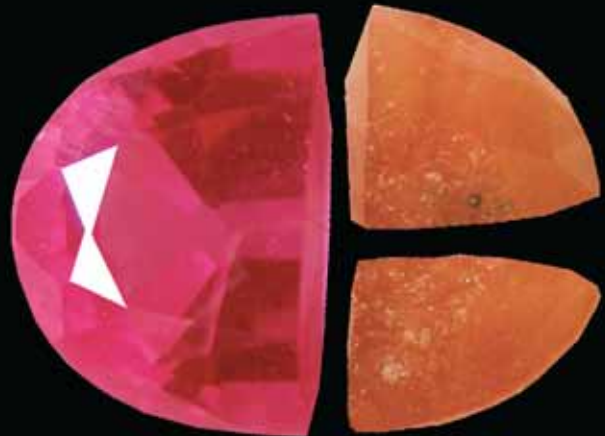
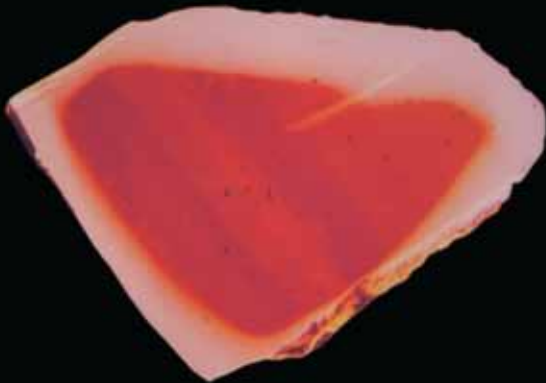
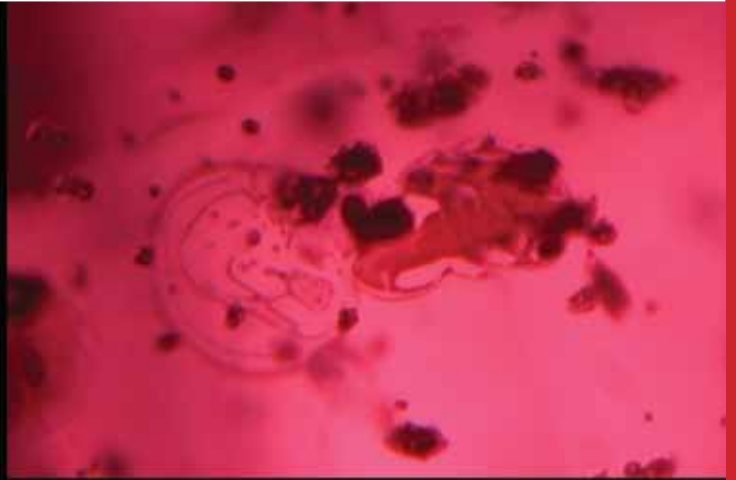
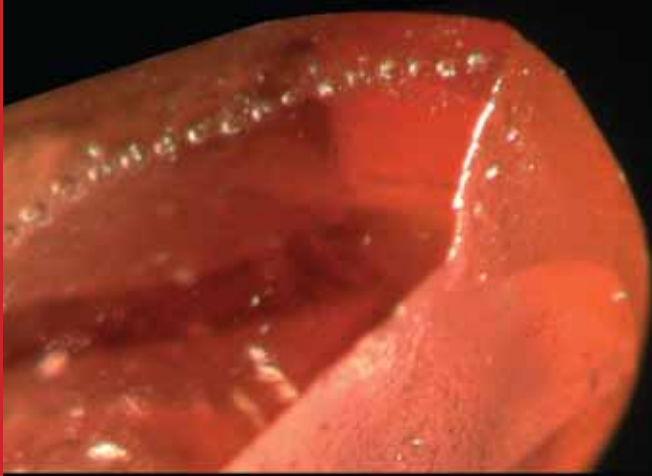


Contributions to Gemology

No.4 December 2005

BERYLLIUM-TREATMENT



GRS

**GEMRESEARCH
SWISSLAB**



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Forward

GRS is honoured and proud to welcome you to our Fourth Issue of Contributions to Gemology. We have named this the "Summary Edition" which compiles almost 5 years of research on the topic of Beryllium-Treatment of Corundum. This continues our tradition on working and striving to share knowledge, research and detailed information concerning the exciting field of modern gemology. In this Summary Edition, we have compiled our previously published research which also includes the results from the co-operation with world-recognized Universities and internationally respected Research Institutes.

GRS strives to continue its in depth research utilizing sophisticated scientific methods. We have invested significant resources in research and development. This includes for example the invention of a new type of Laser Induced Plasma Spectrometer (LIPS) using a UV Laser. This technology is the answer to a non-destructive test to detect Beryllium-Treated corundum. Its calibration is based upon solid scientific research using sophisticated instruments which produced a masterpiece set of unique standards. The collection of this data and standards are summarized in this 4th Issue of Contribution to Gemology. We are convinced that this Edition is a landmark in the world of research on Beryllium-Treated corundum. We, at GRS, believe that international acceptance can be achieved through information and knowledge that is shared with the world.

Thank you and please enjoy our topic-related "Summary Edition" of GRS's Contribution to Gemology.




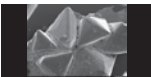



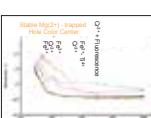








December 2005, Lucerne, Switzerland



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The Beryllium-Treatment of Natural Fancy Sapphires with a New Heat-Treatment Technique Part A

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*(Reprinted with corrections from
Contributions to Gemology, No.1, 2002)*

INTRODUCTION

Sapphires and rubies of different colors are routinely heat-treated to produce products of better clarity and color. As long as the treatment does not involve diffusion of color influencing trace elements - such as Ti, Fe and Cr - into the gemstones surface or irradiation, the trade generally accepts the enhanced gem materials as being highly valuable, depending on size, rarity and beauty. In mid 2001, sapphires and rubies treated with a new method appeared on the market with dominantly orange-pink colors, which are commonly known in the trade as the "Padparadscha" colors .

Natural Padparadschas are among the world's most requested, and rarest, gemstones, and therefore highly-priced. Depending on the exact nature of this new enhancement process, and hence the wording used to disclose and supply these sapphires to the market, the price of these materials may vary considerably. Early Internet published reports initiated a worldwide controversy on the nature of the treatment, ranging from pure heat treatment to a full blown diffusion treatment. The uncertainty about the exact nature of the treatment method, and therefore the lack of investor confidence, caused the worldwide market for the new sapphire materials to collapse (February - March 2002). Of particular interest to the trade is the question: "Are these new materials diffusion-treated?"

This is based on earlier reports of the presence of *Beryllium* in these sapphires, and the occasional presence of color zoning confined to the sapphires' facets (See Internet References found in Lit. 01). A key factor to understand the color giving mechanism is the use of special analytical methods, such as UV-VIS-NIR (origin of color analyses), ED-XRF (e.g. Iron (Fe), Chromium (Cr) and Titanium (Ti) trace element analyses), SEM-EDS (chemical analyses of contaminated substances at the gemstones' surface), visual and spectroscopic cathodoluminescence investigations (analyses of internal growth structures), color-stability measurements (long-term color-stability to UV and visible light), and, most importantly, Laser

Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). The LA-ICP-MS method - used to characterize the content and variation of all trace elements, including light elements such as Lithium (Li), Boron (B) and *Beryllium* (Be) on a micro scale - turned out to be the key factor in understanding the new heat treatment technique .

This report contributes to the understanding of the new heat treatment with Beryllium and to differentiate from conventional heat-enhancement (E) and conventional surface diffusion treatment (T).

MATERIALS

The majority of the tested material included natural fancy sapphires from Tanzania and Madagascar (both enhanced and unenhanced), as well as other comparison materials (described below). The entire collection of materials (320 reference samples) is the property of one of the authors' companies (GRS Gemresearch Swisslab AG (Switzerland) and GRS (Thailand) Co. LTD, and is stored in the companies' reference collections.

The sapphire material can be divided into the following groups:

- a.) Unheated (N).
- b.) Conventional heat-treated (E).
- c.) Conventional diffusion-treated (T).
- d.) Synthetic (Syn) and Irradiated (IR).
- e.) Beryllium-Treatment, short noted as H(Be).(*)
- f.) Beryllium-Treatment, Chantaburi Dec 2001, Table A6, Part A. H(Be)
- g.) With conventional heat treatment and the additional new heat treatment method, Chantaburi Dec 2001 to Jan 2002, Table A6, Part A. Tested before and after Beryllium-Treatment.
- h.) Unheated and conventional heat-treated gemstones, with additional Beryllium-Treatment, Bangkok, Feb 2002, Table A6, Part B. Samples tested before and after treatment with Beryllium.

Details

- a.) GRS acquired 120 rough (pre-polished) fancy sapphires (unheated) of different colors (including "Padparadscha" sapphires) between 1999 and 2002 from K.V. Gems Co., Ltd. (Bangkok), AJS GEMS LTD. (Bangkok), GMR (Gem Mining Resources, Madagascar), and from Bangkok and Chantaburi open markets in Thailand. The material from Madagascar revealed inclusions typical of the Illakaka mining area (clusters of small zircons). This study also includes untreated Songea sapphires from the GRS collection (acquired in 1996)
- b.) For the purpose of comparison with heat-treated natural sapphires from previous years, 30 further heat-treated yellow sapphire samples - as well as "Padparadscha" colors - were investigated.
- c.) For further comparison with diffusion-treated



Fig. A1 GRS Color Names for Selected Natural Colored Sapphires and Rubies

samples, eight diffusion-treated blue sapphires were available, including three samples acquired in 1996 (in Tucson, USA) and five samples acquired in 2002 in Bangkok. These samples from Bangkok were sold as surface diffusion-treated (the element used for diffusion was declared as titanium, and the diffused basic corundum was declared as originally being a natural white sapphire).

d.) More than 50 synthetic corundum samples and 15 irradiated synthetic samples were available for comparison.

e.) Commercially representative products of this new treatment included faceted natural orangy-pink and orange and yellow sapphires (origin Madagascar). They were obtained from three different companies: In November 2001 from K.V. Gems Co. LTD (Thailand), and in December 2001 from 2 other companies in Bangkok. This study also includes samples of African origin (Tanzania), samples obtained in February 2002, and 12 faceted orange-red to vivid orangy-red sapphires, produced by the new treatment in Chantaburi in December 2001.

f.) Further samples of this new treatment were selected from a large lot of sapphires - investigated in Chantaburi on 14th December 2001 - which were heated with the new method, but not repolished. This lot arrived directly at the heat treatment laboratory in Chantaburi after treatment (Fig. A2 and A3). The samples for this report were color sorted, then master sets of different colors were made, including white, blue, yellow, orange and orange-pink ("Padparadscha") colors produced by the new

method. Outside of the dominantly produced typical orange colors in this lot, 12 white and four natural blue sapphires were also sorted. Some of this lot's sapphires were clustered together (due to the melting of non-sapphire materials in the treatment process (Fig. A3)). Three of these clusters were selected for this study from the same lots. Three "Padparadscha" samples from these lots have been re-cut, with 10%, 20% and 50% weight loss respectively.

g.) Typical samples suitable for the new heat treatment include faceted natural purplish-pink sapphires (heart and triangular shape) between 0.3 to 1ct, which were studied in November 2001 and subsequently heat-treated with the new method in commercial runs together with other dealers' samples in Chantaburi (the heat treating laboratory was not aware of GRS making test runs). 15 pieces from this lot were treated in Chantaburi between November and December 2001. The samples were studied before and after treatment.

h.) 15 natural pink sapphire pieces, as well as unheated violet, purple and "padparadscha" sapphires, were treated at a factory in Bangkok in February 2002 through a Thai Gems Jewelry and Trader Association (TGJTA) initiative (Further details see Table A6). The heat treating laboratory was aware of GRS making tests. The material was studied before and after treatment. Treatment details were not disclosed and the treatment laboratory not shown.

(*) "H(Be)" is a trademark of GRS Gemresearch Swissslab AG (Switzerland)

Gemological Testing

During routine gemological testing, samples were checked for fluorescence and subjected to a color-stability test procedure. The samples included sapphires of different colors, origin and treatment (N, E, T, H(Be) and synthetic samples)(See Table A1). Of particular interest are the samples for which the trace element concentration, *Beryllium* in particular, has been analyzed (See Table A6). The samples were first graded for color and saturation according to the GRS Master, and then half-covered with Aluminium Foil. They were then exposed to UV light (Eickhorst lamp, Type Multispec UV-AC) for two days at a distance of 1cm. Two wavelengths were used: 366 and 254nm. After both the covered and uncovered parts were subjected to UV radiation, the samples were subjected to a 100 Watt halogen lamp for two days and, in a repeating experiment, warmed for 30 seconds in a gas flame.

Results UV Fluorescence

Exposed to UV light, the H(Be)-samples showed a particular reaction (Fig. A6) The H(Be)-samples from Madagascar exhibited intense yellowish-orange fluorescence in long wavelength UV (Fig. A6a.) and medium yellowish-orange fluorescence in short wavelength UV. This reaction was not found in the other tested groups (N, E, T and synthetic). This particular reaction to UV light was observed in all samples of the H(Be)-groups, and absent in the reference samples (E,N). Another group of samples thoroughly examined for *Beryllium* (Sample 1999, Table A6), revealed a very particular reaction to UV light – an intense outer rim with whitish-blue (milky) fluorescence was present. This phenomenon was not observed in the unheated half piece from the same sample.



Fig. A2 Dr. A. Peretti selects samples (Chantaburi, 14th December, 2001) heated-treated with *Beryllium*, sorts the different colors of produced sapphires and non-sapphire crystals (as shown in Fig. A8) and then carries out gemological tests (using a portable microscope, portable fiber-optic light source of 100 watt power, Geiger counter, Dichroscope, Polariscope, Refractometer and UV-lamp). Later, in Bangkok, he continues the tests using a vertical trinocular microscope (65x magnification) and a horizontal microscope from Eickhorst with an immersion unit (GEMMASTER SUPERSCOPE).





