NEWS FROM RESEARCH

Cobalt Diffusion of Natural Spinel: a report describing a new treatment on the gem market

Sudarat Saeseaw, Vararut Weeramonkhonlert, Charuwan Khowpong, Nattida Ng-Pooresatien and Supharart Sangsawong, Victoria Raynaud[1], and Claire Ito[2]

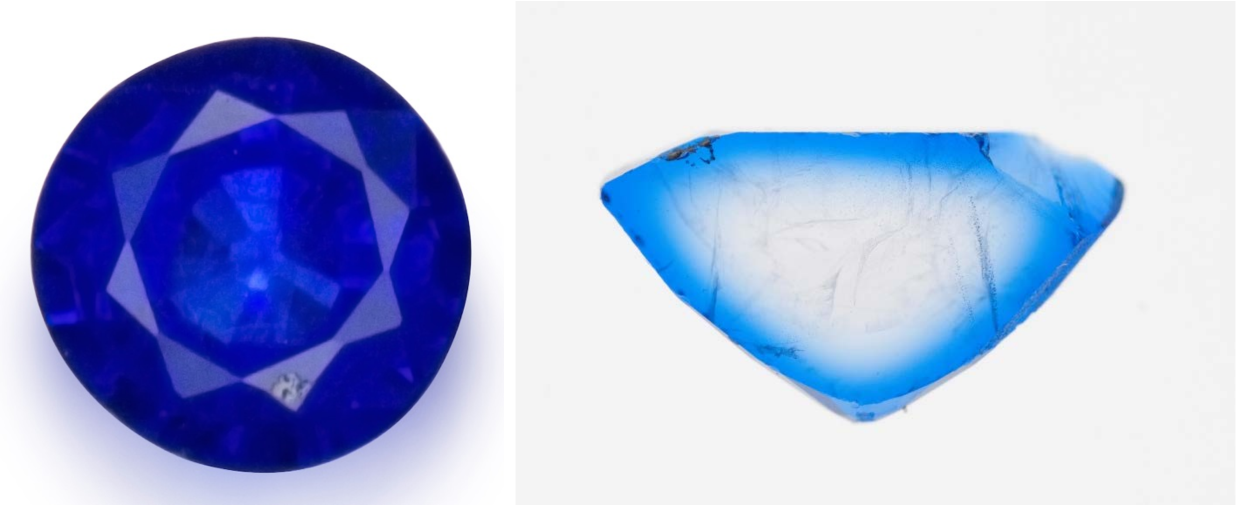


Figure 1: A faceted Co diffused spinel and a cross section though another sample revealing the considerable depth of penetration.

---

[1] GIA Laboratory, Bangkok, Thailand
[2] GIA Laboratory, Carlsbad, CA. USA

Table of Contents

Introduction

Recently (May 2015) several unusual looking faceted spinels were submitted to GIA's New York, Carlsbad, and Bangkok identification laboratories. At the same time and within the social media it was announced by GRS Laboratory that Mr. M.T.M Harris of Emteem Gem Laboratory had reported seeing similar stones coming through his laboratory in Beruwela, Sri Lanka, and that GRS in cooperation with Günther and Harris (Peretti 2012 (updated 2015)) had determined that the stones were diffused with cobalt. From their inclusion scenes these stones appeared to have been heated at high temperatures, in particular this seemed to be so from the dissolved state of numerous solid inclusions and a profusion of fractures that seemed to have been artificially healed in a flux environment.

Cobalt along with iron is known to contribute to the observed color of natural blue spinels from a number of locations (Harder 1986, Chauviré 2015, D'Ippolito 2015) however those colored mostly by cobalt have become sought after both in the general trade as well as with collectors. As such it is important that a clear distinction between natural cobalt spinels and those that owe their color to the artificial addition of cobalt be made and the techniques needed for this distinction be available for all to use.

The following text, images and data set out the detail and results of the authors' examination of eighteen samples supplied to them by the individual responsible for devising the process and placing the material in the market - Mr. Thamrong Charasaiya, who is the President of T.N., High Tech Gems limited, located in Ladprao, Bangkok Thailand. Mr. Charasaiya informed the authors' that his treatment involved the "deep diffusion cobalt" into "low colored natural spinel from Burma" resulting in a strong blue color. He further stated that "cobalt will not diffuse into spinel on its own and that iron had also to be present along with the cobalt for the process to work".

The authors greatly appreciate the assistance of Mr. Charasaiya in donating the specimens for this examination as well as the open discussions that have taken place that have provided further useful information on the process being used. However it should be emphasized at the outset that the details of his process remain proprietary to Mr. Charasaiya and any description of it here results from the conversations we have had with him - the authors have not witnessed the actual treatment taking place and nor do they have details on such important areas as the manner in which the diffusion materials are applied, the temperatures or timescales used.

Figure 2: Eight of the faceted cobalt diffusion treated spinel samples provided to GIA Bangkok for research purposes by Thamrong Charasaiya. Photo by L. Nillapat © GIA

Materials and Methods

Eighteen samples (Table 1) were received from Mr. Thamrong Charasaiya. All samples were of a bright blue color and weighed between 0.35 to 4.99 carats. Internal features were examined using standard gemological (Gemolite) microscopes and horizontally oriented immersion microscopes and captured at up to 180 x magnifications with a Nikon SMZ 1500 system using darkfield, brightfield, and diffused illumination, together with a fiber-optic light source for oblique illumination when necessary.

Chemistry was determined using a Thermo Scientific ARL QUANT'X EDXRF Spectrometer, using an X-ray tube voltage up to 50kV. In this study, the voltage was set to 20 keV, current of 0.14 mA, no filter and a count time of 100 seconds in vacuum. For a more detailed analysis, LA-ICP-MS technology with a Thermo Fisher scientific iCAP-Q induced coupled plasma - mass spectrometer (ICP-MS) coupled with a Q-switched Nd:YAG Laser Ablation (LA) device operating at a wavelength of 213 nm, was used. Laser conditions were 55 μm diameter laser spots, a fluency of around 8±1 J/cm^2, and a 15 Hz repetition rate. Various spots were analyzed on each wafer in different color areas. For the ICP-MS operations, the forward power was set at ~1350 W and the typical nebulizer gas flow was ~0.80 L/min. The carrier gas used in the laser ablation unit was helium, set at ~0.50 L/min. The criteria for the alignment and tuning sequence were to maximize beryllium counts and keep the ThO/Th ratio below 2%. NIST 610 and 612 glasses were used for calibration standards. All elemental concentrations were calculated by applying ^{24}Mg as an internal standard, with Mg concentration calculated from the theoretical value of spinel (17.08 wt%).

Photoluminescence (PL) spectra were collected using a Renishaw inVia Confocal Raman microscope at room temperature. The system was equipped with four laser systems, producing six excitation wavelengths: 324.8, 457.0, 488.0, 514.5, 632.8, and 830.0 nm. The 514.5 nm laser was used for excitation, and spectra range analyzed between 640 nm and 740 nm.

Ultraviolet-visible-near infrared (UV-Vis-NIR) spectra were collected using a Hitachi U-2910 spectrophotometer, integrating with a polarizer accessory controlled by ThorLabs APT. We used 1.5 nm as the slit width, and recorded from 250-1100 nm.

In addition to the specimens studied for the report Mr. Thamrong also provided images of himself (Figure 3) examining his production, his furnace operations (Figure 4 and Figure 5), his production after "pre-heating" (Figure 6), images "after coating (brown in color) with the diffusion material and prior to the diffusion process" (Figure 7), as they emerge from the furnace "following the diffusion process" (Figure 8) and "after repolishing ready for market" (Figure 9).

Note that after the initial use of the full GIA specimen control numbers in Table 1 only the last three digits are used in the following text when referring to a particular specimen.

