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THE RADIOACTIVE DECAY PATTERN OF BLUE TOPAZ TREATED BY NEUTRON IRRADIATION

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A systematic study of 15 neutron-irradiated blue topaz samples was conducted using high-purity germanium (HPGe) digital gamma-ray spectroscopy. The specific activity of the detected radionuclides (^{134}Cs, ^{182}Ta, ^{46}Sc, and/or ^{160}Tb) was measured, and the decay pattern of the irradiated topaz was determined. Based on the time elapsed since their removal from the nuclear reactor, the amount of time required for the residual radioactivity to decay to safe levels was calculated. Most of the samples were safe at the time of the first measurement (95 days after irradiation), but higher concentrations of radionuclide impurities in some samples will require them to be quarantined for several years.

Radioactivity is one of the most discussed topics surrounding blue topaz (figure 1), which is commonly treated by irradiation from near-colorless starting material. To maintain consumer confidence, it is important to ensure that these gems do not contain dangerous levels of residual radioactivity. Three major irradiation methods are used: gamma (γ), neutron, and electron-beam irradiation (Nassau, 1985; Ashbaugh, 1988). Of these, neutron irradiation creates perhaps the most beautiful medium blue color, called "London Blue." Unfortunately, this treatment also produces radioactivity from the nuclides of trace-element impurities in topaz (Crowningshield, 1981; Ashbaugh, 1988), such as Fe, Mn, Co, Zn, Sb, Ta, Cs, Sc, and Tb (Foord et al., 1988; Northrup and Reeder, 1994). These radioactive nuclides, which have various half-lives (table 1), may emit γ-rays and beta (β) particles of varying radiation intensity (Ashbaugh, 1991; Nelson, 1991). While a high dose of γ-rays and β-particles poses danger, a very low dose is not harmful. Therefore, blue topaz colored by neutron irradiation requires a quarantine period to allow the residual radioactivity to reach a safe level (referred to, e.g., as the exemption level) of less than 74 becquerels per gram (Bq/g) or 2 nanocuries per gram (nCi/g; Ashbaugh, 1988).

Investigations of blue topaz have focused mainly on irradiation methods and the cause of the coloration, with less emphasis on the detection of residual radioactivity. Ashbaugh (1988) discussed the radioactivity of colored stones treated by irradiation, as well as potential health hazards and government regulations. Based on these findings, GIA offered testing services for irradiated gems from 1991 through 2006. However, that article did not address blue topaz treated by neutron irradiation. Guo et al. (2000) measured the specific activity of the total alpha (α) and β radioactivity of crushed blue topaz after irradiation using an FJ-2603 low-level α- and β-radiation measuring device and a BH1216A low-background measuring instrument. While that effort was helpful in exploring the radioactive decay of irradiated blue topaz, the specific nuclides involved were not determined. Helal et al. (2006) analyzed the trace elements in topaz samples before and after neutron irradiation using ICP-MS and a high-purity germanium (HPGe) detector. This study proved that radioactivity in blue topaz colored by neutron irradiation is related to variations in the trace elements in the topaz. However, the decay pattern of the radionuclides was unclear. This article studies the residual radioactivity in blue topaz treated by neutron irradiation, identifies the specific radionuclides

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Figure 1. Most blue topaz on the market is irradiated to enhance its color. These stones (~4–10 ct) were treated by neutron irradiation. Photo by J. Zhang.

TABLE 1. Half-lives of radioactive nuclides in irradiated blue topaz.

Radionuclide	Half-life (days)
^{59}Fe	44.51
^{124}Sb	60.20
^{160}Tb	72.30
^{46}Sc	83.81
^{182}Ta	114.4
^{65}Zn	243.8
^{54}Mn	312.2
^{134}Cs	753.7
^{60}Co	1,924

involved, and calculates quarantine periods for the most highly radioactive samples to reach the exemption level.