Fig. A3 Different colors produced by the new treatment (including pink, yellow, orange, and blue) are sorted for this report. Sapphires of different colors are accidentally clustered together by the melting of minerals other than sapphire during heat treatment with Beryllium. Only a small portion of the sapphires showed this accidental cluster. Note: Different colors are produced in the same heating runs.



Sample No.GRS 12925

Sample No.GRS 12922 white

Fig. A4 Natural blue and white Beryllium-Treated sapphires exposed to UV radiation. One half of the piece was kept for reference (left side). Both the blue and white sample developed yellow and orange rims respectively. These rims were found to be the zone of Be-enrichment by LA-ICP-MS (See Fig. A34 and Fig. A45). The color is found to be unstable. The orange rims are fading after mild exposure to heat.

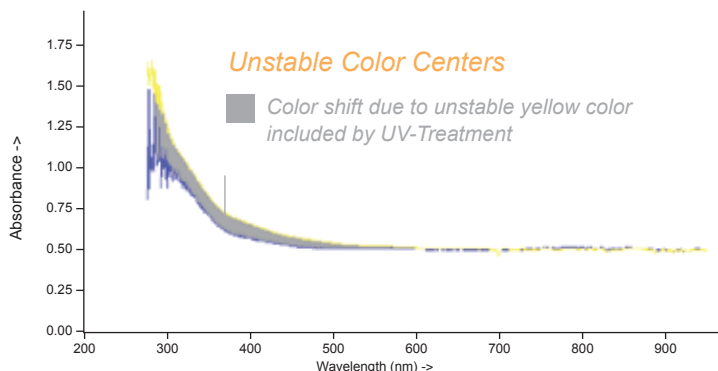


Fig. A5 Polarized UV-VIS-NIR absorption spectra of Beryllium-Treated yellow sapphire before and after treatment with UV light. Yellow curve: Spectrum after exposure to UV. Black curve: After fading of yellow sapphire to white color. Note: Shift of the absorption spectrum towards higher absorptions in the blue causes the yellow color in the sapphires due to the presence of color centers.

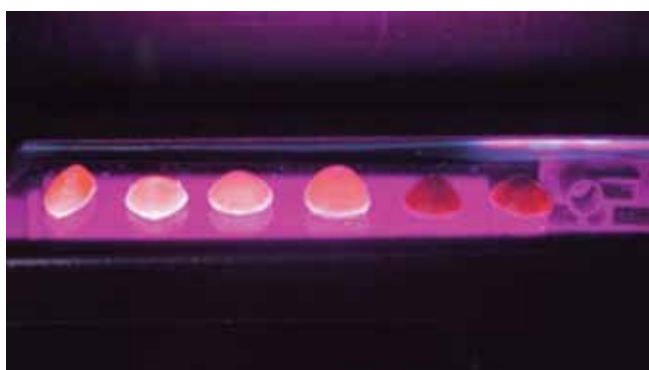


Fig. A6a Fluorescence experiment with Eickhorst UV Lab lamp (long wave 366nm) on faceted sapphires, which had previously been subjected to Beryllium-Treatment. Left: Orangi-pink sapphires (origin: Madagascar) showing intense orangey fluorecence with more yellowish fluorecence at rim. At right: two samples (origin: Songea) with medium orange-red fluorescence (Faceted gemstones between 2 and 5 cts in size). Note: Yellowish fluorescence is confined to the rim of a Beryllium-Treated orangi-pink sapphire (Fig. A6b)

Table A1: UV- Treatment Protocol.

GRS Groups: N = Unheated, E= Conventional Heat Treatment, H(Be) = Beryllium-Treated
T = Conventional Surface Diffusion-Treated, Synthetic

GRS No.	Weight	UV Experiments for color change		Color Change YES/NO	Enhancement Group	Origin Madagascar
		before UV Treatment	after UV Treatment			
12573	0.094	pink	pink	NO	E	Madagascar
12573	0.067	pastel orange	orange	YES	H(Be)	Madagascar
*	0.262	pink	pink	NO	E	Madagascar
*	0.324	orangy-pink	pinkish-orange	YES	H(Be)	Madagascar
12574	0.053	pastel pink	pastel pink	NO	E	Madagascar
12574	0.096	pinkish-orange	orange	YES	H(Be)	Madagascar
12582	0.068	pastel pink	pastel pink	NO	E	Madagascar
12582	0.057	pastel orange	orange	YES	H(Be)	Madagascar
12591	0.044	pastel pink	pastel pink	NO	E	Madagascar
12591	0.091	pastel orange	orange	YES	H(Be)	Madagascar
12580	0.037	pastel pink	pastel pink	NO	E	Madagascar
12580	0.067	sl. pinkish-orange	pastel orange	YES	H(Be)	Madagascar
12575	0.037	pastel pink	pastel pink	NO	E	Madagascar
12575	0.065	pastel orange	orange	YES	H(Be)	Madagascar
12737	0.525	brownish-orangy-pink	brownish-orangy-pink	NO	N	Madagascar
12737	0.195	pastel orange	orange	YES	H(Be)	Madagascar
12702		purple	purple	NO	N	Madagascar
12702	0.228	pastel orange	orange	YES	H(Be)	Madagascar
1999	0.257	purple	lilac	(YES)	N	Madagascar
1999	0.324	brownish-orangy-pink	pinkish-orange	YES	H(Be)	Madagascar
GRS 37	0.065	pastel orange	pastel orange	NO	H(Be)	Madagascar
12567	0.172	pastel orange	orange	YES	H(Be)	Madagascar
12592	0.075	orange	orange	NO	H(Be)	Madagascar
12570	0.166	orange	intense orange	YES	H(Be)	Madagascar
12611	0.328	golden orange	vivid orange	YES	H(Be)	Madagascar
12634	0.458	lime yellow	lime yellow	NO	E	Sri Lanka
12634	0.516	lime yellow	lime yellow	NO	E	Sri Lanka
12642	0.349	golden yellow	golden yellow	NO	E	Sri Lanka
12645	0.687	golden yellow	golden yellow	NO	E	Sri Lanka
12745	0.108	orange	orange	NO	E	Sri Lanka
GRS 20	1.355	modified orange	modified orange	NO	E	Sri Lanka
12740	0.177	sl.orangy-pink	orange	YES	E	Sri Lanka
12561	0.184	pink	pink	NO	E	Madagascar
12569	0.166	pink	pink	NO	E	Madagascar
12588	0.195	pink	pink	NO	E	Madagascar
12593	0.168	pink	pink	NO	E	Madagascar
12563	0.155	pink	pink	NO	E	Madagascar
12584	0.135	pink	pink	NO	E	Madagascar
12559	0.173	pink	pink	NO	E	Madagascar
12583	0.165	pink	pink	NO	E	Madagascar
GRS 11	18.441	colorless	colorless	NO	Synthetic	
GRS 10	8.988	orange	orange	NO	Synthetic	
GRS 14	5.874	pastel pink	pastel pink	NO	Synthetic	
GRS 14b	5.843	pastel pink	pastel pink	NO	Synthetic	
GRS 13	11.640	pink	Sl.orangy-pink	YES	Synthetic	
GRS 12	6.470	yellow	yellow	NO	Synthetic	
GRS 19a	0.297	blue	blue	NO	T (surface diffusion)	
GRS 19b	0.164	blue	blue	NO	T (surface diffusion)	

Table A1 (Continued)

GRS No.	Weight	UV Experiments for color change		Color Change YES/NO	Enhancement Group	Origin
		before UV Treatment	after UV Treatment			
12922	0.113	colorless	pastel yellow	YES	H(Be)	Madagascar
12922	0.084	colorless	pastel yellow	YES	H(Be)	Madagascar
12922	0.222	colorless	pastel yellow	YES	H(Be)	Madagascar
12922	0.091	colorless	pastel yellow	YES	H(Be)	Madagascar
12922	0.109	colorless	pastel yellow	YES	H(Be)	Madagascar
12922	0.173	colorless	pastel yellow	YES	H(Be)	Madagascar
12922	0.165	l.pastel pink	brownish-yellow	YES	H(Be)	Madagascar
12598	0.281	light orangy-pink	orange	YES	H(Be)	Madagascar
12598	0.298	light orangy-pink	orange	YES	H(Be)	Madagascar
12914	0.350	light orangy-pink	orange	YES	H(Be)	Madagascar
12540	0.098	lime yellow	vivid yellow	YES	H(Be)	Madagascar
12540	0.159	lime yellow	vivid yellow	YES	H(Be)	Madagascar
12536	0.276	orange yellow	golden orange	YES	H(Be)	Madagascar
12589	0.156	sl.pinkish- orange	orange	YES	H(Be)	Madagascar
12912	0.415	sl.pinkish- orange	orange	YES	H(Be), recut	Madagascar
12599	0.260	pinkish- orange	orange	YES	H(Be)	Madagascar
12599	0.241	pinkish- orange	orange	YES	H(Be)	Madagascar
12913	0.239	pinkish- orange	orange	YES	H(Be)	Madagascar
12568	0.178	orange	orange	NO	H(Be)	Madagascar
12578	0.174	orange	orange	NO	H(Be)	Madagascar
12586	0.184	orange	orange	NO	H(Be)	Madagascar
12922	0.292	pastel orangy-pink	orangy-pink	YES	H(Be)	Madagascar
12913	0.237	orangy-pink	orangy-pink	YES	H(Be), recut	Madagascar
12922	0.241	v.l.pastel purple	brownish-yellow	YES	H(Be)	Madagascar
12922	0.179	pastel purple	pastel violet with pastel brown	YES	H(Be)	Madagascar
12922	0.057	violet	violet with orange edge	YES	H(Be)	Madagascar
12925	0.208	blue	blue with orange edge	YES	H(Be)	Madagascar
12925	0.184	blue	blue with orange edge	YES	H(Be)	Madagascar
GRS 15	0.142	pastel pink	pink with orange rim	YES	H(Be)	Songea, Tanzania
GRS 15b	0.092	pastel pink	pink	YES	H(Be)	Songea, Tanzania
GRS 16	0.147	colorless	pastel orangy-pink with orange	YES	H(Be)	Songea, Tanzania
GRS 16b	0.093	colorless	pastel orangy-pink with orange	YES	H(Be)	Songea, Tanzania
GRS 21	0.337	medium orange	orange	YES	H(Be)	Songea, Tanzania
GRS 22	0.390	medium orange	orange	YES	H(Be)	Songea, Tanzania
12614	1.517	white	light yellow with yellow rim	YES	N	Sri Lanka
12614b	1.231	white	light yellow with yellow rim	YES	N	Sri Lanka
12626	1.219	colorless	yellow	NO	N	Burma
12627	1.152	colorless	yellow	YES	N	Burma
12613	4.930	v.light yellow	light yellow	YES	N	Sri Lanka
12620	0.758	v.light yellow	V.light yellow	NO	N	Burma
12622	0.816	v.light yellow	V.light yellow	NO	N	Burma
12625	1.226	v.light yellow	V.light yellow	NO	N	Sri Lanka
GRS 43	2.078	v.light yellow	yellow	YES	N	Sri Lanka
12624	0.910	light yellow	light yellow	NO	N	Burma
12629	4.099	yellow	yellow	NO	N	Sri Lanka
12619	1.246	light lime yellow	yellow	YES	N	Sri Lanka
12606	1.379	pink	pink	NO	N	Burma
12607	0.606	pink	pink	NO	N	Burma
12609	0.749	pink	pink	NO	N	Burma
GRS 34	2.113	pink	pink	NO	N	Madagascar
2132	0.926	purple	lilac	YES	N	Madagascar

Results Long Term UV Exposure

Of particular interest to this study, however, is the reaction of the stones after long-term exposure to intense UV light. The Beryllium-Treated samples from Madagascar reacted differently to all other samples, excluding unheated ones (See Table A1). Significant changes in the color were seen in samples heated with Beryllium, and a shift towards more yellow or orange was observed (as shown in the Table A1). A color change from near colorless to yellow was also observed in untreated sapphires of Sri Lankan origin (Table A1). This unheated group of sapphires is known to contain specific color centers (Lit. 16). In Beryllium-Treated gemstones with an orange body color before the UV experiments, the color shift is more difficult to see. The color change towards more yellow or orange could be reversed when exposed to a gas flame for a short time, and within two days when exposed to a 100 watt halogen lamp at slightly elevated temperatures. A set of white sapphires, which did not change color during the Beryllium-treatment process developed a thin layer of yellow color during the long term UV exposure (shown in Fig. A4). This observation was also made on Beryllium-Treated blue sapphires (Fig. A4) which have been exposed to UV. The blue samples developed orange edges, while the body color of the sapphires remained unchanged. The color induced by UV treatment could be reversed by short application of heat to all the samples, beside one exception.

Scanning Electron Microscope Analysis (SEM)

Sampling of colored sapphires heated by the new treatment in Chantaburi included the study of faceted Beryllium-Treated gemstones (Materials group f.). These gemstones were already faceted in briolette and princess-cut style sapphires prior to heat treatment. By sorting the lots after heat treatment, a set of non-sapphire materials were detected (Fig. A8). The colored samples showed a thin film of interference color at the surface, and were indented by craters due to contact with other minerals in the same heating process. These craters were also found indented on the surface of the sapphires (Fig. A13). The materials were identified as consistent with glass-aggregates, zircon and chrysoberyl (Table A2).

Furthermore, clusters of sapphires, sintered together by a whitish matrix, were detected. Only an extremely small portion of the gemstones showed this phenomena and it was clear that these were accidental circumstances.

In order to analyze the surfaces of these materials, and to search for potential trace elements used in the process, the materials were studied with a Scanning Electron Microscope (Philips XL 30 ESEM) in

February 2002 at the University of Basel's Central Laboratory for Microscopy (ZMB) by Chief Technician M. Duggelin and D. Mathys. Five samples were selected (including minerals with an interference film (zircon and chrysoberyl), and sapphire clusters.