Figure 3: Mr. Thamrong Charasaiya examining his production of Co diffused spinels (Photo © T. Charasaiya).

Figure 4: Mr. Thamrong Charasaiya's furnace used for the Co diffusion process. (Photo © T. Charasaiya)

Figure 5: Mr. Thamrong Charasaiya's furnace showing a crucible he uses during the Co diffusion process (Photo © T. Charasaiya).

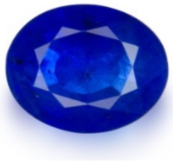
Figure 6: A group of spinels shown here after "pre-heating" (Photo © T. Charasaiya).

Figure 7: A group of spinels shown here as "coated and ready for the Co diffusion process" (Photo © T. Charasaiya).

Figure 8: Co diffused spinel as they emerge from the furnace of Mr. Thamrong Charasaiya (Photo © T. Charasaiya)

Figure 9: Co diffused spinel after repolishing and ready for the market (Photo © T. Charasaiya)

Table 1: Samples used in this study

Samples number#	Weight (ct)	Measurement (mm)			Image
		Length	Width	Depth	
100315603102	2.39	8.91	7.07	5.09	
100315603103	4.29	11.12	8.92	5.12	
100315603104	1.91	8.79	6.99	3.75	
100315603105	1.93	8.97	7.11	3.88	
100315603106	0.96	7.83	5.85	3.04	
100315603107	0.67	6.90	5.12	2.69	

Samples number#	Weight (ct)	Measurement (mm)			Image
		Length	Width	Depth	
100315603108	4.99	12.02	10.13	5.56	
100315603109	0.82	5.84	5.95	3.26	
100315603110	3.93	11.11	9.12	4.53	
100315603111	2.12	9.93	6.95	4.22	
100315603112	1.27	8.04	5.97	3.69	
100315603113	0.93	6.08	5.95	3.37	
100315603114	1.30	8.00	6.20	3.41	

Samples number#	Weight (ct)	Measurement (mm)			Image
		Length	Width	Depth	
100315603115	0.91	6.01	5.92	3.41	
100315603116	3.51	10.98	8.86	4.57	
100315603117	1.12	7.84	5.82	3.18	
100315603118	0.35	4.33	4.23	2.46	
100315603119	0.65	6.04	4.81	3.01	

Examination Results

Standard gemological properties for each of the specimens in Table 1 were determined to be normal for natural spinel. The isotropic refractive indices for the group ranged from 1.715 to 1.719. Most of samples had no fluorescence reaction during exposure to long-wave or short-wave UV light. However, three samples exhibited medium strength red fluorescence under long-wave. All samples had a strong red reaction when viewed through the Chelsea Color Filter in common with most Co colored blue stones. When examined with a handheld spectroscope each stone exhibited strong cobalt-related absorption bands in the green to orange area of the spectrum, and iron bands in blue and violet (Table 2).

Table 2: Gemological properties of the 18 samples of Co diffused blue spinels examined for this report

Samples number#	RI	LWUV	SWUV	Chelsea filter reaction
102	1.718	inert	inert	strong red
103	1.717	inert	inert	strong red
104	1.719	inert	inert	strong red
105	1.718	inert	inert	strong red
106	1.718	inert	inert	strong red
107	1.717	inert	inert	strong red
108	1.719	medium red	inert	strong red
109	1.717	inert	inert	strong red
110	1.717	medium red	inert	strong red
111	1.719	medium red	inert	strong red
112	1.719	inert	inert	strong red
113	1.717	inert	inert	strong red
114	1.716	inert	inert	strong red
115	1.719	inert	inert	strong red
116	1.719	inert	inert	strong red
117	1.715	inert	inert	strong red
118	1.715	inert	inert	strong red
119	1.717	weak red	inert	strong red

Microscopic examination

All samples when examined under magnification were found to contain features that indicated that they had been exposed to a high temperature process. Fractures that had been artificially healed likely by a flux assisted process were clearly evident and if these were viewed in the same manner as laboratories assess ‘flux residues’ the amount of healing in each stone might vary from minor to significant (Figure 10, Figure 11, and Figure 12). Numerous solid and negative included crystals in all samples appeared partially dissolved and or distorted from the heating (Figure 13, Figure 14, Figure 15, Figure 16, Figure 17, Figure 18, Figure 19, Figure 20 and Figure 21). The specimens were immersed in methylene iodide (RI 1.74) or viewed through a white diffuser plate to look for any color concentrations as are often seen in corundum that has been diffused with Ti or Be, however, most samples did not show, or only showed weakly, the expected surface conformal color concentrations. Some color concentrations were noted relating to healed fissures where they met the facet surfaces as well as related to crystal or negative crystal inclusions where these cut the facet surfaces (Figure 22, Figure 23, Figure 24, Figure 25, Figure 26, Figure 27, Figure 28, and Figure 29). But no color concentrations were noted to be associated with flux assisted healed fissures within the depth of each specimen.

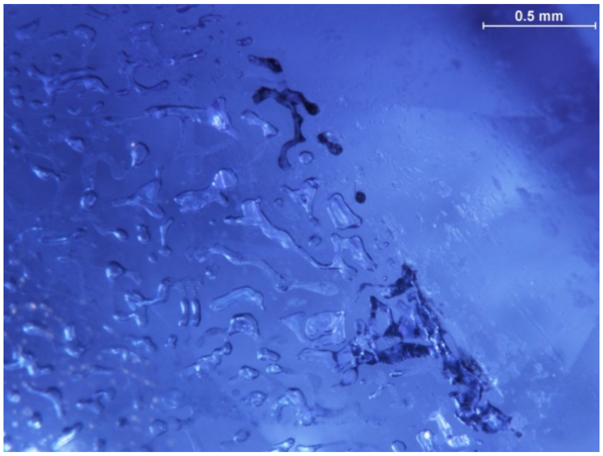


Figure 10: Flux healed fissue seen in sample 103. Photo: C. Khowpong © GIA.

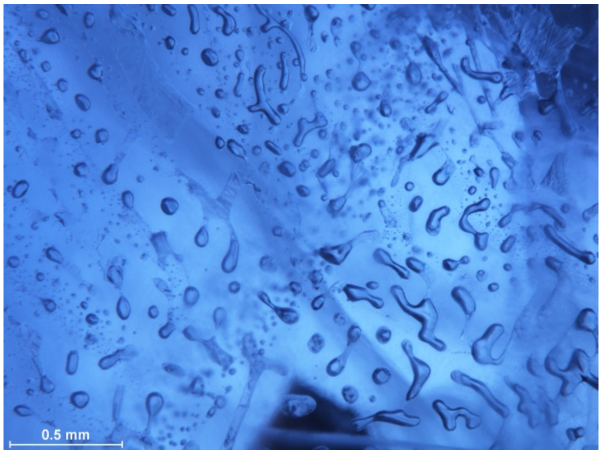


Figure 11: Flux healed fissue seen in sample 103. Photo: C. Khowpong © GIA.

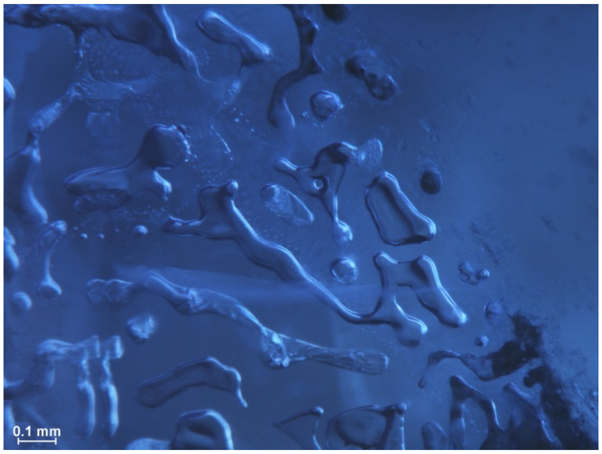


Figure 12: Flux healed fissue seen in sample 103. Photo: C. Khowpong © GIA.

