2011 International Nuclear Atlantic Conference - INAC 2011
Belo Horizonte,MG, Brazil, October 24-28, 2011
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: **978-85-99141-04-5**

MONTEZUMA PRASIOLITE: GAMMA RADIATION EFFECTS

Rainer A. S. Güttler [1], Cyro T. Enokihara [2], André F. M. Helfenberger [1], Paulo R. Rela[2]

[1] Instituto de Geociências - USP
Rua do Lago, 562
05508-080 São Paulo, SP
rainersg@usp.br.

[2] Instituto de Pesquisas Energéticas e Nucleares (IPEN - CNEN / SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
cteiti@ipen.br
prela@ipen.br

ABSTRACT

The amethyst mine of Montezuma, Minas Gerais, is the only one on earth which produces, after heat and irradiation treatment, a quartz of a blue to violetish blue body color, the so-called “safirita” or blueberry in the trade. Beside this , it is possible by heat treatment to produce two types of prasiolite, “type 1” and “type 2” differing in its green color. Prasiolite 1 is a quartz with a yellowish green, prasiolite 2 with a bluish green color. Here are given details about irradiation and heating procedures of heated amethyst from Montezuma to show the changes in color after each step. This allows to select the best conditions for the production of the ideal quality of “safirita” or blueberry and prasiolite 2. Finally it can be concluded that the irradiation of material from Montezuma always produces an increase in grayish black tons and heating always leads to lighter tons in the colors. It is possible that there exists two processes on atomic scale with opposite reactions.

1. INTRODUCTION

The Montezuma deposit, located in the Northern part of State of Minas Gerais, near the border with Bahia, has been worked for amethyst since the Decade of the 60s. Since then the amethysts were being burned for the production of so-called prasiolite [1], green quartz produced by heating amethyst crystals between 380 and 450ºC. Recently, a new variety of quartz is being produced in the region through the irradiation of prasiolite with gamma rays. The product is a violet blue quartz commercially called "safirita" [2]. Figure 1 shows amethyst, prasiolite and “safirita” with gem quality in raw state and cut.

Figure 1. (1) Natural amethyst Montezuma; (2) Prasiolite (burnt amethyst); (3) Prasiolite cut and polished; (4) “Safirita” (burnt amethyst and irradiated); (5) “Safirita” cut and polished.

This, however, is the only record in the world of a deposit whose amethyst crystals become blue, after being heated and irradiated with gamma rays [3]. A recent study of irradiation of samples of Brazilian quartz was undertaken by Güttler et al. [4], where samples of colorless quartz from the Paraná basin were subjected to gamma radiation, and showed a greenish coloration. Still no study exists addressing the reason of the differences in results between the treatment of quartz of Rio Grande do Sul, and Montezuma (MG). Also there are no publications and studies related to the geology of the deposit of Montezuma, and the mineralogical characterization of mineral products extracted. The mineral quartz, relatively pure in its natural state (compared with other minerals), may contain solid , fluid and structural inclusions. Solid and fluid inclusions are those that do not occur related to the mineral's crystal structure, corresponding to solid or liquid material included by crystallization in the mineral. However, the structural impurities are those where the trace elements occur related to the crystalline network. According to Weil [5] [6], cited in Götze et al. [7], the small size of the ion, Si^{4+} (4,2nm), and the structure of quartz, allow only small quantities of trace elements in their structure. When this occurs, the Si can be replaced by Al, Fe, Ti, Ge, Ga, H and P. If there is a deficit of charge after the replacement, there may be a compensation by cations located in structural channels parallel to the axis c. These cations correspond mainly to Li +, Na +, K + and H +, though in some cases, ions of Cu, Ag, Al, Fe, Ti, Co, Cr and Ni can also accomplish this compensation.

Since most quartz is colorless numerous methods of treatment of gemstones have been applied to alter the color characteristics. Treatment methods used in this work are: heating, and the irradiation with gamma rays.

The heating of amethysts is already done for a long time, with the objective to improve the color of attractive little gems. By heating crystals of amethyst a few hundred degrees, one can obtain samples with yellow, brownish red, green or milky white colors. Almost all citrine for sale on the market and all prasiolite are products of the heat treatment of amethyst [8].

Monteiro [9] conducted a study involving heating tests and irradiation experiments of amethysts of 17 Brazilian occurrences, where she describes the darkening of the color as a result from the gamma irradiation, and the bleaching of the samples as function of heating . Samples from Montezuma deposit have not been studied in this work.

Neumann and Schmetzer [10] studied the behavior to heating of samples of amethyst of several locations in the world, including Montezuma, and describe the reasons that lead to color change after heating.