Results SEM

Analyses of zircon and chrysoberyl did not reveal any further information on chemicals present, other than expected from their chemical compositions and attention was placed on the sapphire clusters and the white matrix around the sapphire materials. Cracks and intended craters were investigated, and a series of newly formed crystallizes were detected in these cracks (Fig. A15-A17), mostly composed of Zr-oxide, plus additional element Silicon (Si), Aluminium (Al), Magnesium (Mg), Calcium (Ca) and Fluorine (F). *Beryllium* can not be measured with SEM, and no indications for Chromium (Cr), Titanium (Ti), or Iron (Fe), were found on the surfaces of the enhanced gemstones. Most of the detected elements can be explained as originating from decomposed minerals present in the runs (Silicon (Si) and Zirconium (Zr) from zircon, Aluminium (Al) from corundum, or chrysoberyl), yet the source of Fluorine (F) is unclear. Melting on the surface of these minerals is very visible, as different craters are present on the surface of the former faceted materials (Fig. A8) and also by the craters produced at the surface of the sapphires (Fig. A13, A14). They were formed when they came into contact with other chemical compositions present in other minerals - of the same shape, cutting style and size - in the heating run. Chrysoberyl is a potential source for *Beryllium*. Its role in the heat treatment process has been confirmed (See later publications Lit. 23-33).

Weight	Color	Density	DR	RI	ID
1.153	pastel yellowish-green	3.70	yes	1.743-1.750	chrysoberyl
1.223	pastel yellowish-green	3.70	yes	1.745-1.751	chrysoberyl
0.665	almost colorless	4.66	yes	OTL	zircon
0.716	almost colorless	4.66	yes	OTL	zircon
0.316	colorless	2.78	intr.	not readable	glass
0.366	colorless	2.78	intr.	not readable	glass
0.424	colorless	2.60	intr.	not readable	glass
0.481	colorless	2.60	intr.	not readable	glass

Table A2: Selected representative ID Data on the identified minerals accompanying the sapphires heat-treated in the presence of Beryllium. Samples cut in half and polished.



Fig. A7 An example of a SEM-EDS recently used for research is shown from the University of Fribourg, Earth Science Department, Switzerland. On the left: Prof. B. Grobety operating the SEM (FEI XL 30 Sirion FEG). To the right details of the SEM: An opened sample chambre, surrounded by a variety of detectors, such as Secondary Electron Detector (SE), Backscattered Electron Detector (BSE) and an X-Ray Detector (EDS) with a Polymer Window (S-UTW), for microchemical analysis.



Fig. A8 A set of non-sapphire materials sorted after heat treatment experiments. In December 2001, heat treatment was carried out with the new method in Chantaburi (Thailand) on a lot of briolette sapphires and then inspected by GRS at the source. First row: Melted non-sapphire materials transformed to whitish glass-aggregates. Second row: Zircon minerals (radioactive). Third row: Chrysoberyl minerals. (Note: Craters on the surface of the zircon and chrysoberyl crystals due to contact with other minerals in the heat treatment process and partial melting of the surface, See arrows). Overgrowing layers of thin films with interference colors were found on zircon and Chrysoberyl samples, indicating some chemical reactions on their surfaces. Samples collection GRS.



Fig. A9 Dr. A. Peretti mounts the chrysoberyl samples for SEM-EDS analysis in February 2002 at the University of Basel (Switzerland).

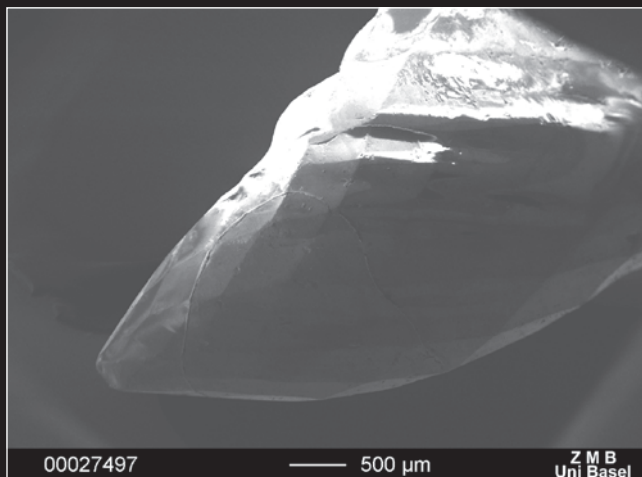


Fig. A10 SEM-SE image of a faceted chrysoberyl crystal after heat treatment. The crystal has a thin film overgrowth with interference color. Sample not carbon-coated for analysis. Acceleration voltage 20kV



Fig. A11 Macrophotograph of glass-aggregate formed by the melting of non-sapphire materials during heat-treatment with Beryllium.

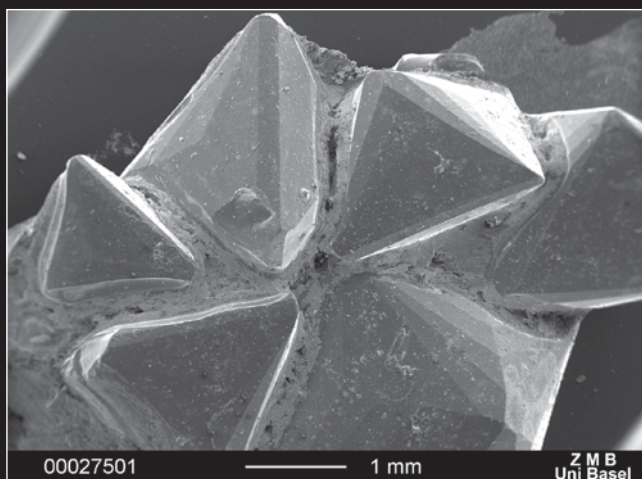


Fig. A12 SEM-SE image of different colored sapphires clustered together in accidental circumstances during the Beryllium treatment experiments. Acceleration voltage 15kV.

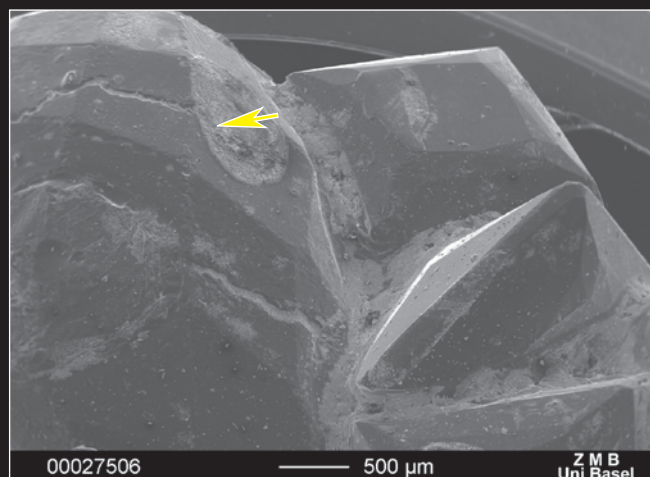


Fig. A13 SEM-SE image of sapphire showing craters due to surface melting of the sapphire material (See arrow). Acceleration voltage 30kV.

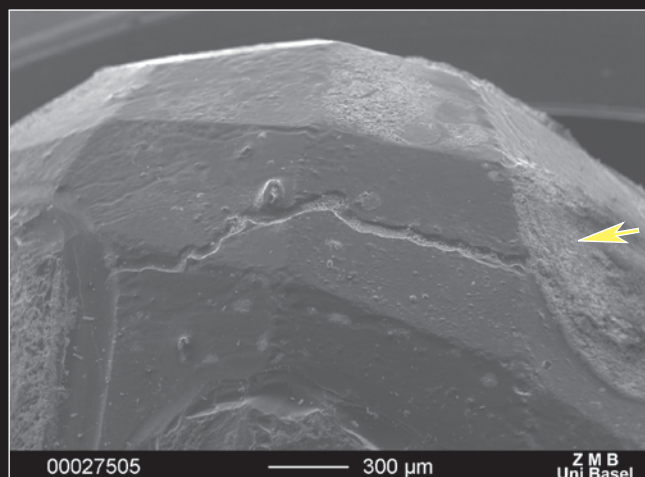


Fig. A14 SEM-BSE image of enlarged area of Fig. A13. The crack is shown as well as a melting crater in the sapphire (arrow) in course of the Beryllium-Treatment. Acceleration voltage 30kV.

Surface Analysis (SEM-SE, SEM-BSE and SEM-EDS) of Beryllium-Treated Sapphires

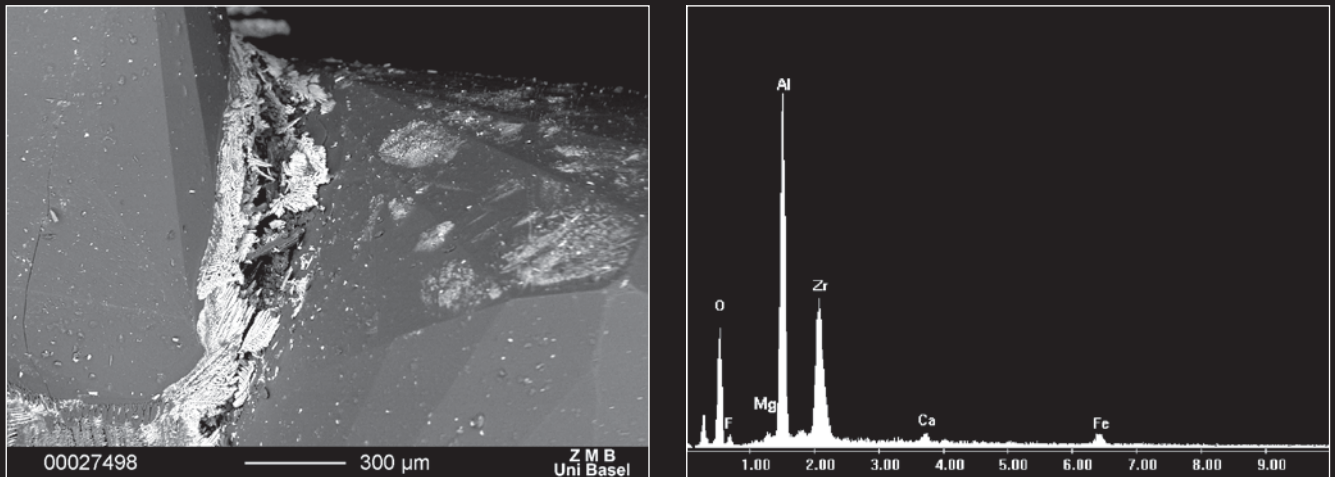


Fig. A15 SEM-BSE image of the matrix between sapphires. Note: Presence of more heavy elements is seen as a white color. These heavy elements are mostly composed of Zirconium (Zr)-oxide of unknown crystal structure (Aluminium (Al) from corundum contamination) as shown by SEM-EDS spectrum on right (Acceleration Voltage 20kV). Note also: Presence of fluorine (F). Samples carbon (C) coated.

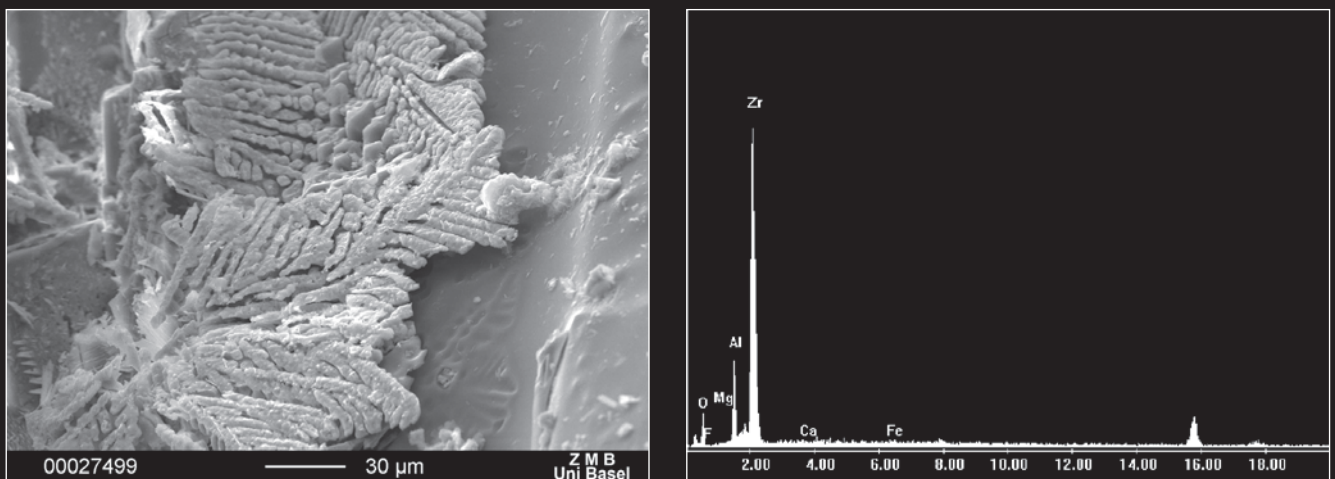


Fig. A16 SEM-SE enlarged portion of the crack shows the growth of dendrites of Zirconium (Zr)-oxide and SEM-EDS spectrum of the same area (Aluminium (Al) from corundum). No high concentrations of iron (Fe), titanium (Ti) or chromium (Cr) were detected as shown by SEM-EDS spectrum on right (Acceleration Voltage 30kV).