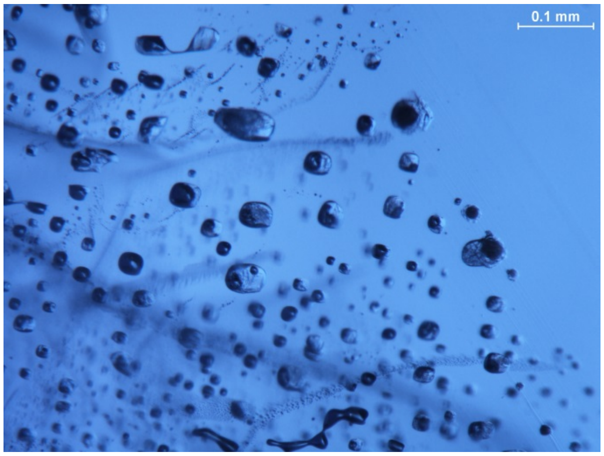


Figure 13: Altered crystals in a feather formation present in sample 103. Photo: C. Khowpong © GIA.

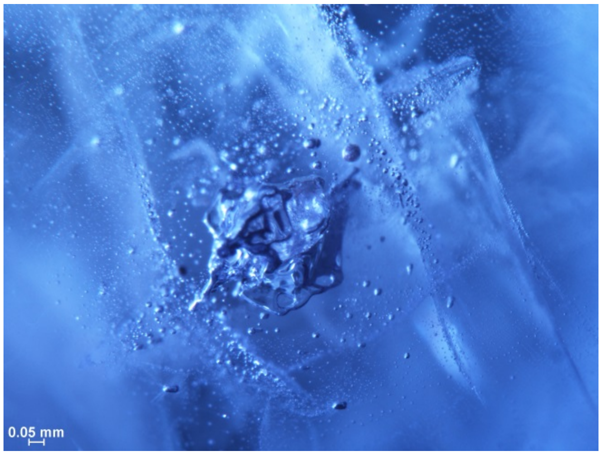


Figure 14: Altered crystal with healed fractures observed in sample 105. Photo: N. Ng-Pooresatien © GIA.

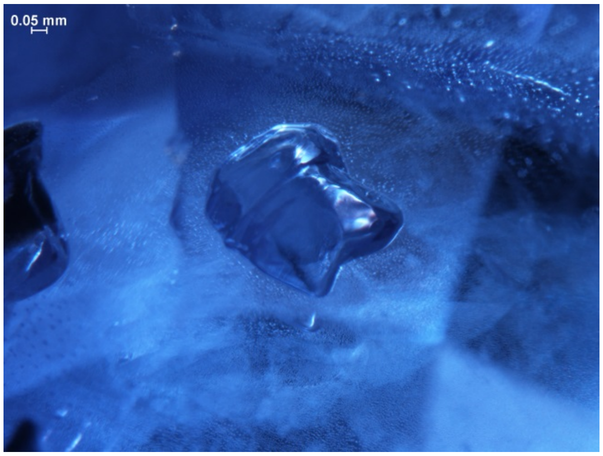


Figure 15: Altered crystal observed in sample 105. Photo: C. Khowpong © GIA.

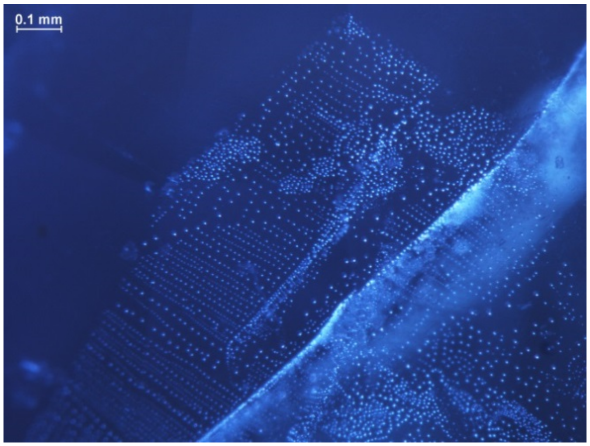


Figure 16: Altered rows of crystals observed in sample 109. Photo: C. Khowpong © GIA.

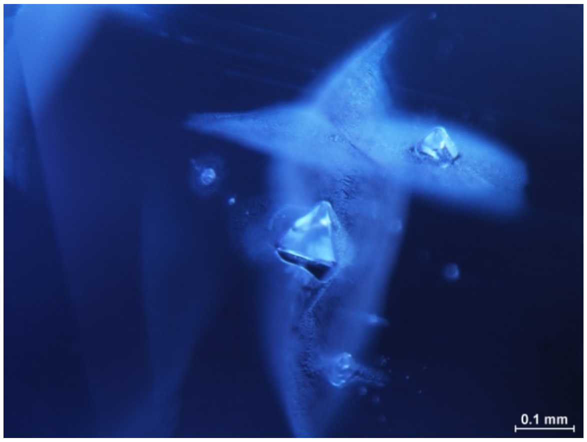


Figure 17: Distorted crystals observed in sample 107. Photo: N. Ng-Pooresatien © GIA.

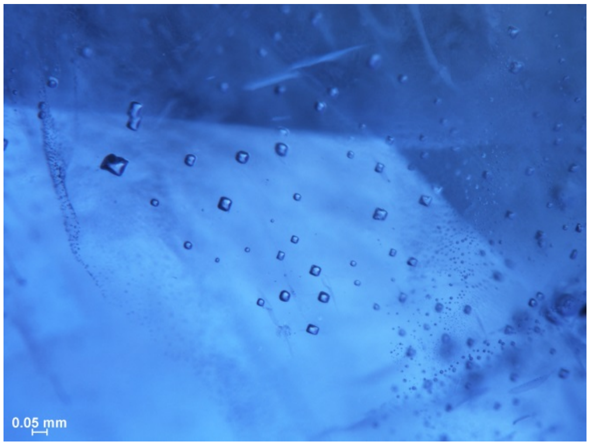


Figure 18: Rows of altered crystals found in sample 104. Photo: C. Khowpong © GIA.

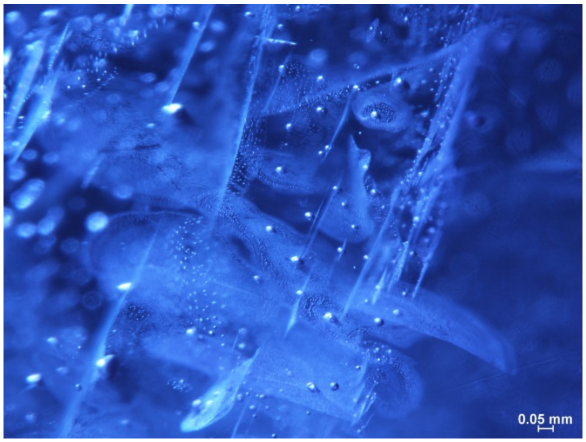


Figure 19: Altered crystals with healed fractures observed in sample 104. Photo: C. Khowpong © GIA.

