2024 International Nuclear Atlantic Conference – INAC 2024
Escola de Guerra Naval, Rio de Janeiro, RJ, May 6 – 10, 2024

ISBN: 978-65-594-1256-3

Analysis of hydrothermal quartz from States Rio Grande do Sul, Bahia and Minas Gerais induced by gamma radiation

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1. Introduction

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. In the present work the hydrothermal quartz samples studies were from following regions: Quaraí (Rio Grande do Sul), located in the Paraná Basin, Brejinho (Bahia) and Curvelo (Minas Gerais) located in Serra do Espinhaço. The quartz from Quaraí, formed at low temperature, has high concentration of molecular water, silanol (Si-OH) [1], hydroxyl (OH) 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. This content of molecular water and silanol in hydrothermal quartz of Quaraí is responsible for the formation of NBOHC (Non-Bonding Oxygen Hole Center) defects that produce, by gamma radiation, the green color [2]. Studies on hydrothermal green quartz, from some regions of the Paraná Basin, were presented by Henn & Schultz-Güttler [3] and Schultz-Güttler et al. [4].

2. Methodology

Some representative hydrothermal quartz crystals from Quaraí, Brejinho and Curvelo have been selected for chemical and spectroscopic characterization. The chemical composition has been analyzed by the techniques of Optical Emission Spectrometry, with Argon Plasma (ICP-OES), at the Chemical Laboratory from IPEN-CNEN/SP. The Near-Infrared NIR and FTIR Spectroscopy were made by using the FTLA 2000 – ABB Bomem Spectrometer, at the Radiopharmacy Center of IPEN-CNEN/SP. To analyze the defects of growth or "Realbau" of samples of quartz, with regard to twinning, the Polariscope and Horizontal Gemological Research Microscope, installed on Gemological Laboratory of the Institute of Geosciences of the University of São Paulo, were used.

3. Results and Discussion

The results of chemical analysis carried out by ICP-OES indicate that the chemistry of quartz samples of hydrothermal origin, from Quaraí, are dominated mainly by impurities of Fe , Al, Na, and K. The results of the samples analyzed were: Na (109 µg/g), Al (148 µg/g), K (81 µg/g), Fe (80 µg/g), Ca (< 2.0 µg/g), Cr (< 8.0 µg/g), Mn (< 1.5 µg/g), Zn (< 5.0 µg/g), Ni (< 16.0 µg/g), Cu (< 25.0 µg/g), Ba (< 3.0 µg/g), Mg (< 1.5 µg/g).
As it has been shown by Ihinger et al. [5], the concentrations of trace elements 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.

The graph presented in Fig. 1 shows the FTIR spectra of transmittance of the samples from Quaraí, Brejinho and Curvelo regions. The graph shows the distribution of H_2O contents in various molecular forms in the samples. Quaraí samples show strong absorptions of H_2O and Si-OH, respectively, near the regions of 5300 cm^{-1} and 4500 cm^{-1}. These concentrations may be related to the presence of polysynthetic twinning of Brazil Law [6] 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 H_2O 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 Quaraí samples.

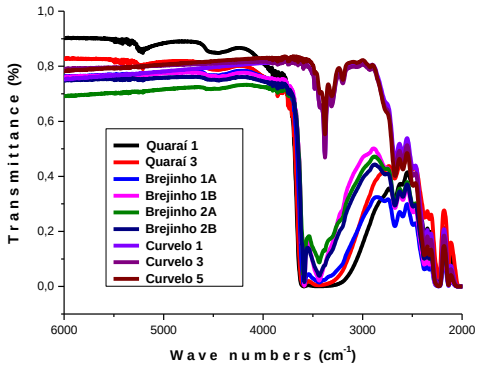


Figure 1: FTIR spectra of quartz samples from Quaraí, Brejinho and Curvelo regions.

According to Lias et al. [7], 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 [8], 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. 2, 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, Quaraí quartz plate shows absorptions between 4300 cm^{-1} - 4700 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. [9], 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 Quaraí sample shows very well defined molecular water and silanol content.