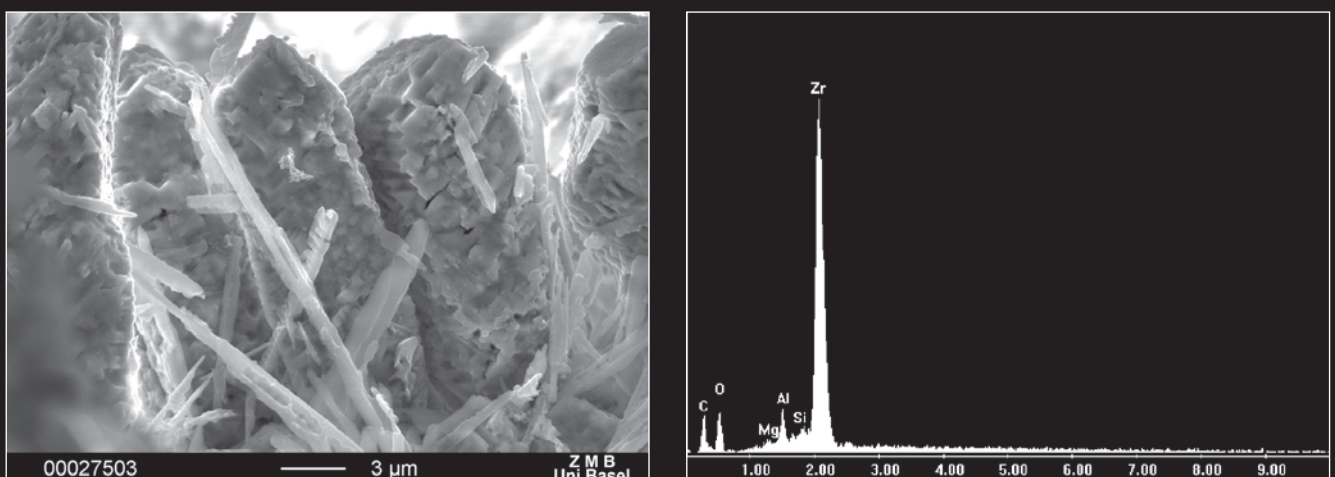


Fig. A17 SEM-SE image of crystallites composed of Zirconium (Zr)-oxide. This crystallite must have been formed over the course of the Beryllium-heating experiments. SEM-EDS spectrum on right (Acceleration voltage 15kV). Sample carbon (C) coated.

Energy Dispersive X-Ray Fluorescence Analysis (ED-XRF)

The ED-XRF analyses were carried out by Dr. A. Burkhardt at the IFZAA Laboratory (Institute for Non-Destructive Analysis + Archaeometry), in Basel, Switzerland, using an ED-XRF Spectrometer

Methods

For the excitation an X-ray tube with a rhodium target and a 125 micron Beryllium-window was used. The X-ray generator was operated in a series of KV increments between 4 KV to 50 KV with current adjustable in 0.02 mA increments and a maximum power of 50 W, using cellulose, aluminium, palladium and copper filters. The background was optimised in combination with the acceleration voltage. A thermoelectric cooled Si(Li)-detector with a comfortable Peltier system with a detector window of 12 microns thickness was used. For the light elements (Na to Ti), the system was operated in vacuum which was required to improve the sensitivity. A complex measurement procedure was optimised for the measurement conditions for all elements of the periodic table from atomic number 11 (Na) to 92 (U). A collimator with a diameter of 2 mm was used to condense and focus the X-Ray beam. The average weigh of the samples was 0.5 to approx. 5 ct. For each corundum sample four different energy spectra were collected with a total of 600 seconds lifetime. To avoid strong diffraction peaks, the sample were rotated. The penetration depth of the x-rays in the sample for a particular analysed element and the intensity of the excited signals (M-L-K lines) are correlated with the acceleration voltage and the atomic number. The penetration depth is increasing from microns for the K-lines of the light elements (Na, Mg, Al) to millimetres (Ga-K, Sr-K, Zr-K) as well as for the L-lines of the heavy elements such as Pt-L, Au-L, Pb-L, Bi-L. In a corundum matrix the penetration depths is for example: 3 microns for Na, 10 microns for Cl, 75 microns for Cr, 120 microns for Fe; from Ga to Sr the penetration depth is increasing from 360 microns to 1.3 mm and for the L-lines of Pt to Bi it is increasing from 390 microns to 1.5 mm. The penetration depth of the strong K-lines of silver (Ag) is 4.7 mm in an Al₂O₃ matrix. After the primary energy spectrum was saved on a Pentium-PC the raw intensities for four energy spectra for each sample were calculated and combined in an intensity file. The "Fundamental Parameter Programme" was used to quantify the raw data and the results were normalized to 100% (weight-percent). Standards were used to setup a standard-table. The quality of the quantitative ED-XRF data (accuracy, precision and detection limits) were found to be critically related to the correct selection of the analytical parameters (collimator, voltage, current, filter) as well as on the quality of the standards. The standards are used to obtain calibration curves. The ED-XRF method cannot be



Fig. A18a Example of an ED-XRF Spectrometer used for chemical testing of corundum at GRS. A sample is positioned at the window above a X-ray generator by Dr. A. Peretti.

used to differentiate between thin layers or in-homogeneities in the samples, such as natural inclusions or small scale chemical layering. Therefore, the data are averaged chemical analyses, with the additional inconvenience of the different penetration depth of the M-, L-, and K-lines. In the first survey of our project a database of 1200 ED-XRF spectra have been collected and only 20 elements including Na, Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Ge, Rb, Sr and Au were quantified. All spectra can be recalculated and quantified for a selection of other elements (atomic number $Z = 11$ to 92). The ED-XRF quantitative data are compared with the data of LA-ICP-MS for selected samples. (Tab A5b). LA-ICP-MS have already compared to another ED-XRF instrument on a larger scale and found to be compatible (Lit. 05) with the exception of Gallium (Ga), therefore confirming that trace element determinations have been checked for accurate consistency with other methods as to the best of our possibilities at this stage. The analytical error on the concentrations for TiO₂ is given here as maximal approx. +/-0.01 wt-%, for Cr₂O₃ approx. +/-0.01 wt-%, for Fe₂O₃ approx. +/- 0.01 wt-% and for Ga₂O₃ approx. +/- 0.002 wt-% and for V₂O₃ approx. +/- 0.01 wt-%. These errors are small enough to allow us to interpret the data (See Fig. A18, A19). Errors on the lighter elements (such as Mg) are considerably higher for this method. Li, B, and *Beryllium* are not measurable by ED-XRF analyses due to limited detection capabilities.

ED-XRF Results

The trace elements used for this report's results are given in Table A3 and shown in Fig. A18, A19, A21 and A30a,b. The data revealed considerable variation mainly in the trace elements Iron (Fe), Chromium (Cr), Vanadium (V), Titanium (Ti), and Gallium (Ga). The elements Na, Mg, Ca, K, Mn, Ni, Cu, Zn, As, Rb, Zr, Tl, Bi, Ge and Sr concentrations are occasionally found. No final conclusion are given here to interpret the presence of these trace elements.

Chemical Composition of Fancy Sapphires from Songea (Tanzania), Unheated and Beryllium-Treated and Origin of Color Analysis of Unheated Natural Fancy and Natural Pink Sapphires from Madagascar

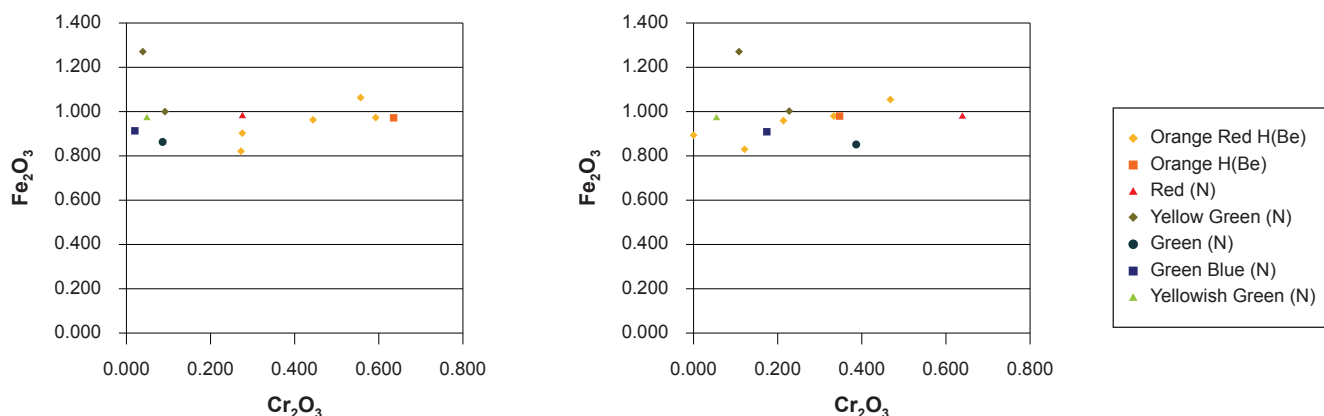


Fig. A18 Representation of ED-XRF data on the dominant trace element concentrations in natural colored sapphires unheated (N) and heat-treated in the presence of Beryllium, in oxide wt.-%. These intense saturated colors are found in the sapphires originating from Songea (Tanzania).

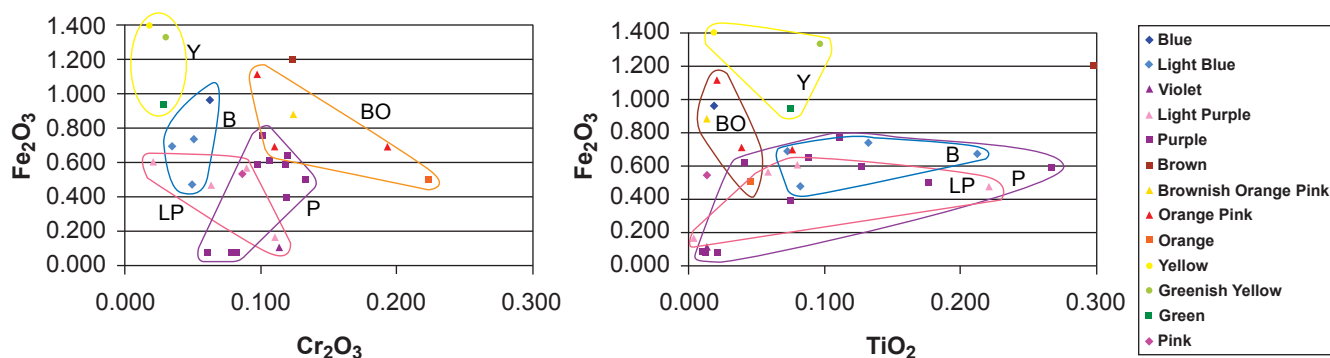


Fig. A19 Representation of ED-XRF data on the dominant trace element concentrations (in oxide wt.-%) in natural colored sapphires unenhanced by heat (N) from Madagascar. Color groups: Y = yellow, greenish yellow, green; BO = brown, orange-pink; B = light blue, blue; LP = light purple and purple; P = purple violet

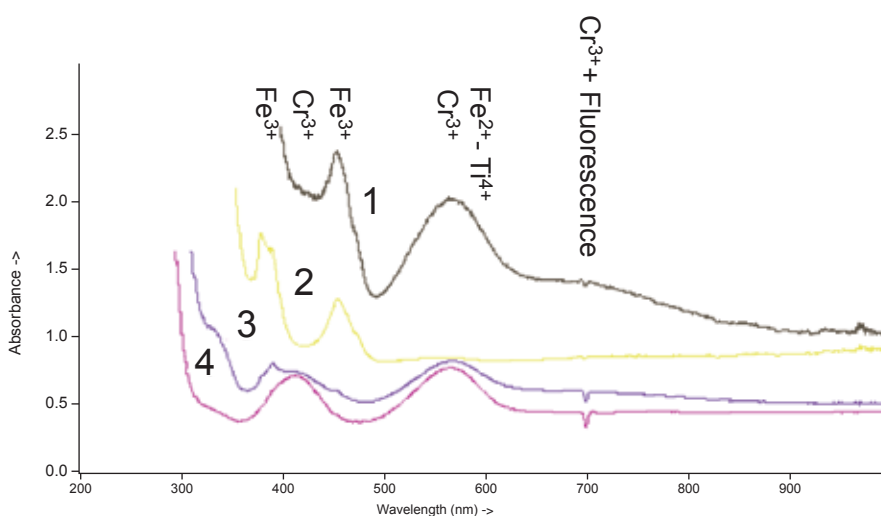


Fig. A20a UV-VIS-NIR non-polarized absorption spectra of natural unheated Fancy Sapphires (origin Madagascar). The observed absorption bands and lines can be explained by variable concentrations in chromium (Cr^{3+}), iron (Fe^{2+} , Fe^{3+}) and titanium (Ti^{4+}) (Trace elements confirmed by ED-XRF analyses). See Fig. A19 and Compare Lit. 20.

Fig. A20b The samples of four different colors of Natural Sapphires spectroscopically measured (Fig A20a).