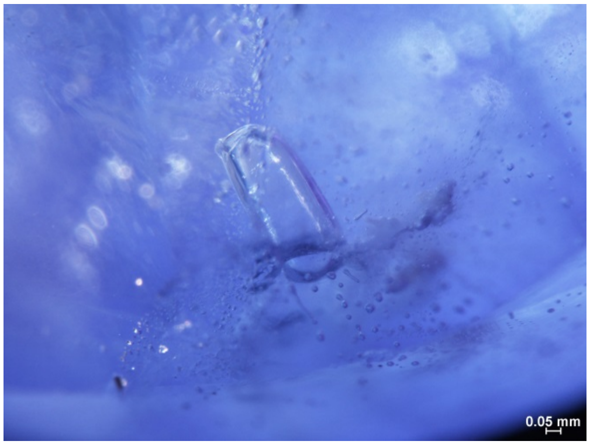


Figure 20: Altered crystal observed in sample 111. Photo: N. Ng-Pooresatien © GIA.

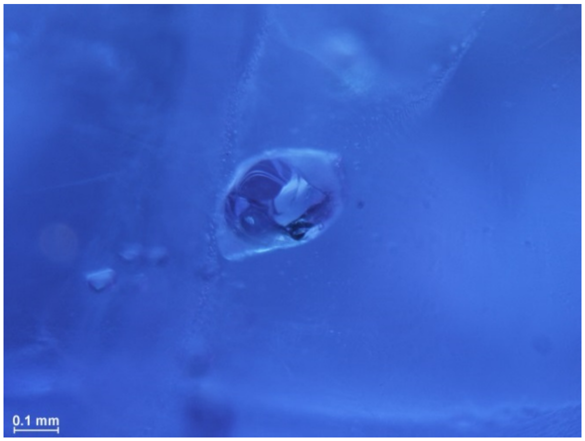


Figure 21: Altered crystal observed in sample 109. Photo: C. Khowpong © GIA.

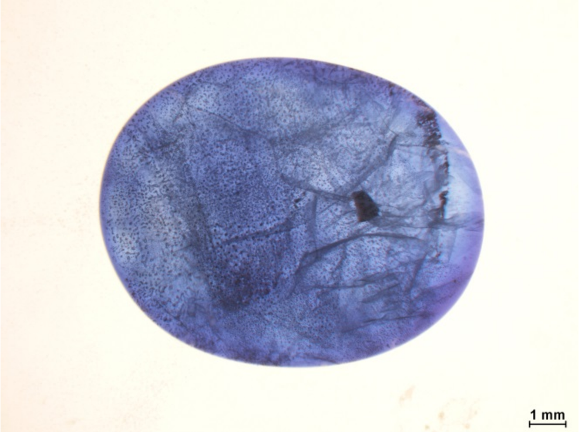


Figure 22: A faceted sample 103 immersed methylene iodide table down. Photo: S. Saeseaw © GIA.

Figure 23: A faceted sample 103 immersed methylene iodide - profile view. Photo: S. Saeseaw © GIA.

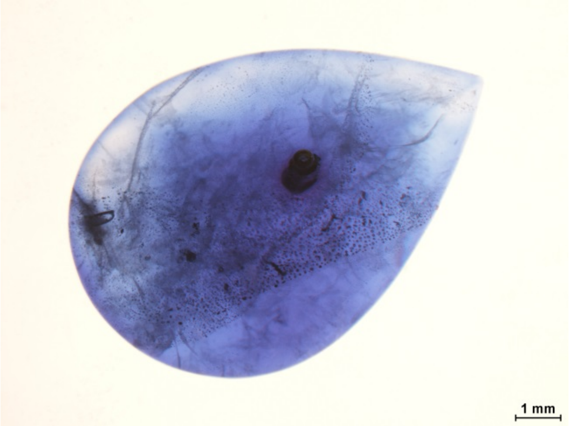


Figure 24: A faceted sample 111 immersed methylene iodide table down. Photo: S. Saeseaw © GIA.

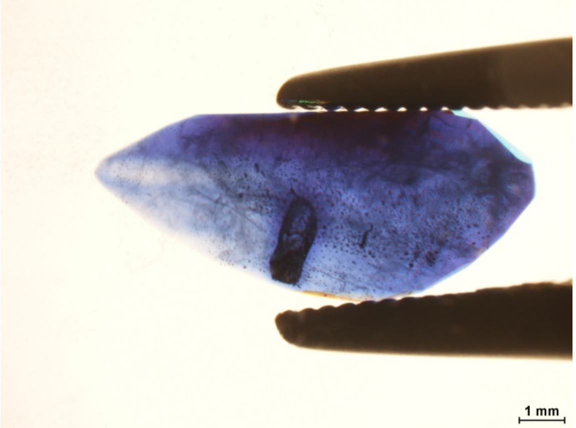


Figure 25: A faceted sample 111 immersed methylene iodide - profile view. Photo: S. Saeseaw © GIA.

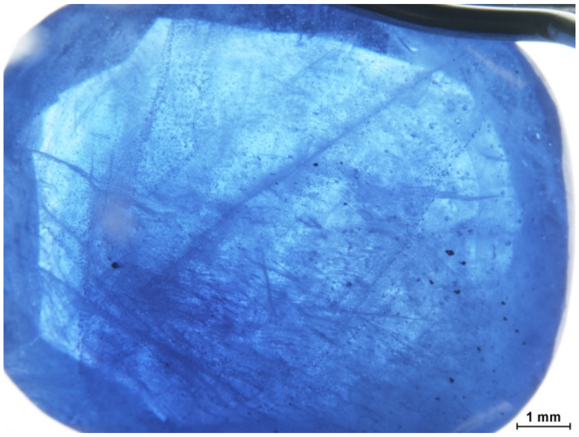


Figure 26: A faceted sample 111 presents color concentrations along fissures using a white diffuser plate. Photo: N. Ng-Pooresatien © GIA.

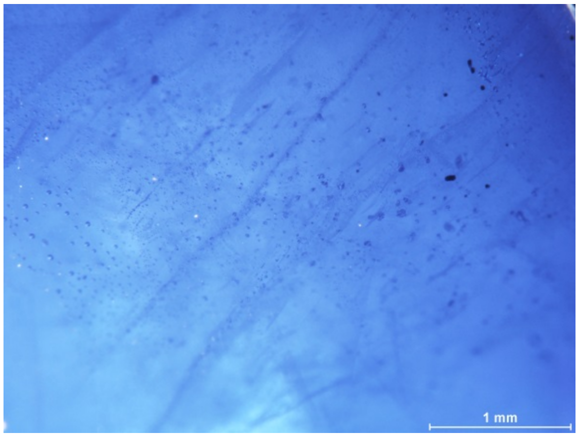


Figure 27: A faceted sample 111 presents color concentrations along fissures using a white diffuser plate. Photo: N. Ng-Pooresatien © GIA.

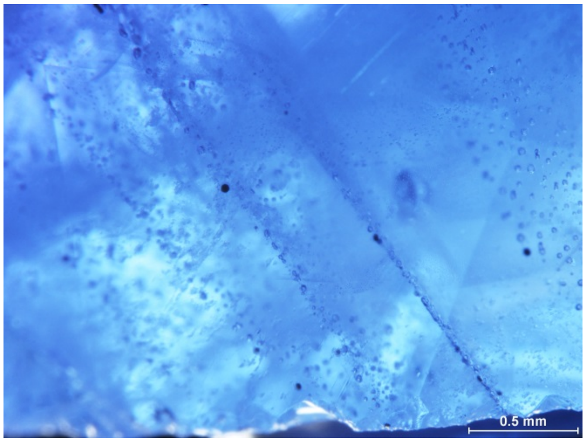


Figure 28: Color concentration along fissures seen in sample 108. Photo: N. Ng-Pooresatien © GIA.