MATERIALS AND METHODS

Fifteen samples of cut but unpolished near-colorless topaz (weighing 0.75 to ~2.0 g) of pegmatite origin from China's Guangdong Province were studied. EDXRF chemical analysis was performed on all 15 samples (after irradiation) and on one additional untreated sample from the same locality, using an ARL Quant'X spectrometer at the National Gemstone Testing Center in Beijing.

The important color centers in topaz are produced after 12 hours of irradiation at 1.2×10^{19} neutrons/(cm^2 × sec). These conditions were used in this study to produce the colors shown in figure 2. The irradiation was conducted in a "light water" (ordinary water) nuclear reactor at the China Institute of Atomic Energy in Beijing. The samples were placed in cadmium-lined containers to reduce the amount of the thermal neutrons caused by absorption, and also to increase the amount of the fast, color-producing neutrons.

A GEM-30185-Plus Despec HPGe digital gamma-ray spectrometer (figure 3) was used to measure the residual radioactivity of the irradiated blue topaz. The Ge semiconductor detector had a relative efficiency of 25%, an energy resolution of 1.96 keV at 1332.5 keV for ^{60}Co, and a peak ratio of 48. The values measured represent the combined radioactivity of specific nuclides in the process of decay. The measurements were semiquantitative, obtained for 40,000 seconds of active time.

Figure 2. These irradiated topaz samples (weighing 0.75 to ~2.0 g) were used in this study. From left to right, the top row shows samples numbered Topaz-1 to Topaz-7, and the bottom row shows Topaz-8 to Topaz-15. Photo by J. Zhang.

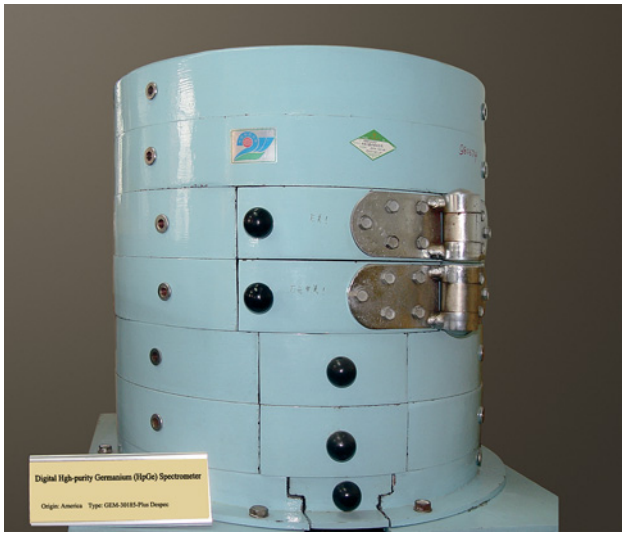

Figure 3. The HPGe digital spectrometer at the China Institute of Atomic Energy in Beijing was used in this study. Photo by J. Zhang.

To explore the decay pattern of the irradiated blue topaz, we conducted four measurements of the residual radioactivity in the 15 samples. The samples were removed from the reactor on September 28, 2005, and gamma-ray spectroscopy was subsequently performed on January 1, 2006 (day 95); March 14 (day 167); April 19 (day 203); and November 30 (day 428). We tested all samples at day 95, and then focused on four samples (figure 4) with residual radioactivity higher than the exemption value (74 Bq/g).

TABLE 2. Residual radioactivity (Bq/g) of irradiated blue topaz samples after four periods of decay.[a]

Sample no.	Nuclide	Decay time (days)			
		95	167	203	428
Topaz-8	^{134}Cs	417.6	392.1	379.2	309.3
	^{182}Ta	19,800	12,800	10,290	2,668
	Total	20,218	13,192	10,669	2,977
Topaz-9	^{134}Cs	1,617	1,512	1,462	1,187
	^{46}Sc	296.3	162.1	120.7	18.4
	^{182}Ta	495.9	321.1	258.1	66.8
	Total	2,409	1,996	1,840	1,273
Topaz-10	^{182}Ta	195,000	125,800	100,800	25,750
	Total	195,000	125,800	100,800	25,750
Topaz-15	^{134}Cs	106.2	100.2	96.5	78.7
	^{46}Sc	237.9	132.1	98.6	15.0
	^{160}Tb	3,909	1,961	1,389	160.5
	Total	4,253	2,193	1,585	254.2