**Table A3: ED-XRF Chemical Analysis of Natural Sapphires of Different Colors
Unheated (N), Enhanced by Heat (E) and Beryllium-Treated (H(Be))
Origin: Madagascar and Tanzania (in oxide wt-%, Al₂O₃ by 100% difference)**

SAMPLE	Origin Madagascar			TiO ₂	V ₂ O ₅	Cr ₂ O ₃	MnO	Fe ₂ O ₃	Ga ₂ O ₃
	Color	Treatment							
VIOLET1-0.179	blue	H(Be)	0.088	0.061	0.096	0.020	0.106	0.023	
BROWN2-0.166	brown	H(Be)	0.132	0.000	0.088	0.010	0.278	0.033	
BROWN3-0.214	brown	H(Be)	0.109	0.000	0.079	0.018	0.099	0.032	
BROWN4-0.203	brown	H(Be)	0.060	0.000	0.016	0.014	0.098	0.019	
BROWN5-0.126	brown	H(Be)	0.079	0.000	0.107	0.002	0.269	0.030	
BROWN6-0.146	brown	H(Be)	0.139	0.020	0.088	0.000	0.153	0.026	
YELLOW1-0.326	golden-yellow	H(Be)	0.037	0.000	0.009	0.000	0.072	0.027	
YELLOW3-0.170	golden-yellow	H(Be)	0.052	0.000	0.003	0.000	0.113	0.015	
YELLOW4-0.142	golden-yellow	H(Be)	0.057	0.029	0.002	0.000	0.217	0.016	
LAVEND1-0.268	lavendar	H(Be)	0.025	0.002	0.068	0.000	0.071	0.019	
LAVEND3-0.289	lavendar	H(Be)	0.029	0.000	0.072	0.000	0.056	0.023	
LAVEND10-0.239	lavendar	H(Be)	0.074	0.000	0.045	0.007	0.063	0.021	
LAVEND12-0.137	lavendar	H(Be)	0.081	0.056	0.045	0.000	0.170	0.029	
LAVEND11-0.093	lavendar	H(Be)	0.110	0.014	0.147	0.008	0.203	0.026	
LEMON1	lemon	H(Be)	0.072	0.003	0.014	0.004	0.125	0.025	
LEMON2	lemon	H(Be)	0.060	0.009	0.028	0.000	0.114	0.016	
LEMON3	lemon	H(Be)	0.014	0.006	0.029	0.005	0.126	0.016	
LEMON4	lemon	H(Be)	0.059	0.000	0.016	0.002	0.100	0.036	
LEMON5	lemon	H(Be)	0.050	0.014	0.049	0.001	0.121	0.032	
LEMON6	lemon	H(Be)	0.037	0.031	0.015	0.003	0.278	0.025	
LEMON7	lemon	H(Be)	0.051	0.002	0.039	0.000	0.126	0.019	
12548-0.255	lime yellow	H(Be)	0.035	0.014	0.010	0.000	0.144	0.021	
ORANGE1	orange	H(Be)	0.051	0.038	0.121	0.000	0.116	0.014	
ORANGE2	orange	H(Be)	0.028	0.009	0.062	0.000	0.060	0.019	
ORANGE3	orange	H(Be)	0.016	0.000	0.149	0.001	0.264	0.017	
ORANGE4	orange	H(Be)	0.033	0.000	0.047	0.001	0.352	0.022	
ORANGE5	orange	H(Be)	0.123	0.000	0.112	0.000	0.100	0.017	
ORANGE6	orange	H(Be)	0.050	0.000	0.058	0.000	0.219	0.240	
ORANGE7	orange	H(Be)	0.041	0.000	0.024	0.003	0.190	0.017	
ORANGE8	orange	H(Be)	0.048	0.001	0.066	0.000	0.292	0.029	
ORANGE9	orange	H(Be)	0.052	0.006	0.082	0.007	0.392	0.028	
ORANGE10	orange	H(Be)	0.029	0.023	0.001	0.000	0.179	0.005	
ORANGE11	orange	H(Be)	0.037	0.013	0.072	0.000	0.390	0.025	
ORANGE12	orange	H(Be)	0.067	0.038	0.111	0.000	0.217	0.027	
ORANGE13	orange	H(Be)	0.039	0.000	0.051	0.000	0.318	0.020	
ORANGE14	orange	H(Be)	0.020	0.000	0.018	0.000	0.109	0.012	
ORANGE15	orange	H(Be)	0.018	0.008	0.040	0.000	0.467	0.024	
ORANGE16	orange	H(Be)	0.039	0.000	0.022	0.003	0.175	0.016	
ORANGE17	orange	H(Be)	0.066	0.000	0.107	ND	0.135	0.031	
12586-0.184	orange	H(Be)	0.038	0.017	0.045	0.000	0.317	0.016	
12527-0.93	orange-pink	H(Be)	0.040	0.004	0.076	0.000	0.254	0.029	
12528-0.667	orange-pink	H(Be)	0.024	0.006	0.009	0.001	0.070	0.026	
12538-0.314	vivid golden orange	H(Be)	0.097	0.001	0.030	0.000	0.089	0.014	
WHITE1	white	H(Be)	0.054	0.021	0.021	0.000	0.080	0.020	
WHITE2	white	H(Be)	0.025	0.008	0.032	0.000	0.070	0.019	
WHITE3	white	H(Be)	0.039	0.028	0.087	0.000	0.207	0.039	
WHITE4	white	H(Be)	0.059	0.062	0.038	0.004	0.062	0.069	
WHITE5	white	H(Be)	0.122	0.000	0.030	0.006	0.178	0.025	
WHITE6	white	H(Be)	0.055	0.000	0.067	0.008	0.670	0.068	
MIX4-0.291	white	H(Be)	0.063	0.036	0.047	0.000	0.163	0.056	
MIX3-0.112	white-blue	H(Be)	0.050	0.011	0.028	0.005	0.221	0.022	
YELLOW2-0.286	yellow	H(Be)	0.126	0.021	0.117	0.017	0.263	0.011	
MIX5-0.159	yellowish-blue	H(Be)	0.014	0.004	0.056	0.005	0.158	0.017	
01994-0.494	orange	H(Be)	0.016	0.008	0.086	0.002	0.499	0.018	
01994-0.476	orange	H(Be)	0.000	0.018	0.087	0.004	0.106	0.023	
01994-0.834	orange-pink	H(Be)	0.021	0.000	0.098	0.000	0.093	0.022	
01994-0.621	orange-pink	H(Be)	0.019	0.000	0.092	0.000	0.064	0.017	
01994-0552	orange-pink	H(Be)	0.009	0.000	0.056	0.001	0.302	0.015	
01994-1.885	orange-pink	H(Be)	0.022	0.007	0.080	0.000	0.622	0.021	
01995-1.213	orange-pink	H(Be)	0.018	0.008	0.080	0.002	0.401	0.015	
01995-1.265	orange-pink	H(Be)	0.019	0.000	0.112	0.000	0.219	0.021	
01995-0.556	orange-pink	H(Be)	0.051	0.010	2.268	0.000	0.327	0.027	
01995-.0574	orange-pink	H(Be)	0.019	0.003	0.056	0.001	0.339	0.030	
01995-1.562	orange-pink	H(Be)	0.009	0.011	0.117	0.000	0.754	0.021	
01995-1.240	orange-pink	H(Be)	0.023	0.009	0.087	0.003	0.064	0.020	
01995-1.689	orange-pink	H(Be)	0.009	0.005	0.101	0.000	0.427	0.018	
01995-1.478	orange-pink	H(Be)	0.016	0.000	0.076	0.000	0.086	0.020	
12912-0.414	orange-pink	H(Be)	0.018	0.011	0.079	0.000	0.052	0.017	
12914-0.350	orange-pink	H(Be)	0.024	0.012	0.077	0.002	0.136	0.021	
12914-0.350	orange-pink	H(Be)	0.027	ND	0.077	0.004	0.108	0.022	
01994-0.607	vivid yellow	H(Be)	0.007	0.009	0.005	0.001	0.029	0.019	
01994-0.658	vivid yellow	H(Be)	0.008	0.006	0.015	0.000	0.721	0.020	
01994-0.597	vivid yellow	H(Be)	0.036	0.000	0.019	0.001	0.413	0.015	
SAMPLE	Origin Songea			TiO ₂	V ₂ O ₅	Cr ₂ O ₃	MnO	Fe ₂ O ₃	Ga ₂ O ₃
	Color	Treatment							
TUN5-0.83	dark blue	N	0.156	0.082	0.084	0.002	0.030	0.009	
TUN8-0.755	green	N	0.043	0.000	0.316	0.000	1.263	0.013	
TUN4-1.73	pastel blue	N	0.102	0.008	0.004	0.000	0.100	0.019	
TUN7-0.90	violet	N	0.027	0.002	0.126	0.000	0.143	0.009	

Table A3 (Continued)

Origin Madagascar								
SAMPLE	Color	Treatment	TiO ₂	V ₂ O ₅	Cr ₂ O ₃	MnO	Fe ₂ O ₃	Ga ₂ O ₃
12559-0.170	pink	E	0.010	0.011	0.115	0.000	0.176	0.023
12560-0.138	pink	E	0.016	0.010	0.104	0.000	0.067	0.021
12562-0.151	pink	E	0.029	0.008	0.084	0.005	0.106	0.011
12563-0.159	pink	E	0.041	0.008	0.124	0.000	0.145	0.024
12564-0.181	pink	E	0.006	0.042	0.131	0.000	0.069	0.023
12565-0.165	pink	E	0.027	0.038	0.093	0.007	0.107	0.026
12566-0.191	pink	E	0.044	0.020	0.072	0.002	0.107	0.016
12570-0.179	pink	E	0.018	0.020	0.103	0.002	0.174	0.022
12571-0.199	pink	E	0.026	0.000	0.157	0.005	0.421	0.027
12572-0.152	pink	E	0.034	0.034	0.128	0.000	0.060	0.026
12573-0.212	pink	E	0.027	0.015	0.079	0.003	0.132	0.022
12574-0.185	pink	E	0.018	0.015	0.123	0.000	0.070	0.020
12675-0143	pink	E	0.013	0.010	0.075	0.000	0.057	0.025
12579-0.178	pink	E	0.027	0.000	0.108	0.000	0.149	0.021
12581-0.176	pink	E	0.042	0.022	0.062	0.004	0.045	0.018
12582-0.163	pink	E	0.043	0.006	0.134	0.000	0.203	0.022
12584-0.136	pink	E	0.006	0.000	0.105	0.006	0.034	0.018
12585-0.154	pink	E	0.052	0.018	0.137	0.000	0.081	0.019
12588-0.194	pink	E	0.136	0.000	0.093	0.000	0.057	0.019
12590-0.173	pink	E	0.022	0.000	0.138	0.000	0.084	0.016
12591-0.149	pink	E	0.048	0.004	0.088	0.000	0.184	0.026
12592-0.163	pink	E	0.024	0.000	0.137	0.000	0.135	0.024
12593-0.170	pink	E	0.043	0.010	0.105	0.019	0.214	0.015
12594-0.176	pink	E	0.007	0.000	0.092	0.006	0.085	0.019
12612-1.073	light purple	N	0.004	0.009	0.111	0.001	0.167	0.023
12671-1.915	purple	N	0.111	0.018	0.102	0.000	0.764	0.021
12672-1.860	purple	N	0.089	0.021	0.120	0.005	0.643	0.012
12673-4.436	purple	N	0.689	0.011	0.206	0.003	1.062	0.019
12680-1.050	purple	N	0.177	0.000	0.133	0.001	0.502	0.015
12691-1.222	purple	N	0.042	0.000	0.107	0.000	0.615	0.020
12692-1.100	purple	N	0.076	0.000	0.119	0.000	0.390	0.011
12693-1.833	purple	N	0.128	0.020	0.118	0.000	0.592	0.017
12704-2.647	violet	N	0.013	0.015	0.114	0.000	0.109	0.029
12669-1.201	purple	N	0.268	0.026	0.097	0.000	0.588	0.020
12668-1.418	light purple	N	0.059	0.009	0.090	0.001	0.565	0.016
12690-1.010	light purple	N	0.080	0.010	0.021	0.003	0.608	0.011
PURPLE-1.769	purple	N	0.012	0.009	0.061	0.002	0.077	0.018
12703-2.27	purple	N	0.011	0.008	0.082	0.000	0.083	0.016
12611-SILVERB		N	0.020	0.000	0.079	0.005	0.082	0.025
12677-2.506	light blue	N	0.213	0.003	0.239	0.000	0.666	0.019
12689-2.801	light blue	N	0.082	0.003	0.050	0.000	0.470	0.011
12670-1.719	green	N	0.076	0.014	0.029	0.006	0.935	0.010
12675-1.272	light blue	N	0.590	0.020	0.092	0.001	0.659	0.013
12679-2.051	light purple	N	0.221	0.000	0.064	0.000	0.472	0.015
12681-1.561	light blue	N	0.133	0.011	0.051	0.003	0.735	0.014
12684-1.469	blue	N	0.019	0.002	0.062	0.000	0.967	0.016
12686-0.924	green	N	0.824	0.023	0.111	0.000	1.106	0.020
12688-1.191	light blue	N	0.074	0.009	0.035	0.000	0.690	0.018
12630-0.729	yellow	N	0.019	0.000	0.018	0.006	1.401	0.019
12674-1.398	padparadscha	N	0.040	0.001	0.193	0.005	0.703	0.011
12676-1.676	padparadscha	N	0.076	0.007	0.110	0.000	0.692	0.013
12685-1.646	orange	N	0.046	0.007	0.223	0.000	0.501	0.010
MAD-1.888	brown	N	0.298	0.000	0.123	0.000	1.197	0.020
MAD-1.703	padparadscha	N	0.021	0.008	0.097	0.000	1.112	0.028
12738-1.36	brownish padparadscha	N	0.014	0.000	0.124	0.001	0.880	0.240
12737-PINK	pink	N	0.014	0.000	0.087	0.005	0.542	0.027
Origin Songea								
SAMPLE	Color	Treatment	TiO ₂	V ₂ O ₅	Cr ₂ O ₃	MnO	Fe ₂ O ₃	Ga ₂ O ₃
SONG3-0.30		N	0.012	0.011	0.231	0.000	0.871	0.013
SONG5-0.44	red	N	0.048	0.000	0.273	0.000	0.980	0.016
SONG8-0.71	green	N	0.029	0.002	0.084	0.000	0.851	0.012
SONG10-0.87	green blue	N	0	0.000	0.042	0.000	0.874	0.013
SONG11-0.82	green blue	N	0.013	0.018	0.019	0.001	0.902	0.011
SONG6-0.488	yellow green	N	0.017	0.001	0.080	0.004	1.003	0.015
SONG7-0.50	yellow green	N	0.008	0.004	0.036	0.000	1.259	0.017
SONG12-0.97	yellowish green	N	0.004	0.011	0.046	0.000	0.975	0.012
121004-0.687	orange red	H(Be)	0.009	0.004	0.269	0.005	0.826	0.011
TU-0.24	orange red	H(Be)	0.025	0.003	0.589	0.002	0.975	0.015
TU-0.26	orange red	H(Be)	0.035	0.002	0.555	0.009	1.053	0.020
TU-0.32	orange red	H(Be)	0	0.004	0.272	0.001	0.895	0.010
TU-0.40	orange red	H(Be)	0.016	0.000	0.440	0.000	0.955	0.007
121002-0.824	orange red	H(Be)	0	0.000	0.190	0.004	0.941	0.010
TU-0.37	orange red	H(Be)	0.026	0.008	0.634	0.000	0.976	0.014
SONG1-0.26	orange red	H(Be)	0.016	0.022	0.162	0.000	1.177	0.013
SONG4-0.31	orange red	H(Be)	0.015	0.001	0.071	0.000	0.518	0.010