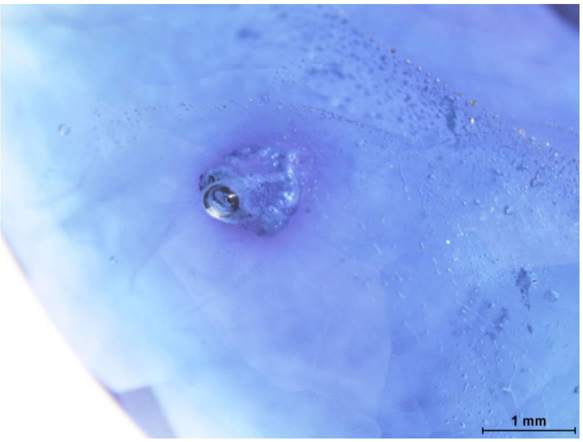


Figure 29: Color concentration examined in sample 111. Photo: N. Ng-Pooresatien © GIA.

EDXRF Analysis

EDXRF analysis was carried out on the majority of the faceted samples used in this investigation. In all instances Al and Mg dominated the resulting spectrum with strong intensities for Fe and Co. Zn and Ga were also revealed to be present indicating a natural (rather than synthetic, (Muhlmeister, Koivula et al. 1993)) origin for the original material (Figure 30). For detailed chemistry see LA-ICP-MS analysis later.

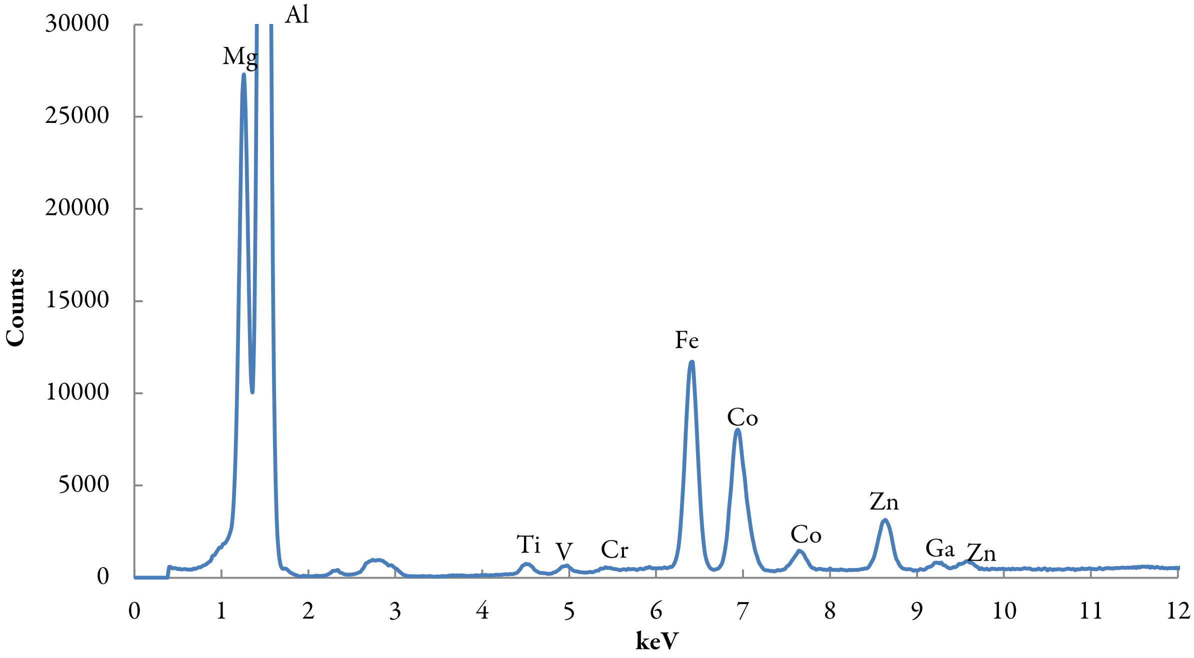


Figure 30: EDXRF spectra on faceted sample #108 taken from the table facet of the stone.

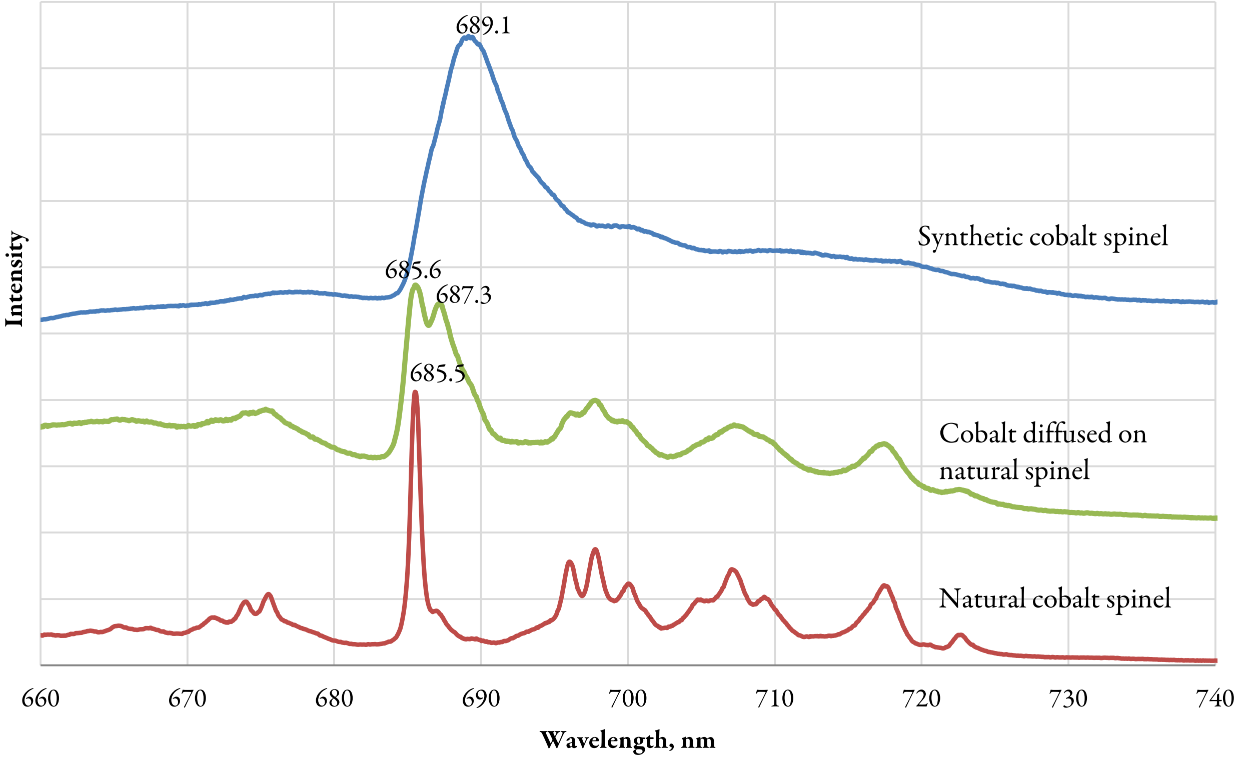


Figure 31: The PL spectra under room temperature for natural cobalt spinel from Luc Yen, Vietnam (red), cobalt diffused on natural spinel (green) and synthetic cobalt spinel from our GIA collection (blue). Spectra have been shifted vertically for clarity.

Photoluminescence Analysis

Photoluminescence (PL) is a high sensitivity technique useful in detecting Cr^{3+} in spinel. Indeed the collection of PL spectra allows for the separation of natural and synthetic spinel (Shen A.H. 2004, Saeseaw 2009). PL spectra in natural spinel showing a sharp peak complex when compared with normal heated or in this case cobalt diffused natural spinel. Synthetic cobalt spinel revealing a distinctly broadened series of peaks when compared with the natural and cobalt diffused material (Figure 31).