Color changes would be related to interstitial and cationic substitutions according to the model described by the equation:

$$(x + y)Fe^{3+} (S_1) + xFe^{3+}(I_4) \xleftrightarrow{T \geq 300\ ^{\circ}C} xFe^{4+}(S) + xFe^{2+}(I_4) + yFe^{3+}(S_2)$$

where,

(S) = Silicon replacement
(S_1) = replacement of silicon with charge compensation by an alkaline metal ion
(S_2) = replacement of silicon with charge compensation by a hydrogen ion
(I_4) = interstitial channel with tetrahedral symmetry

In the case of prasiolite, the green colour would be generated by the color center $Fe^{2+}(I_6)$, i.e., Fe^{2+} on the sites of octahedral symmetry structural channels. The $Fe^{2+}(I_6)$ is however formed by a change in oxidation and migration of Fe^{3+} of interstitial channels of tetrahedral symmetry (I_4), to the sites of the interstitial channels of octahedral symmetry (I_6), being then the $Fe^{3+}(I_4)$, the precursor of prasiolite color center.

About the darkening of crystals after irradiation with gamma rays, Rossman [11] mentions that the smoky color of quartz is associated with the color centers of substitutional Al^{4+} ions. These centers can be generated by the combination of irradiation and heating processes.

2. MATERIALS AND METHODS

2.1. Materials

A batch of l,5 kg of amethyst fragments from Montezuma, heated already on-site, at a temperature between 380 and 450º C, without much control of time and temperature, has been used in this study. These limits have been established according to the appearance of shades of green, indicating normal temperature.

Within the batch there could be found samples with different shades of color: light green, dark green, yellowish green, brown and bluish green of course. The size of samples varied between 10 to 20 mm. Most of the samples show color zoning, possibly generated during the crystallization of crystals. All these varieties have been arbitrarily separated into 5 groups according to their tonality and color depth as shown in Table 1.

Table 1. The five groups of colors produced by heating amethyst from Montezuma, Minas Gerais

	Colouring	Trade Nomenclature
Group 1	Clear green	Prasiolite (type 1)
Group 2	Yellowish green	Green gold quartz
Group 3	Dark green	Prasiolite (type 1)
Group 4	Brown	Quartz pardo
Group 5	Bluish green	----------------

.

2.2. Tests with Gamma Radiation

All trials involving gamma irradiation, with those five groups of samples, were made in the Technology Center of Radiation (CTR) of IPEN-CNEN/SP, using the Multipurpose Co^{60} Irradiator. The samples were inserted into baskets of stainless steel wire and fixed to a steel structure. This was then submerged in the pool of irradiation that contains 32 bars of Co^{60}. The total dose of radiation given to samples varies with the distance of the samples to the bars and also of the exposure time. The radiation dose was then measured with dosimeters for gamma radiation "Red Perspex 4034" in all tests performed.

Irradiation in the first trial samples of 5 groups were limited to a dose of 160 kGy. Later there was a set of irradiation tests with samples of Group 3, which underwent irradiation of 5, 20, 35, 50, 65, 85 and 100 kGy to document the influence of increasing radiation doses. In the third test a small batch of samples of groups 1 and 3 were subjected to 371 kGy and of samples of the Group 2 to 256 kGy. In all cases of irradiation, the samples acquired an intense black color and were totally opaque.

2.3. Heating Tests

For heating of samples was used an cylindrical oven “Cobel” brand, model SH-1. The samples were put in pure quartz sand in a porcelain bowl, at all stages of heating, so that the temperature remained more homogeneous. Heating tests were made in samples of groups 1, 2, 3 and 4.

To study the behavior of black samples and to investigate the formation of the blue tone, several tests of heating with temperatures ranging from 200 to 300º C were undertaken. Samples of groups 1, 2, 3 and 4, irradiated to 160 kGy, were heated to 200, 250 and 300º C during time intervals of 30, 60 and 90 min Later, additional tests on samples of Group 3, irradiated with 5 kGy and 371 kGy to confirm the results of former runs. Group 1 Samples irradiated with 371 kGy were heated under the same conditions. Heating of samples of groups 1, 2 and 3 with higher temperatures of 380, 420 and 430º C has been tried to perform the reverse reaction, transforming both black samples and "safirita" (produced after heating to 250º C) to prasiolite again. As a result prasiolite of type 2, with a bluish green color has been formed. Details about the experimental and heating procedures can be found in Helfenberger [12].

3. RESULTS AND DISCUSSION

After the first heating at temperatures of 380 to 450º C, done at the mine, products of this heating step can be classified as prasiolite type 1, green gold quartz and honey quartz.