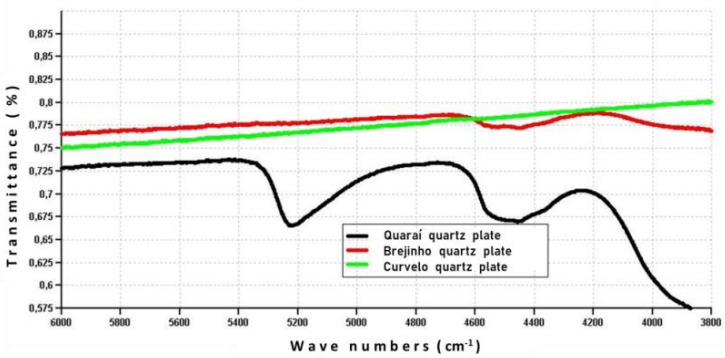
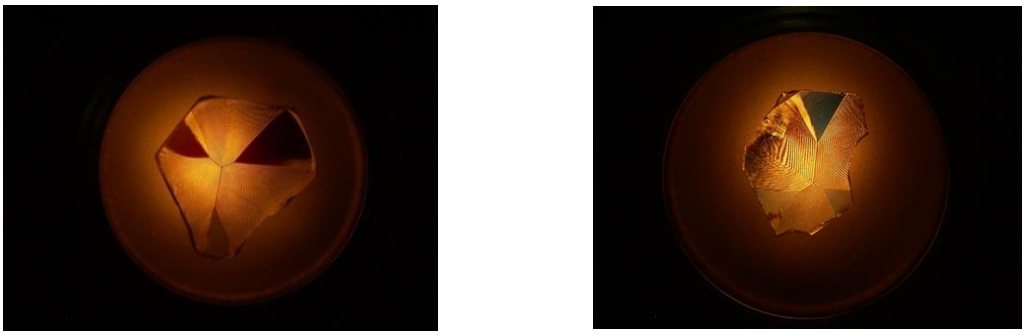


Figure 2: Spectrum in the near infrared range of quartz samples from Quaraí, Brejinho and Curvelo regions, with various water specifications.

The quartz samples of Quaraí 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.

The Figs. 3 (a) and (b) show the samples of the locality of Quaraí 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 [2].



(a) **(b)**

Figure 3: Images in the polariscope of quartz plates from Quaraí (a) and (b) with Brazil Law twinning.

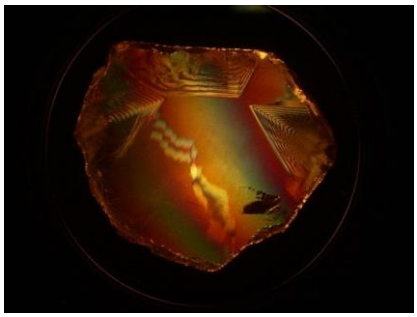


Figure 4: Image of a quartz plate from Brejinho.

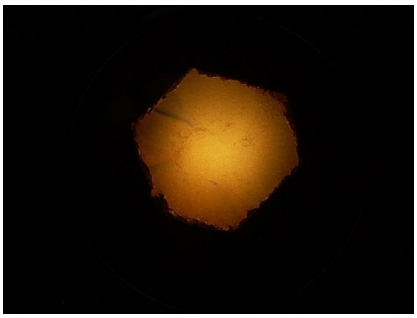


Figure 5: Image of a quartz plate from Curvelo.

The Fig. 4 above 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. 5 above which does not show any Brazil Law twinning.

4. Conclusions

The FTIR spectroscopy analyses performed on Quaraí 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 responsible for the formation of defects 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. Differentely 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.

Acknowledgements

The important collaboration of the technical staff and colleagues from the Multipurpose Irradiator and the Electron Beam Accelerator of the Radiation Technology Center (IPEN-CNEN/SP), and the Geological Institute of USP are acknowledged.

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