LA-ICP-MS Analysis

In order to gain a detailed chemical analysis two specimens were sliced and polished into wafers and LA-ICP-MS employed (Figure 33 and Figure 36). Results revealed high concentration of cobalt (Co) and iron (Fe) at the rim that gradually reduced towards the center. In sample 108 (Figure 32) Co was found to be present up to 1231 ppma and Fe was present up to 1718 ppma. Additionally other elements, namely Li, Ti, Mn and Ga were detected at higher concentrations at the rim in comparison with the center. It is interesting that Zn showed lower concentrations at the rim than at the center. Figure 35 shows the distribution of Co, Fe, Mn, Zn and Ga across the cross section, shown in Figure 33. The detailed chemistry for each spot examined for sample 108 is given in Table 3.

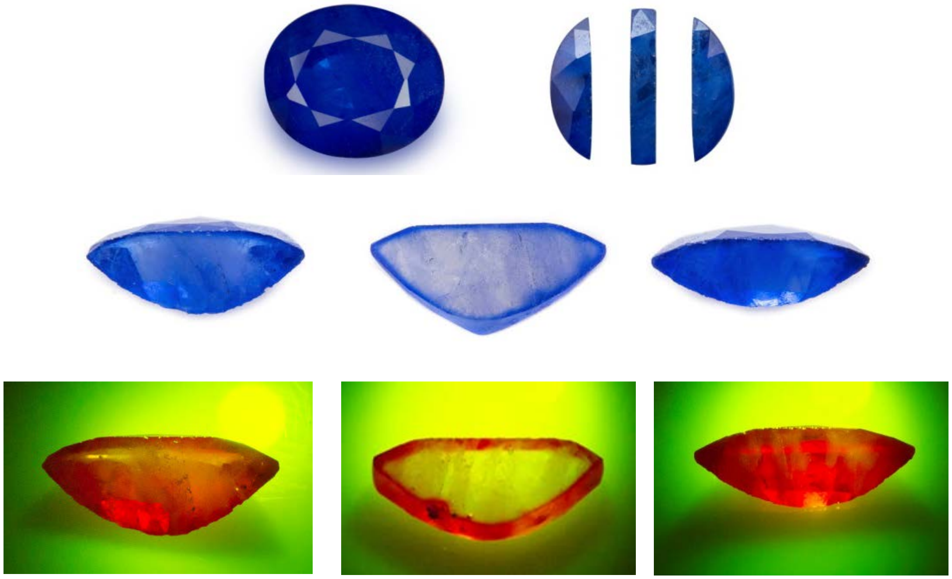


Figure 32: A faceted sample #108 before and after being cut in to wafers. Bottom: Wafers viewed through the Chelsea Color Filter showing the Co rich areas appearing red.

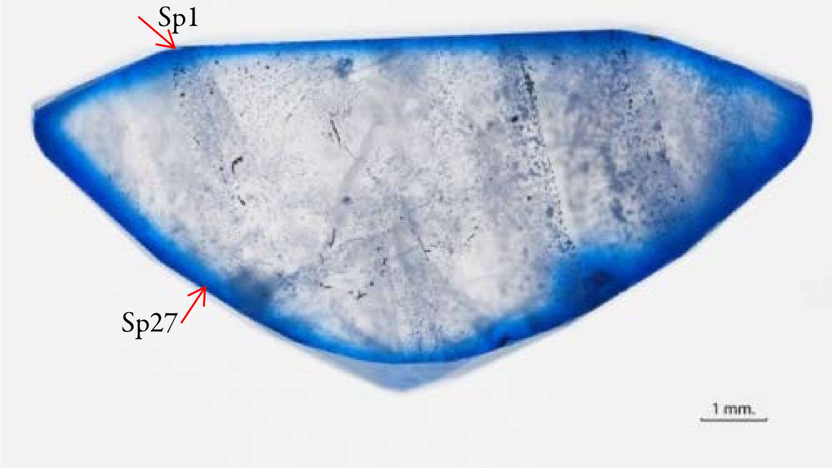


Figure 33: The cross-section of cobalt diffused natural spinel (sample #108) was tested with LA-ICP-MS.

Figure 34: Enlargement from Figure 33 showing position of the ablation spots more clearly

Table 3: LA-ICP-MS results on a cross section of sample #108; ppma is parts per million atomic.

Spot number	**7Li**	**9Be**	**47Ti**	**51V**	**52Cr**	**55Mn**	**56Fe**	**59Co**	**66Zn**	**69Ga**
sp1	137	17	115	70	16	17	1718	1231	224	36
sp2	133	17	79	84	15	11	1186	783	267	28
sp3	125	18	63	97	16	6	859	466	326	25
sp4	112	15	50	96	16	4	630	241	351	24
sp5	98	14	46	99	17	3	550	143	361	23
sp6	79	13	44	98	18	2	517	67	379	24
sp7	77	12	43	102	19	2	495	52	376	23
sp8	71	12	42	105	19	2	477	41	382	23
sp9	66	11	42	101	19	2	484	28	398	23
sp10	64	11	41	104	20	2	480	26	407	24
sp11	69	11	44	118	20	2	466	8	410	24
sp12	62	11	41	114	21	1	491	10	413	23
sp13	59	9	39	106	21	1	488	11	401	24
sp14	59	10	37	104	22	1	466	10	404	25
sp15	60	9	36	111	24	2	499	11	410	24
sp16	64	9	29	110	23	1	480	12	407	24
sp17	65	11	29	108	24	1	473	11	401	24
sp18	73	10	30	111	25	2	484	10	407	25
sp19	81	10	28	112	24	2	499	11	401	26
sp20	85	10	29	109	25	2	484	11	395	25
sp21	94	11	25	111	25	1	491	16	407	25
sp22	97	13	30	113	27	2	509	26	410	26
sp23	102	13	27	111	25	2	528	48	379	25
sp24	107	12	30	110	28	3	586	92	376	26
sp25	107	17	41	111	28	4	677	183	357	26
sp26	110	18	56	108	28	6	768	348	320	27
sp27	110	18	95	101	29	10	997	645	277	31
Detection limit	0.19	0.04	0.38	0.05	0.62	0.09	2.04	0.02	0.13	0.03