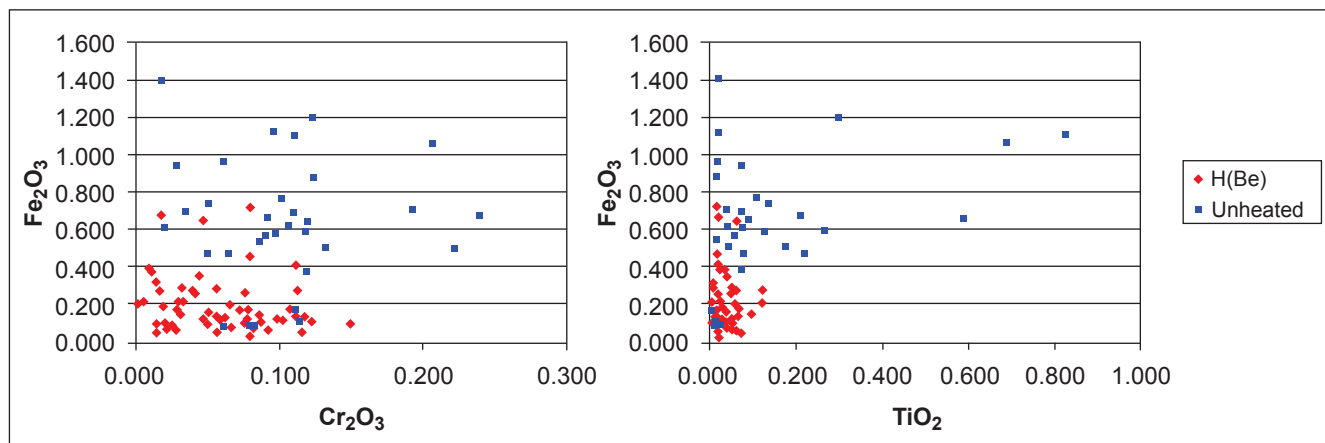


Fig. A21 Iron (Fe), chromium (Cr) and titanium (Ti) concentrations (ED-XRF analysis in oxide wt.-%, See Tab. 5) of natural fancy color sapphires, unheated (blue), and Beryllium-Treated (red). Origin: Madagascar. Note: Beryllium-Treated sapphires are not enriched in these trace elements (Fe, Cr and Ti) in comparison to those unheated (N).

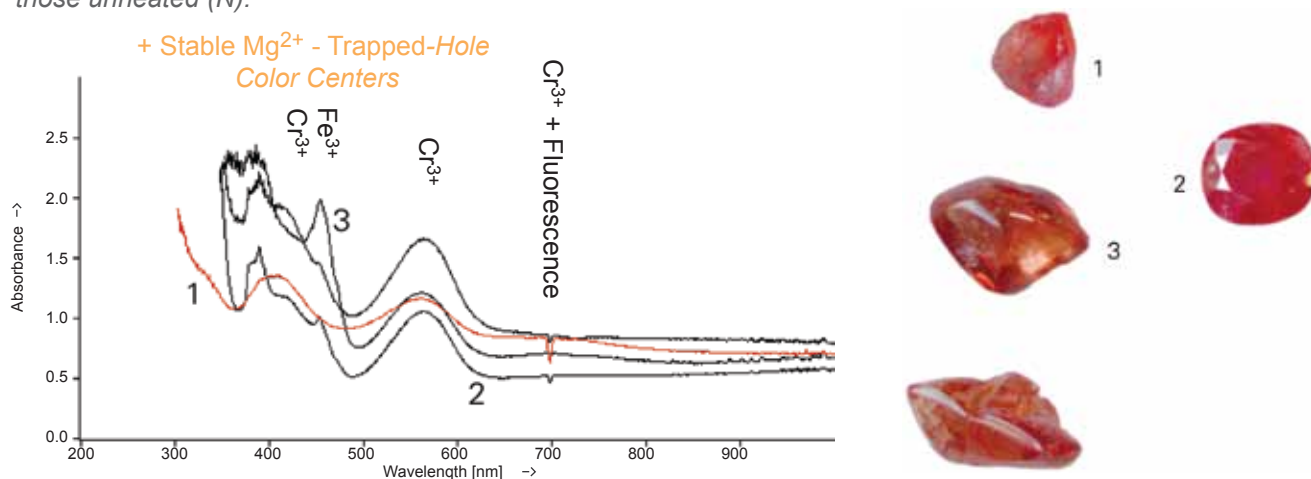


Fig. A22 Representative absorption spectra of natural brownish orangy-pink sapphires from Madagascar unenhanced by heat. Some of the samples are reminiscent of "Padparadscha" colors. Note: Similarity of the absorption spectra of the samples treated with Beryllium (See Fig. A23). The interpretation of origin of color, indicated for chromium (Cr^{3+}), iron (Fe^{3+} and Fe^{3+} pairs) as well as color centers, based on chemical compositions determined by ED-XRF (Fig. A19), LA-ICP-MS analysis and literature (Lit. 04 and 24). Representative LA-ICP-MS analysis: Mg= 91 wt.-ppm, Ti= 89 wt.-ppm, V=21 wt.-ppm, Cr=521 wt.-ppm, Fe= 4937 wt.-ppm, Ga= 101 wt.-ppm (Average 17 analysis, sample No. GRS 12737, LA-ICP-MS, Table A6, Part B).

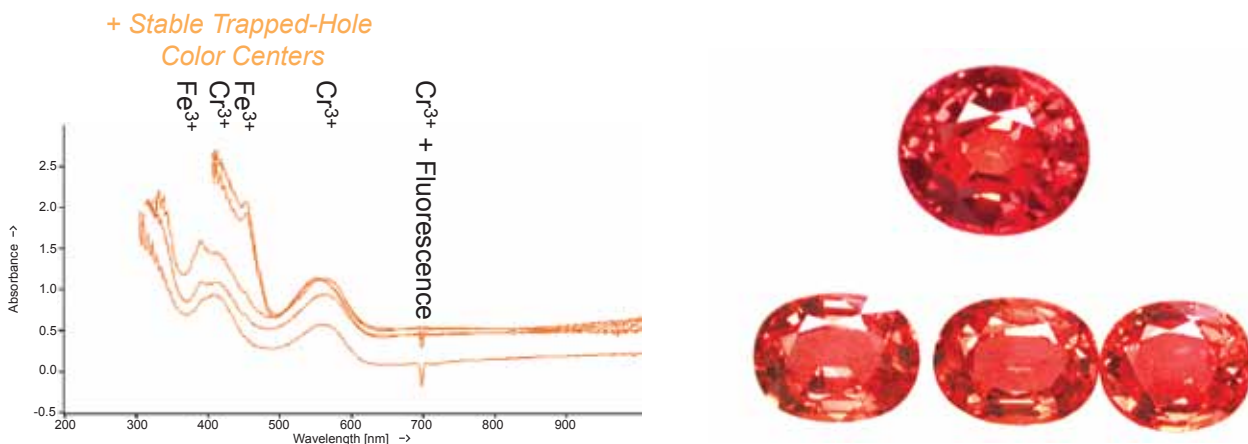


Fig. A23 Polarized UV-VIS-NIR absorption spectra of natural pastel orangy-pink sapphires (origin: Madagascar) to vivid orange-red sapphires (origin: Songea, Tanzania) heat-treated with Beryllium. Absorption spectra can be interpreted as absorption bands and lines caused by trace elements iron (Fe^{3+} , Fe^{3+} -pairs) and chromium (Cr^{3+}) and magnesium (Trapped Hole Color Centers). Chemical analyses by ED-XRF and LA-ICP-MS (See Fig. A18, A30 and Tables 3, 4 and 7b,c).

Origin of Color Analysis of Natural Beryllium-Treated Fancy Sapphires from Madagascar

Sample	Color	No. Analyses		Be	Mg	Ti	Cr	Fe
12922	Orange	4	Average	27.6	87.6	177	346	1165
	rim analysis		Std Dev	9.8	14.9	48.3	88.9	158
12925.1	Blue	24	Average	4.3	75.6	260	265	1166
			Std Dev	7.1	13.5	156	40.9	162
12598	Padparadscha	32	Average	4.7	55.4	62.4	383	670
			Std Dev	4.4	8.2	7.2	55.1	99.5
12540	Yellow	15	Average	8.5	118	94.7	35.2	800
			Std Dev	3.8	22.9	18.1	6.4	112.8
12922	White	19	Average	3.2	129	156	67.8	548
			Std Dev	5	21.8	22.9	15.2	76

Table A4: Averaged chemical compositions (LA-ICP-MS data in wt.-ppm) of samples investigated by UV-VIS-NIR absorption spectroscopy (Fig. A24). Detection limits See page 20.

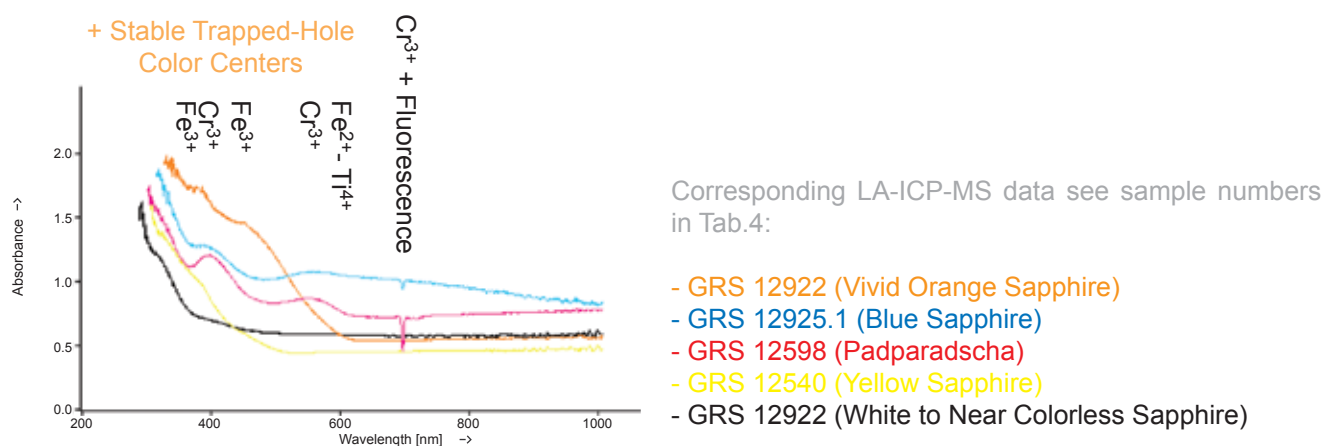


Fig. A24 UV-VIS-NIR absorption spectra of natural sapphires from Madagascar heat-treated with Beryllium. Sapphire Colors: White (black line), yellow (yellow line), pinkish-orange - "Padparadscha" - (pink line), vivid orange (brown line) and blue sapphire (blue line). The chemical compositions are dominated by Mg, Fe, Cr and Ti (Beryllium subordinate). All samples are as produced from pastel colors after heat-enhancement in the same heating run. ED-XRF and LA-ICP-MS data on chemical compositions See Tab.A3 and A4. Effect of unstable color centers to the absorption spectra See Fig. A5 and Fig. A26. Interpretation of color centers based on measured divalent-cation-concentrations and absorption in the blue region of the spectrum (See also Lit. 04, Lit. 24).

BOX: Methods UV-VIS-NIR Absorption Spectroscopy

Spectroscopic analysis was carried out with a multi-channel TIDAS spectrometer with 1024 diode arrays and an 80Watt Xenon lamp. Quartz fiberoptics of 2mm diameter, and quartz lens optics, were used to condense the signal to the sample, with another quartz lens optic utilized to collect the signal. Before the sample, and after the condenser optic, a diffuser was implemented, then, after the signal, and before the second quartz lens optics, a UV-VIS polarizing filter was used to obtain polarized absorption spectra. This set-up enabled the spectra to be recorded from 260nm to 1024nm. Below 300nm, an increase in background noise was present due to the characteristics of the Xenon lamp and the increase in absorption of the UV filter towards the lower UV region. The resolution of the absorption lines is restricted by the number of diodes used to approx. 1nm, as lines narrower than this constraint could not be seen. The measuring time was 10 milliseconds. 20 spectra were collected in one run and averaged to obtain one spectrum. The data was computed by software from the manufacturer.

The Zero absorption line was collected for each set up which allows correcting for the absorption characteristics of the polarizing filter before every measurement. Due to the nature of multi-channel spectroscopy, fluorescent emission lines (as seen, for example, as a white fluorescent line in a hand-held



Fig. A25 The GRS UV-VIS-NIR multi-channel spectrometer used for recording the absorption spectra of the gemstones. A special measuring chamber set-up (Center of picture) enables the collection of non-polarized, or polarized absorption spectra, between 290nm (UV) and 1024nm (NIR) on rough or faceted gemstones in all different crystallographic directions within milliseconds.

spectroscope) will also appear in an absorption spectrum as a negative peak towards lower absorptions. Results of these analyses are given in Fig. A5, A20a, A22, A23, A24, A26, A27, A28 and A29.