[a] *Although Fe was detected in the samples by EDXRF analysis, no iron radionuclides were detected by gamma-ray spectroscopy.*

RESULTS AND DISCUSSION

EDXRF spectroscopy showed traces of Mg, Ca, Na, K, and Cl in all samples, while Fe, Cs, Sr, Sc, Ta, and Tb were detected in some of them. Gamma-ray spectroscopy revealed the variable presence of four radionuclides in the irradiated topaz: ^{134}Cs, ^{182}Ta, ^{46}Sc, and/or ^{160}Tb (table 2). When the samples were first tested 95 days after irradiation, four of them showed residual radioactivity above the exemption level. The residual radioactivity of the other 11 samples had decayed below the exemption level or the detection limit of the spectrometer.

NEED TO KNOW

- Neutron irradiation is commonly used to create an attractive "London Blue" color in near-colorless topaz.
- Topaz may contain trace impurities that become radioactive after neutron irradiation.
- Gamma-ray spectroscopy showed that irradiated topaz samples from China contained up to four radionuclides.
- Most of the samples were safe to handle when measured 95 days after irradiation, but some will require several years to "cool down."

The goal of studying the decay pattern of irradiated blue topaz is to determine the time needed for the residual radioactivity to decay to a safe level (Miraglia, 1986; Miraglia and Cunningham, 1988). The half-life decay formula of radioactive nuclides is necessary for these calculations. De Soete et al. (1972) defined the formula as follows: If the probability of decay for radioactive elements in unit time is $1/\tau$, and if the number of radioactive elements is N, then the number of decayed radioactive elements in the time span of dt should be dN, where

$$dN/N = -1/\tau\, dt \qquad (1)$$

In formula (1), the negative sign indicates a reduction in the number of subatomic particles that constitute ionizing radiation. Integrating both sides of the equation yields:

$$N = N_0 e^{-t/\tau} \qquad (2)$$

In formula (2), N_0 is the original value of radioactivity from a given nuclide, and τ represents the decay time constant, after which the element has been reduced to e^{-1} of the original value of radioactivity. The relationship between τ and half-life ($T_{1/2}$) can be expressed as:

$$T_{1/2} = 0.693\tau \qquad (3)$$

Applying formula (3) to formula (2), we can derive the half-life decay formula of radioactive nuclides:

$$N = N_0 e^{-0.693t/T_{1/2}} \qquad (4)$$

Figure 4. These four samples (9.5–16.5 mm long) had residual radioactivity higher than the exemption level when initially measured after 95 days. From left to right: Topaz-8, Topaz-9, Topaz-10, and Topaz-15. Photo by J. Zhang.

In formula (4), N_0 is the initial value of radioactivity and N is the unknown value of radioactivity, expressed in units of Bq. $T_{1/2}$ is the half-life of the nuclide, and t is its decay time.

The specific activity of each radionuclide present in a given sample was calculated. The values obtained at the first stage of radiation detection (after 95 days) can be set as the initial values. Values for each subsequent stage can then be calculated and compared with the detected values, as shown in table 3. In addition, the radioactivity of the samples upon their removal from the reactor (day 0) can be calculated. Most importantly, the time required for the residual radioactivity to decay below the exemption level (74 Bq/g) can be derived using the formula; these times are shown in table 4 for the four samples.

CONCLUSIONS

Blue topaz (e.g., figure 5) typically takes two to three years to decay below the exemption level after neutron irradiation. The actual quarantine time necessary for specific samples depends on several factors. There are three scenarios that can contribute to high levels of residual radioactivity in irradiated gems.

The first is the presence of activated impurities with a long half-life (i.e., a comparatively slow rate of decay). For example, ^{134}Cs has a half-life of 2.06 years. This radionuclide was present in three of the four topaz samples showing residual radioactivity, and for Topaz-9 the time required to decay below the exemption level was calculated at 3,440 days (~9.4 years).