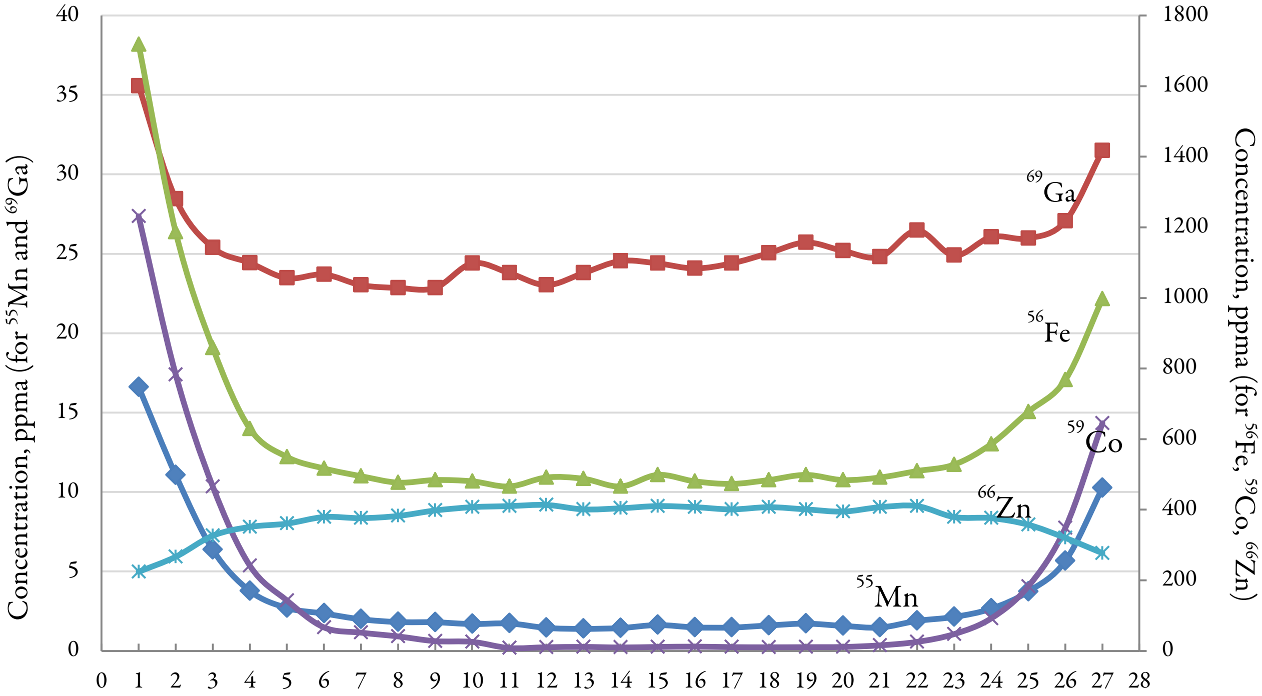


Figure 35: The distribution of Co, Fe, Mn, Ga, and Zn across the cross-section of cobalt diffused natural spinel sample #108.

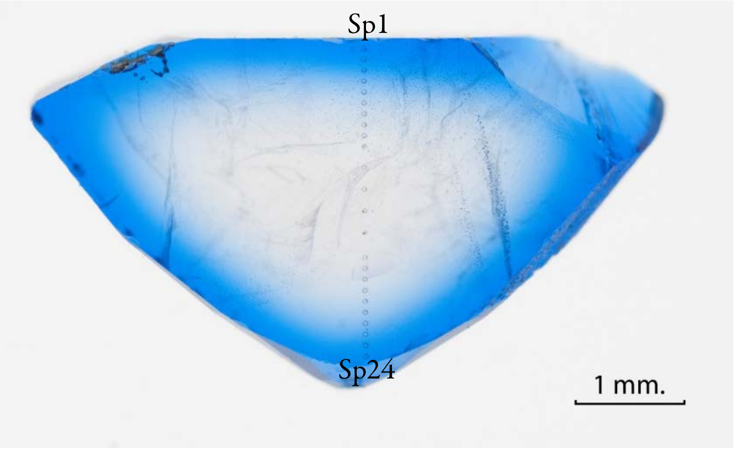


Figure 36: The cross-section of cobalt diffused natural spinel (sample #109) showing the ablation spots from which the chemical data detailed in Table 4 and Figure 37 were obtained.

Sample #109 exhibited deeper Co penetration resulting in a deeper blue penetration of the sample (Figure 36). The distribution of Co showed clearly in the graph (Figure 37) indicating that a longer diffusion period may have been applied. The Co concentration detected was about 466 ppma at the rim and 9 ppma at the center. Fe content was found to be up to 1070 ppma at the rim. The correlation of Co, Fe, Mn, Zn and Ga are presented in Figure 37. In sample #109 the Ga concentrations analyzed across the cross-sections appeared to be the inverse of those analyses in sample 108 in terms of their pattern. These data are yet to be fully understood, however Mr. Thamrong disclosed that the samples in this study were treated at different times and under different conditions.

Table 4: LA-ICP-MS data gained from a cross section of sample #109; ppma is parts per million atomic unit.

Spot number	**7Li**	**9Be**	**47Ti**	**51V**	**52Cr**	**55Mn**	**56Fe**	**59Co**	**66Zn**	**69Ga**
sp1	131	19	43	78	9	11	1070	466	376	59
sp2	164	16	37	98	5	10	972	366	376	67
sp3	179	15	35	118	5	10	881	263	373	76
sp4	189	17	33	124	5	9	782	177	370	79
sp5	188	14	38	137	4	9	786	125	376	86
sp6	174	13	33	144	5	8	724	77	336	83
sp7	163	14	36	132	5	7	702	53	317	84
sp8	146	14	37	140	6	7	728	41	317	87
sp9	130	11	38	136	6	6	710	30	293	85
sp10	121	12	37	153	6	6	761	23	298	89
sp11	83	10	38	138	7	5	670	10	252	88
sp12	67	10	40	144	7	5	684	9	241	87
sp13	61	9	38	147	8	5	677	11	257	87
sp14	65	11	42	148	8	5	688	15	250	85
sp15	80	10	40	161	9	5	702	32	271	83
sp16	98	11	46	169	11	6	782	43	288	89
sp17	111	11	53	178	12	7	786	61	302	89
sp18	118	14	48	174	13	7	782	82	317	86
sp19	125	13	52	193	12	7	786	109	317	84
sp20	129	13	53	176	13	8	844	150	342	80
sp21	133	12	53	175	12	9	881	204	357	77
sp22	138	13	55	168	14	10	917	279	389	77
sp23	124	14	56	146	13	10	1001	345	382	66
sp24	117	17	57	107	14	10	1077	386	367	57
Detection limit	0.19	0.04	0.38	0.05	0.62	0.09	2.04	0.02	0.13	0.03

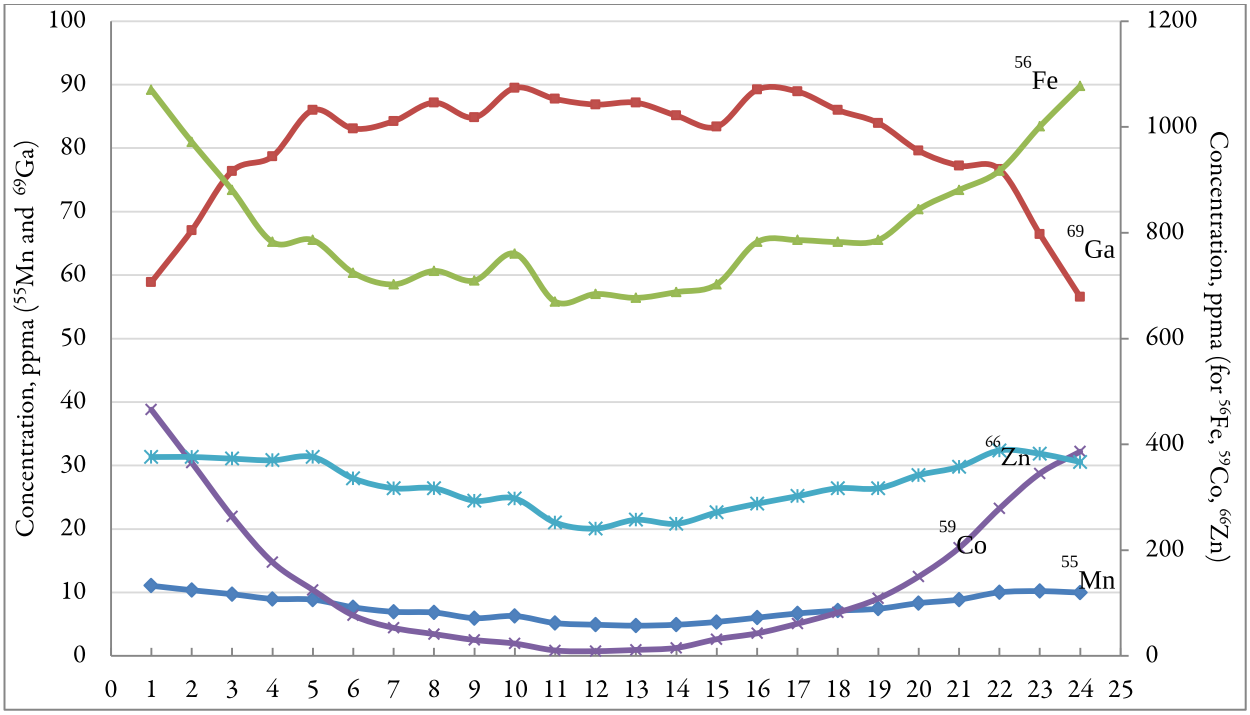


Figure 37: The distribution of Co, Fe, Mn, Ga, and Zn across a cross-section of cobalt diffused natural spinel (sample #109).