Irradiation tests carried out on 5 groups, regardless of the amount of radiation received (either 5 kGy or 371 kGy), showed these groups have the same characteristics after this stage of the treatment. The percentage of black color of the samples was greater than 90%.

By heating of the black samples at temperatures between 200 to 300° C, it was observed that at the low temperature of 200° C, bleaching was very weak, with average percentages of black still up to 63%, and traces of cyan and magenta are less than 10%. However, it is only from 250º C that samples presented a significant change in color.

Another important observation can be made about bleaching. Figure 2 shows the variation of the amount of black color with increasing temperature. Compared to the variation of the black color as a function of time (for a same temperature), one can observe that the bleaching is much more pronounced at temperatures between 200 and 250° C. Between 250 and 300^{o} C, the variation of saturation virtually stabilizes, varying slightly.

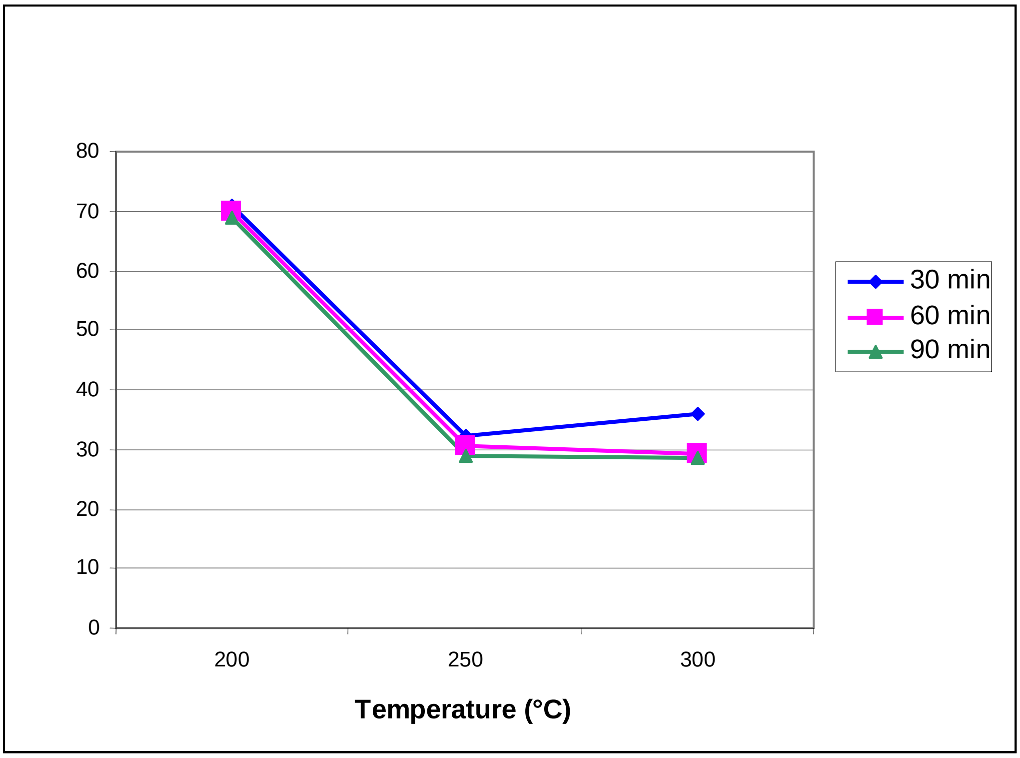

Figure 2. Decrease of amount of black as a function of Time and Temperature

Figure 3 shows all the main variations of hue obtained in these heating tests, showing tones more purple (samples 1, 2, 3 and 4) to tones more blue (samples 5 and 6), and even nearly total bleaching, represented by sample 7.

Figure 3. Variations of the shade of blue produced by heating of opaque samples

Tests of heating with temperatures varying between 380 and 430° C indicated that only half of the samples of groups 2 and 3 heated to 380° C became purple whereas the other half does not changed.

All samples were then heated again to 430º C and at this temperature all samples have become green, including those that had remained violet to 380º C. The same test was performed directly with Group 2 samples irradiated with 160 kGy, where it was noted that at 380° C only half of the samples changed from black to green.

Comparing the results between the prasiolite type 1, produced by previous gamma irradiation and heating with prasiolite type 2 obtained one observes that there is a difference between the percentages of cyan and yellow and this produce the difference of the hue of prasiolite. The prasiolite type 2 has a smaller percentage of yellow (47% to 60.3%) and cyan (27.6% to 20.1%), producing a more bluish color than prasiolite type 1, as shown in Figure 4.