Second, high concentrations of activated impurities (even those that do not have a long half-life) may produce high residual radioactivity. Sample Topaz-10, for example, contained a large amount of ^{182}Ta (half-life of 114 days). Consequently, the sample's radioactivity upon removal from the reactor was 347,600 Bq/g, and it took 1,391 days (~3.8 years) for the sample to decay below the exemption level.

The third scenario contributing to high levels of residual

TABLE 3. Detected and calculated specific activity (Bq/g) of radionuclides in irradiated blue topaz.

Sample no.	Nuclide	Method	Decay time (days)				
			0	95	167	203	428
Topaz-8	^{134}Cs	Detected		417.6	392.1	379.2	309.3
		Calculated	455.8		390.8	378.0	307.2
	^{182}Ta	Detected		19,800	12,800	10,290	2,668
		Calculated	35,280		12,780	10,270	2,664
Topaz-9	^{134}Cs	Detected		1,617	1,512	1,462	1,187
		Calculated	1,764		1,513	1,464	1,190
	^{46}Sc	Detected		296.3	162.1	120.7	18.4
		Calculated	650.0		163.4	121.3	18.9
	^{182}Ta	Detected		495.9	321.1	258.1	66.8
		Calculated	877.7		320.1	257.2	66.5
Topaz-10	^{182}Ta	Detected		195,000	125,800	100,800	25,750
		Calculated	347,600		125,900	101,100	25,770
Topaz-15	^{134}Cs	Detected		106.2	100.2	96.5	78.7
		Calculated	115.7		99.2	96.0	78.0
	^{46}Sc	Detected		237.9	132.1	98.6	15.0
		Calculated	521.8		131.1	97.4	15.1
	^{160}Tb	Detected		3,909	1,961	1,389	160.5
		Calculated	9,717		1,960	1,388	160.6

TABLE 4. Decay time needed for irradiated blue topaz samples to reach the exemption level of 74 Bq/g.

Sample no.	Nuclide	Decay time (days)						
		0	95	428	703	1,391	1,975	3,440
Topaz-8	^{134}Cs	455.8	417.6	309.3	238.4	139.8	73.8	
	^{182}Ta	35,280	19,800	2,668	491.5	14.5	0.2	
	Total	35,736	20,218	2,997.3	729.9	154.3	**74.0**	
Topaz-9	^{134}Cs	1,764	1,617	1,187.3	922.5	540.7	285.6	74.0
	^{46}Sc	650.0	296.3	18.4	1.9	0	0	0
	^{182}Ta	877.7	495.9	66.8	12.2	0.4	0	0
	Total	3,291	2,409	1,272	936.6	541.1	285.6	**74.0**
Topaz-10	^{182}Ta	347,600	195,000	25,750	4,843	73.9		
	Total	347,600	195,000	25,750	4,843	**73.9**		
Topaz-15	^{134}Cs	115.7	106.2	78.7	60.5			
	^{46}Sc	521.8	237.9	15.0	1.6			
	^{160}Tb	9,717	3,909	160.5	11.5			
	Total	10,350	3,434	254.2	**73.6**			

Figure 5. Treated blue topaz (here, 85.79–243.66 ct) is commonly encountered in the global gem market, and neutron-irradiated samples must undergo appropriate safeguards to ensure that they do not contain dangerous levels of residual radioactivity. Photo by Robert Weldon; from top to bottom, GIA Collection nos. 16203, 30886, 31942, 30889, and 31947.

radioactivity is the presence of activated impurities with a long half-life combined with relatively high concentrations.

The Chinese topaz studied for this article should be assumed to contain different trace-element impurities than starting material from other sources (e.g., Brazil), and therefore the decay times presented in this study are not representative of all neutron-irradiated topaz on the market. Still, the procedure and data presented here provide useful information for evaluating the residual radioactivity in topaz treated by neutron irradiation, regardless of locality.

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