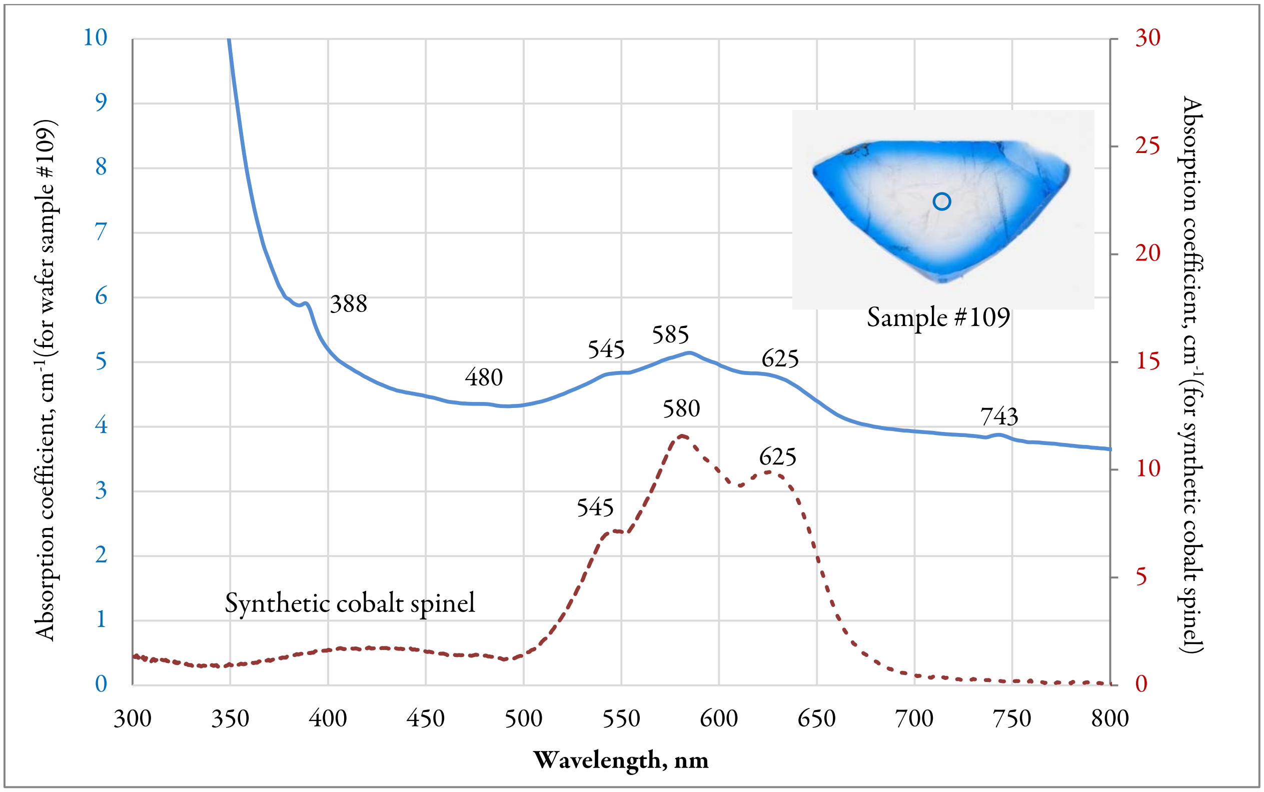


Figure 38: UV-Vis absorption spectra of wafer sample #109 and synthetic cobalt spinel (90 ppma Co and no Fe detected).

UV/visible spectra:

UV-Vis spectra recorded for wafer sample #109, revealed a combination of cobalt and iron features (Figure 38). Much blue spinel color is caused or impacted by a combination of iron and cobalt, and these two elements overlap to each other in UV-Vis spectrum. Figure 38 shows the spectrum of sample # 109 overlaid with that of a synthetic cobalt spinel. While this clearly shows that sample #109 has a cobalt related spectrum, as indicated by the LA-ICP-MS analysis, sample #109 was too heavily included to produce a valid baseline to the spectrum.

Observations:

Cobalt diffusion is a new treatment being applied in spinel which to some extent mimics the fact that some blue spinel naturally owes its color to this important trace element. Cobalt diffusion artificially changes the color appearance of natural spinel that lacks any significant natural color to a deep blue. The identification of cobalt diffused spinel using a microscope, even when immersed on methylene iodide or using a white diffuser plate, may prove inconclusive as unlike titanium or some beryllium diffused sapphires, surface conformal color zoning may not be obvious. It will however be clear that the stones have been subject to a high temperature treatment which is currently unusual for spinel and when this is combined with an EDXRF chemical analysis where unusually high intensities for Co compared with Zn and Ga are present, these two factors should be sufficient to indicate that this treatment had taken place in any given stone.

As much of the inclusion scenes within the spinels used for this treatment process are considerably altered, due the high temperatures employed, it may be challenging in some cases to determine if the starting material is of natural or synthetic origin. However, photoluminescence (PL) spectroscopy may assist in this separation.

From the data it appears, as stated by Mr. Charasaiya, that Fe may play a part in this diffusion process as in both cross-sections examined here the Fe concentrations at the edges were greater than they were in the center of the specimens. However, Mn behaved similarly and more empirical data is needed to understand the nature of this diffusion process.

Acknowledgements:

The authors gratefully acknowledge the assistance given by Mr. Thamrong Charasaiya in providing the samples and background information. Mr. Charasaiya has applied for a patent for his diffusion techniques in Thailand as “The process procedure to improve value and quality of blue and other colors of spinel by diffusion processes”, the application number being 10503000761. His address for correspondence is 38/34 Soi 78 Chokchai 4 road, Ladprao, Bangkok 10230 Thailand or mteeranuth@hotmail.com. The authors also thank the teams in the GIA Laboratory located in Bangkok and Carlsbad for their support.

Bibliography:

Chauviré, B., Rondeau, B. Fritsch, E., Ressigeac, P., Devidal, J-L. (2015). "Blue Spinel from the Luc Yen district of Vietnam." Gems and Gemology **51**(1): 2-16.

D'Ippolito, V., Andreozzi, G.B., Halenius, U., Skogby, H., Hametner, K., Gunther, D. (2015). "Color mechanisms in spinel: cobalt and iron interplay for the blue color " Phys Chem Minerals **42**: 431--439.

Harder, H. (1986). "Natürliche kobaltblaue spinelle von Ratnapura, Sri Lanka." Neues Jahrbuch für Mineralogie Monatshefte(3): 97-100.

Muhlmeister, S., et al. (1993). "Flux-grown synthetic red and blue spinels from Russia." Gems and Gemology **29**(2): 81-98.

Peretti, A., , Günther,.D, Haris MTM (2012 (updated 2015)). "New type of treatment of spinel discovered involving heat-treatment and cobalt-diffusion (updated 22 may 2015)." Contributions to Gemology.

Saeseaw, S. W., W., Scarratt, K. Emmett, J., Douthit, T. (2009) Distinguishing heated from unheated natural spinels - A short review.

Shen A.H., D., . D. (2004). "Natural spinel identified with Photoluminescence." Gems and Gemology **40**(2): 168-169.