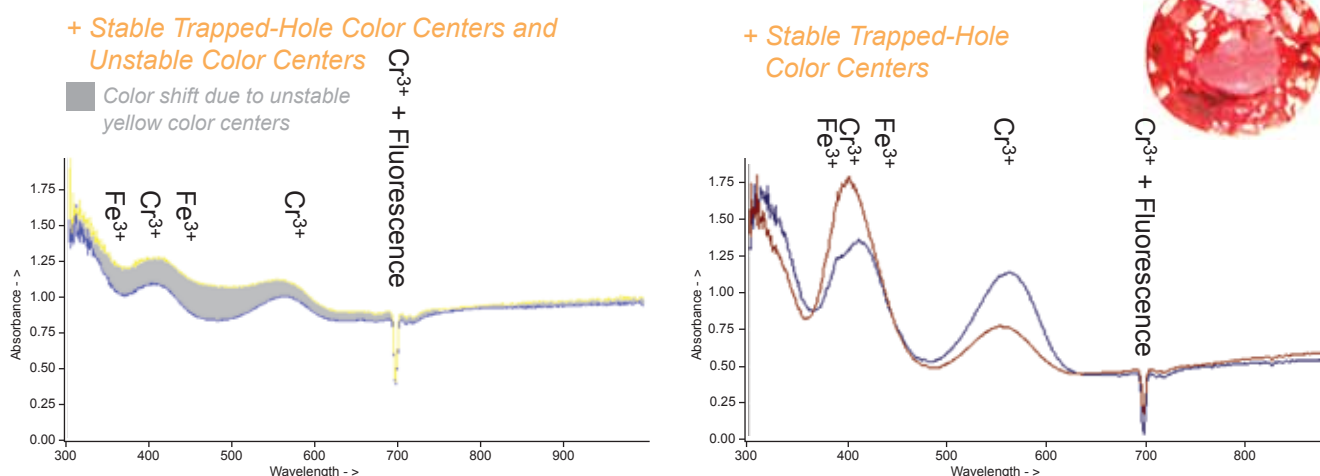
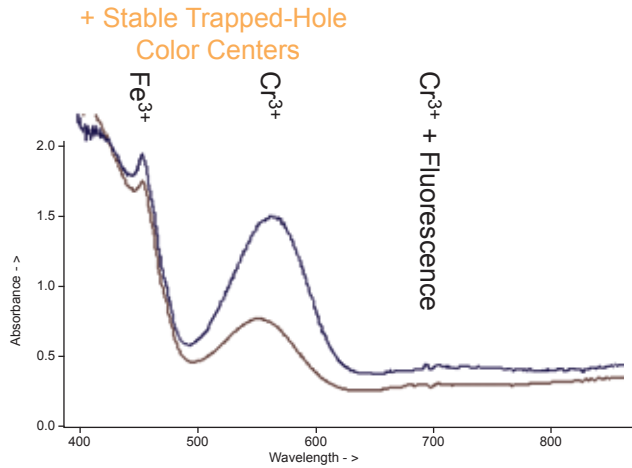


Fig. A26 Right side: Polarized UV-VIS-NIR absorption spectra of a pastel orange-pink sapphire heat-treated with Beryllium. Absorption parallel and perpendicular to the c-axis are shown, responsible for orange-pink to pink pleochroism in the gemstones.

Left side: Color shift after long term UV- exposure (shift to higher absorption in the blue region of the spectrum). Two absorption curves due to the presence of different types of color centers are indicated. Trapped-hole color centers are interpreted as stable (See blue curve at lower absorptions in the blue region of the spectrum) (Compare Lit. 04 and Lit. 24).

UV-VIS-NIR Absorption Spectroscopy of Beryllium-Treated Natural Yellow Sapphires, Orangy-Red and Blue Sapphires, and Surface Diffusion-Treated Blue Sapphires.



Sample No. GRS 782



Fig. A27 Polarized UV-VIS-NIR absorption spectra of a vivid orange sapphire heat-treated in the presence of Beryllium. Absorption parallel and perpendicular to the c-axis are shown, responsible for yellow-orange to orange-red dichroism in the gemstone. Note: Strong effect of pleochroism to the development of the 550nm band and the presence of a prominent 450nm line (Due to higher Fe³⁺-concentrations) in the spectra. Chemical composition for Mg, Be, Cr, Fe see Table A18. (Mg- concentrations 10x higher than Be-concentrations if expressed in wt.-ppm).

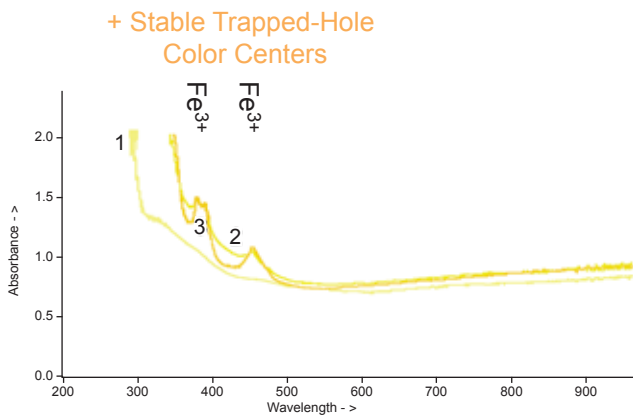
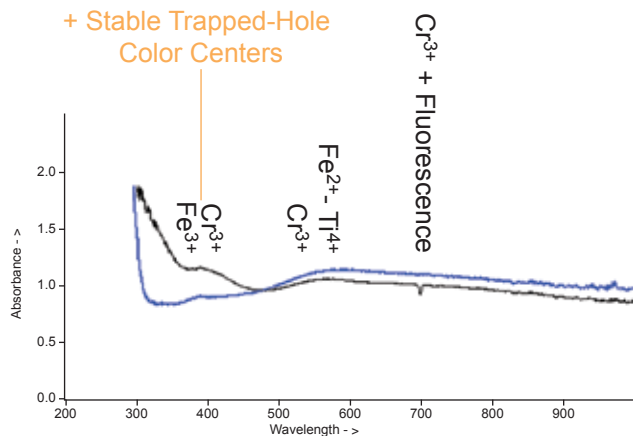
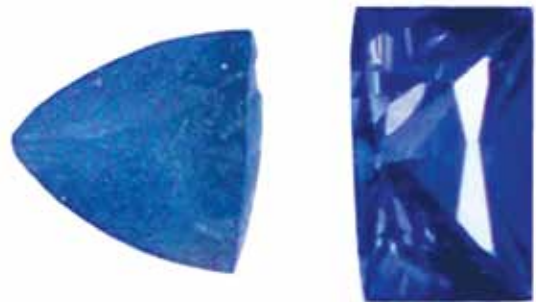


Fig. A28 Polarized UV-VIS-NIR absorption spectra in the direction of the c-axis of yellow sapphires with increasing saturation produced by heat-treatment with Beryllium. The spectra is dominated by iron (Fe³⁺ and Fe³⁺-pairs) for spectrum No. 3. Increase of Fe-concentrations (from 1 to 3) as determined by ED-XRF analyses. Presence of color centers based on spectral curve (absorption in the blue region of the spectrum) and divalent cation (Be+Mg)-concentrations (See LA-ICP-MS Data Table A4). Compare also with Lit. 04 and Lit 24.



Sample No. GRS 12925



Sample No. GRS T-Blue

Fig. A29 Polarized UV-VIS-NIR absorption spectra of a diffusion-treated blue sapphire (T) (See blue line), and Beryllium-Treated blue sapphire. Note: Major differences in the absorption characteristics in the UV region of the spectrum. Surface diffusion-treated sapphires (T) show more transparency in the lower UV and blue region of the spectrum between 300 and 450nm.

Conclusions on Origin of Color (ED-XRF, UV-VIS-NIR)

The chemical analysis and spectroscopic study were carried out on fancy sapphires of different colors from Madagascar, both for gemstones unenhanced by heat (N) and, in comparison, for gemstones heat-treated with Beryllium (Compare Fig. A19, A21, A30a). Comparing the quantitative data, (e.g. focusing on the concentration of trace elements between H(Be) and unenhanced (N) sapphires of the same color, and the intensity of the absorption lines, Compare Fig. A20a, A22 with Fig. A23 and A24), the following major differences were noticed:

For the large group of sapphires heat-treated in the presence of Beryllium, it was found that chemical concentrations (Fe and Cr) were much lower than those found in the natural counterparts of the same color family.

The presence of iron (Fe^{3+} , Fe^{3+} -pairs) cause absorptions in the gemstones typical for yellow sapphires. Chromium (Cr^{3+}) and iron (Fe^{3+} , Fe^{3+} -pairs) were found to contribute to the color of orangy-pink sapphires. However, the iron caused absorptions as determined by UV-VIS-NIR absorption spectroscopy are too weak to explained the extent of the orange color contribution (See Fig. A23 and A24).

Two different reasons can be given to explain this:

- The presence of other origins of color are present such as color centers related to light elements (such as Mg or Be) (Compare Lit. 04 and Lit. 24).

- The origin of color must be concentrated in certain levels within the gemstones, not necessarily accessible by ED-XRF analysis. This is confirmed by the microscopic studies. ED-XRF cannot see these layers within the gemstones due to the restricted analytical sampling volume. Therefore, the color, as seen face up, cannot be explained sufficiently by the chemical analysis as determined by ED-XRF on the surface. Similar trends, however, such as the correlation of the color with the dominant trace element present, were still possible. The correlation of the chemistry with UV-VIS-NIR spectroscopy is restricted, because UV-VIS-NIR is a bulk analysis which measures the light absorbed in certain colored levels of the gemstone. The intensity of the absorption spectrum depends on the light path through the gemstone. The layers of color measured by UV-VIS-NIR spectroscopy may not be at the same position as the part of the gemstone measured by ED-XRF analysis. Therefore, further conclusions are difficult for samples with color zoning.

To further clarify the origin of color, it is therefore necessary to extend the ED-XRF to another method which focuses precisely on the micro-chemical

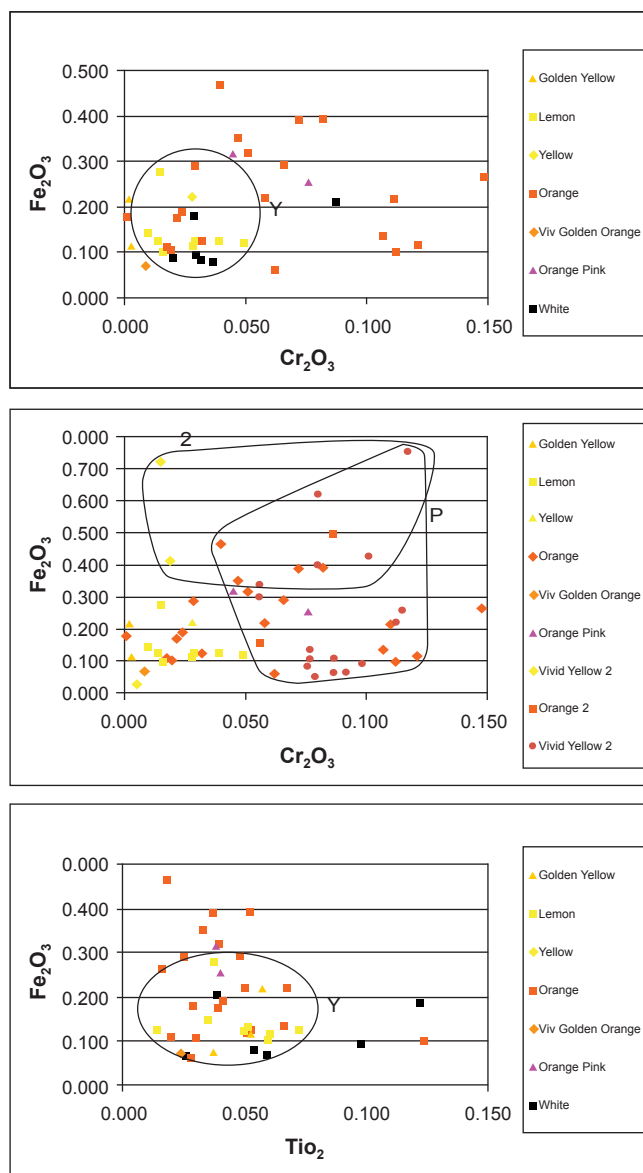


Fig. A30a,b ED-XRF chemical analyses (in oxide wt.-%) of different natural colored sapphires heat-treated with Beryllium. The samples from the first two graphs originate from the same heat treatment run of pastel colored sapphires from Madagascar (See materials f.). The group of colors indicated via No. 2 corresponds to samples which were re-polished after treatment, and which are not from the same heating run or the same heat treatment laboratory. The golden yellow, and lemon and yellow, group (Y) is indicated, as well as the field of orange to orangy-pink colors (P). Note: White sapphires are those that did not change after heat-treatment with Beryllium. Compare group P (these figures) with counterparts in Fig. A19 (the field BO) and the fields Y in both figures Fig. A30b and Fig. A19. It can be noted that the chemical compositions (as determined at the surface of the gemstones by ED-XRF analysis, See Fig. A30) are much lower than the natural unenhanced counterparts with the same color (compare Fig. A19).

variations within the gemstone, and which allows correlation of micro-banding of chemical compositions with microscopic color banding. Further tests require a complicated sampling procedure (See Table A6) and extensive measurements by LA-ICP-MS as shown in the following pages.

Methods: LA-ICP-MS

Inductively coupled plasma mass spectrometry (ICP-MS) has developed rapidly and is now a routine method for multi-elemental analysis of many types of samples. As the use of aqueous solutions is not very convenient when working with solid samples (dissolution, contamination, etc), alternative solid sample introduction techniques, such as laser ablation, are used with ICP-MS. Ablation of solid samples, using a laser with a flow of carrier gas to carry the ablated material from a suitable cell to the ICP, is a very powerful technique. The development of new laser systems (Quadrupled ND:YAG [Lit. 05], excimer [Lit. 08]), homogenization optics, increased mass spectrometer sensitivity, accompanied by an increased linear dynamic range, has led to a large number of new applications (Lit. 05).

In this work, an ArF excimer laser (193nm; Compex 110I, Lamda Physik, Goettingen, Germany), coupled with a quadrupole mass spectrometer (Elan 6100 DRC Perkin Elmer/Siex, Toronto, Canada), was used (See Fig. A32). A homogenized laser beam with a flat top beam profile was imaged onto the sample surface using mirror optics, homogenizer arrays, and a petrographic microscope. This system allows the laser beam onto the sample, while allowing the operator to observe the sample during ablation. An in-house fabricated ablation cell, which can hold five samples, including a reference material for calibration, had a total volume of 2 cm³. Helium was used as the sample carrier gas (1.2 l min⁻¹), introduced into the cell using a nozzle with an inside diameter of 100 micrometers.

An argon gas flow (0.85 l min⁻¹) was mixed with the helium gas flow at .5cm after the cell, and this mixture was transported though 1m length PVC-tubing (inside diameter 0.4cm) to the ICP.

For data collection, the LA-ICP-MS system was operated in time resolved mode. Every 520 ms, the intensities of 40 selected isotopes are measured and stored. At this data acquisition repetition frequency (approximately 2 Hz), no significant fluctuation of the time resolved signal was observed.

