak of quartz as a general term. It is necessary, therefore, to characterize each type before applying any treatment to know which color may be imparted and what will be the final result.

From these preliminary results, it appears that the formation conditions of natural quartz crystals impart special trace element characteristics and defect features, which will define the final color obtained by radiation treatment. From the above, it could be shown that the compositional factor is not as important as the role of structurally bound water. The latter can even quench the formation of certain colors like the violet shades of amethyst or citrine. More studies correlating these two parameters are needed to understand the fine tuning of colors obtained by standard irradiation procedures.

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