Figure 4. Prasiolite of type 1 (left) und type 2 (right)

These variations in color observed by irradiation and heating of different samples may be related to compositional differences of the material.

Detailed studies of compositional differences does not exist yet. Semi-qualitative analyses on samples of amethysts obtained at by X-ray Fluorescence at the Universidade Federal de Minas Gerais (UFMG) however showed the presence of Zn, Fe, Ni, Co, Ti and K as trace elements. The largest concentration detected was Zn (388 ppm), Fe (188 ppm) and Ni (98 ppm). Another analysis performed in the laboratory of X-ray Fluorescence of IGc/USP of samples of prasiolite type 1 belonging to the Group 1 (light green coloring) showed 0,59% of iron, 0,11% of Al and traces of zinc.

4. CONCLUSIONS

According to the results of this work it can be concluded that, generally speaking, gamma radiation and heating produce changes in colour of crystals of amethyst and/or prasiolite of the deposit of Montezuma, and that these changes apparently vary depending on the chemical composition of samples.

The treatment of samples with gamma rays cause in all cases the darkening of samples making some of them opaque and black. On the other hand, it was concluded that all steps of heating cause the bleaching effect of samples, i.e. decrease in saturation of the color black, changing the color of the samples to various tones of blue and green.

Two types of prasiolite can be produced by heating: prasiolite type 1 and type 2 . The prasiolite type 1 can be produced by direct heating of natural Amethyst between 380 and 450^{o} C, resulting in a material with a slightly yellowish green tone. Irradiating prasiolite type 1, and heating the product between 380 and 420º C, produces prasiolite type 2, with a bluish green colour.

During tests of producing prasiolite type 2, it was noted that there is a minimum temperature for the bleaching of the samples. This temperature can vary between 380 and 420º C as a function of composition.

To produce the "safirita" one has to irradiate samples of prasiolite type 1 with gamma rays, with subsequent heating between 250 and 300º C. If this heating step reach temperatures close to 380º C one starts to produce prasiolite type 2.

REFERENCES

1. Cassedanne J. P.; Cassedanne J. O. " Axinite, hydromagnesite, amethyst, and other minerals from near Vitória da Conquista (Brazil) " , *Mineralogical Record*, v. **8**, p. 382-387 (1977).
2. Güttler, R. A. S. " Safirita: the brazilian blue quartz ", *Diamond News*, v. **25**, p. 45, (2006a).
3. Güttler, R. A. S. " Treated violetish blue to violet quartz from Brazil ", *Gem News International – Gems and Gemology*, v. **42**, nº 4, p. 285-286, (2006b).
4. Enokihara, C. T.; Güttler, R. A. S.; Rela, P. R. " Gamma irradiation of quartz from Parana Basin, South America ". *International Nuclear Atlantic Conference INACC 2007*, Santos, Brazil , (2007).
5. Weil, J.A., "A review of electron spin spectroscopy and its application to the study of paramagnetic defects in crystalline quartz" , *Phys Chem Min* ,**10** , p.149-165, (1984).
6. Weil, J.A. "A review of EPR spectroscopy of the point defects in α-quartz: the decade 1982-1992". *In: Helms, C.R. Deal, BE (ed), The Physics and Chemistry of SiO_2 and the Si-SiO_2 Interface.2, Plenum Press, New York*, p.131-144, (1993).
7. Götze, J.; Plötze, M.; Graupner, T.; Hallbauer, D.K.; Bray, C.J.; "Trace elements incorporation into quartz: A combined study by ICP-MS, electron spin resonance, cathodoluminescence, capillary ion analysis and gas chromatography" , *Geochimica et Cosmochimica Acta*, v. **68**, nº 18, p. 3741-3759, (2004).
8. Schumann, W. " Gemas do Mundo " . *Ao Livro Técnico.* 3ª edição, Rio de Janeiro. 625p. (1985).
9. Monteiro, C. V. " Caracterização das ametistas brasileiras em face aos efeitos da radiação gamma e seu tratamento térmico ". Dissertação de Mestrado. Instituto de Geociências e Ciências Exatas - UNESP (Rio Claro). 65p. (2001).
10. Neumann, E.; Schmetzer, K. " Mechanism of thermal conversion of colour and colour centers by treatment of amethyst " . *N. Jb. Miner. Mh. Jg.* H. **6**, P. 272-282 (1984).
11. Rossman, R. R. " Colored varieties of the sílica minerals " *Reviews of Mineralogy*, v. **29**, p. 433-467, (1994).
12. Helfenberger, A. F. M. " Estudo da interferência da radiação gama na cor das ametistas de Montezuma, MG ". Trabalho de Formatura. Instituto de Geociências – USP. 61p. (2007).