The integration intervals (background and gross analyte) were selected manually, and then the gross signal was background corrected using the preablation signal.

The concentrations in the samples were calculated using SRM NIST 612 glass as external standard, with Al being used as internal standard. Using Al normalized sensitivity, the changes in the volume (mass) of the sample, which was ablated, was corrected. The data for samples slightly exceeding 100% have not been corrected, because the correction results in insignificant concentrations changes (smaller than the detection limit). A small drift

of the normalized sensitivity over 20 analyses (run) was corrected by measuring the reference material four times - twice at the beginning, and twice at the end of an analytical run using a linear interpolation of the sensitivity with time. For this study more than 30 samples were analyzed – with mainly Be, Mg, Al, Cr, Mn, Ti, and some 30 other trace elements, measured in all samples.

Detection limits for selected elements:

Be	= 0.3 to 0.5 ppm
Mg	= 0.2 to 0.5 ppm
Ti	= 1 ppm
Cr	= 2 ppm
V	= 0.1 - 0.2 ppm
Fe	= 3 ppm
Ga	= 0.06 to 0.12 ppm

(variation depending on the concentrations measured)

In most samples, a profile across the gemstones was probed using an 80 micron crater diameter to determine the edge rim concentration. Blank level determinations were placed randomly across the sample (e.g. See Fig. A55) to determine differences between enhanced (E), unheated (N) and in Beryllium-treated samples, shortly noted as H(Be) in Table A6.



Fig. A31 LASER ABLATION ICP-MS Analyses by Prof. D. Günther in early 2002 (details see Fig. A32).



Fig. A32
Laser Ablation Mass Spectrometry (LA-ICP-MS) at the Laboratory for Inorganic Chemistry, SFIT ZH, Switzerland (Prof. D. Günther)

Explanation of method

The laser ablation technique (LA) uses a 193 nm excimer laser (1) which is focused onto the sample surface via microscope lenses (2). The laser is ablating (carrying away) the material (crater diameter 4 to 80 microns) (3). The mobilized material is suspended in a carrier gas (4) and transported via transport tube into an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (5). The material/elements (except those that cannot be ionized, such as gases and fluorine) are vaporized, atomized and ionized within the ICP. The created ions are then transferred to the mass spectrometer and separated by their mass divided by charge (5). The detector allows measuring major, minor and trace elements within a single analysis. Very light elements, such as boron, lithium or beryllium, can be detected, along with a large series of other elements at concentrations of less than 1 ppm. The quantification at low concentrations is possible by LA-ICP-MS due to a matrix-independent calibration, including special computer analysis and specific software (6). The use of complementary solid-analysis methods (such as EMPA and XRF) for comparison and validation purposes (e.g. for quantitative measurement of silicon and aluminium) must be applied (see Table A5b).

	Repeated Measurement		Average 5	Ratio	Repeated Measurement		Average 17	Ratio	Average 15		Ratio
Sample	12914-0.350		12914-0.350		12737-1.25		12737-1.25		12737-Or	12737-Or	
	ED-XRF	ED-XRF	LA-ICP-MS	ED-XRF/LA	ED-XRF	ED-XRF	LA-ICP-MS	ED-XRF/LA	ED-XRF	LA-ICP-MS	ED-XRF/LA
Average	1	1			1	1			1		
BeO	ND	ND	0.0033		ND	ND	0.0000		ND	0.0175	
MgO	ND	ND	0.0129		ND	ND	0.0152		ND	0.0192	
Al ₂ O ₃	99.648	99.693	99.4997		99.183	99.242	99.4997		98.972	99.4997	
K ₂ O	0.068	0.041			0.038	0.049	0.0002	257.9398	0.097	0.0022	44.5873
CaO	0.009	0.023			0.005	0.029	0.0020	8.5622	0.065	0.0059	11.0956
TiO ₂	0.024	0.027	0.0164	1.5541	0.020	0.014	0.0149	1.1378	0.069	0.0639	1.0790
V ₂ O ₅	0.012	ND	0.0032	1.8666	0.003	0.000	0.0031	0.4909	0.009	0.0031	2.9091
Cr ₂ O ₃	0.077	0.077	0.0543	1.4184	0.095	0.087	0.0763	1.1926	0.102	0.0880	1.1588
MnO	0.002	0.004			0.003	0.005			ND		
Fe ₂ O ₃	0.136	0.108	0.1359	0.8974	0.625	0.542	0.7060	0.8265	0.646	0.8121	0.7955
Ga ₂ O ₃	0.021	0.022	0.0091	2.3654	0.027	0.027	0.0136	1.9879	0.033	0.0140	2.3608

Table A5b Comparison of LA-ICP-MS and ED-XRF data (in oxide-wt.-%). Values given for ED-XRF represent bulk analysis, whereas LA-ICP-MS data is multiple local analysis (averaged). Therefore, variation of concentrations are sample dependant. ND = Below detection limit or not detectable. CaO- and K₂O-concentrations are due to surface contaminations. Repeated measurements include repositioning of the sample.

Table A5a: Averaged LA-ICP-MS Data of Various Natural Sapphires of Different Colors Beryllium-Treated and Untreated

Table A5a Averaged LA-ICP-MS trace element concentration (in wt.-ppm) of natural sapphires of different colors heat-treated in presence of Beryllium and two unheated natural sapphires (purple and violet).

Sample	Color	Average		Be	Mg	Ti	V	Cr	Fe	Ga
12922	Orange	4	Average	27.6	87.6	177	4.0	346	1165	67.4
			Std Dev	9.8	14.9	48.3	0.3	88.9	158	2.3
12925.2	Blue	20	Average	5.0	68.3	251	42.1	247	1190	64.9
			Std Dev	7.7	18.9	167	8.4	39.1	236	12.1
12925.1	Blue	24	Average	4.3	75.6	260	39.5	265	1166	63.2
			Std Dev	7.1	13.5	156	4.3	40.9	162	9.2
12599	Padparadscha	20	Average	4.9	66.7	73.6	26.9	462	1154	78.5
			Std Dev	5.0	10.6	9.7	2.8	39	124	7.9
12911	Padparadscha	26	Average	2.7	56.6	61.1	27.1	351	668	75.5
			Std Dev	4.3	6.7	8.7	3.0	36.6	84.3	9.2
12598	Padparadscha	32	Average	4.7	55.4	62.4	27.5	383	670	73.2
			Std Dev	4.4	8.2	7.2	3.4	55.1	99.5	10.0
12914	Padparadscha	5	Average	12.0	77.8	98.3	21.8	371	950	67.7
	rim analysis		Std Dev	2.4	7.5	6.9	0.3	26.9	69.4	5.8
12540	Yellow	15	Average	8.5	118	94.7	10.2	35.2	800	60.0
			Std Dev	3.8	22.9	18.1	1.4	6.4	112.8	8.3
12922	White	19	Average	3.2	129	156	62.1	67.8	548	88.5
			Std Dev	5	21.8	22.9	6.5	15.2	76	11.6
12922.1	White	19	Average	3.1	142	167	66.0	59.7	615	90.5
			Std Dev	4.9	28.2	23.9	10.2	10.2	111	16.8
1498	Purple	10	Average	<0.1	73.6	81.6	21.8	457	1311	85.5
			Std Dev		5.9	5.5	0.6	30.1	92.7	9.0
12702	Violet	17	Average	<0.1	60.2	73.2	26.1	461	1032	78.1
			Std Dev		7.4	8.6	2.2	32.8	114	7.7

GRS Table A6: Sampling and Probing Strategy for LA-ICP-MS Analysis (Part A and Part B)

	Sample	Weight (ct)	Color	Material	Treatment	Preparation	Source	Origin	LA-ICP-MS Profile
PART A	1498	1.49 2 pieces same original sample	purple	Natural Purple Sapphire	N	1. rough 2. cut half	GRS's collection	Madagascar	1 profile 13 spot analysis
	12914	0.35 recut	orangy-pink	Natural Pastel "Padparadscha"	H(Be)	1. treated new method 2. faceted	Chantaburi market	Madagascar	girdle analysis 5 spot analysis
	12910 Peretti1	0.021 center slice	pinkish-orange	Natural Pastel "Padparadscha"	H(Be)	1. faceted 2. treated new method 3. cut thick section	GRS supply to Chantaburi Factory Jan 2002	Madagascar	scattered 2 dim. 32 spot analysis
	12911 Peretti2	0.22 center silce	pinkish-orange	Natural Pastel "Padparadscha"		same as above		Madagascar	scattered 2 dim. 26 spot analysis
	12599	0.26 0.24	pinkish-orange	Natural Pastel "Padparadscha"	H(Be)	1. faceted 2. treated new method 3. cut half for profile	GRS supply to Chantaburi Factory Dec 2001	Madagascar	1 profile 20 spot points
	12598	0.28 0.29	pinkish-orange	Natural Pastel "Padparadscha"	H(Be)	same as above	same above	Madagascar	4 profiles 66 spot points
	12540	0.09 0.16*	vivid yellow	Natural Yellow Sapphire	H(Be)	same as above	same above	Madagascar	1 profiles 3 control points 20 spot points
	12925	2 pieces	blue	Natural Sapphire	H(Be)	same as above	same above	Madagascar	4 profiles 50 spot points
	12922	0.13 0.084	colorless to light cream	Natural White Sapphire	H(Be)	same as above	same above	Madagascar	4 profiles 46 spot points
	12922		vivid orange	Natural Orange Sapphire	H(Be)	1. faceted 2. treated new method (surface analysis)	same above	Madagascar	surface analysis 4 spot analysis
	782	0.33 0.39	vivid orangy-red	Fancy Sapphire "Intense Padparadscha"	H(Be)	1. heated 2. faceted 3. cut half	Chantaburi market Jan 2002	Songea (Tanzania)	2 dim. mapping (2 pieces) 37 spot analysis
	T-blue	2 pieces	blue	Diffusion-treated Sapphire	T heat-treatment and diffusion treatment with Titanium	1. treated 2. faceted 3. cut half	Bangkok Mar 2002	natural white sapphire origin not known	2 dimensional mapping 16 spot analysis
PART B	12571	0.08	purplish-pink	Natural Pink Sapphire	E	cut half piece (keep for reference before treatment)	GRS supplied to Bangkok Factory Feb 2002	Madagascar	1 profile 14 spot analysis
	12571	0.07	pinkish-orange	Natural Pastel "Padparadscha"	H(Be)	heat treated (not repolished)	same above	Madagascar	surface profile depth profile 34 spot analysis
	12573	0.09	purplish-pink	Natural Pink Sapphire	E	cut half piece (keep for reference before treatment)		Madagascar	1 profile 14 spot analysis
	12573	0.06	pinkish-orange	Natural Pastel "Padparadscha"	H(Be)	1. faceted 2. cut half 3. heated new method 4. cut half for profile	same above	Madagascar	Surface profile depth profile 34 spot analysis
	12702	0.43	violet	Natural Violet Sapphire	N	keep half piece for ref not heated		Madagascar	17 spot analysis profile
	12702	0.55	pinkish-orange	Natural Pastel "Padparadscha"	H(Be)	1. cut half 2. treatment for half piece	same above		surface profile depth profile 42 spot analysis
	12702	0.22 quarter piece	pinkish-orange	Natural Pastel "Padparadscha"	H(Be)	1. cut half piece 2. treatment 3. cut half after treating	same above		core/rim 3 analysis
	12737	half-piece	"pinkish-orange slightly brown"	Natural Pastel "Padparadscha"	N	keep half for reference untreated		Madagascar	17 spot analysis 34 spot analysis
	12737	0.22	orange-pink	Natural Pastel "Padparadscha"	H(Be)	1. cut half 2. treatment of half piece	same above	Madagascar	surface profile depth profile
	1999	0.26	purplish-pink	Natural Purplish-Pink Sapphire	E	keep half for reference untreated		Madagascar	profile 14 spot analysis
	1999	0.32	orange-pink	Natural Pastel "Padparadscha"	H(Be)	1. cut half 2. treatment of half piece	same above	Madagascar	surface profile depth profile 31 spot analysis
	12570		orange-pink	Natural "pastel" Padparadscha	H(Be)	1. faceted 2. treated 3. cut half piece	same above		1 profile 16 spot analysis surface analysis 4 spot analysis
	121001	0.69	vivid orange-red	Fancy Sapphire "Intense Padparadscha"	H(Be)	1. heated 2. faceted 3. recut to expose inclusion with halo	Chantaburi market Jan 2002	songea (Tanzania)	porfile over inclusion 8 spot analysis
	12636	.045	vivid yellow	Natural Yellow Sapphire	E at elevated pressures (oxidizing conditions)	1. heated 2. recut	Rogers (Bangkok)	Sri Lanka	2 profiles 40 spot analysis

Results LA-ICP-MS

The different colors analyzed (Table A6, Part A) are discussed below, including orangy-pink, white, blue, and yellow sapphires heat-treated with Beryllium. Details of sampling strategy and preparation are summarized in Table A6, and discussed in more details below. The results are given in Tab. A7, A8, A9, A10, A11, A12 and presented on page 61-63 in more details.

Natural Orangy-Pink Sapphires Heat-Treated with Beryllium: Results LA-ICP-MS

The color of the starting material of the orangy-pink sapphire (prior to heat-enhancement) was pink. The samples were each approx. 1 ct in size, and one sample was kept untreated. The samples were first checked by routine gemological testing, including recording of the absorption spectrum, and subsequently sent for heat experimentation in Chantaburi in December 2001. To recognize the stone after heat-enhancement, heart shaped samples were chosen and placed together in a lot with pink sapphires of different shapes. After the heat experiments, the samples were cut in half and their profiles analysed with LA-ICP-MS (See Laser probing ablation craters Fig. A35 and Fig. A40). Two of the samples were later sliced into a 3mm thick plate and checked with Cathodoluminescence, as shown on page 40. Pink sapphires and unheated samples were measured for comparison, with the number of measured points by LA-ICP-MS indicated in Table A6. Typical measured profiles are shown in Fig. A35, A39, A40 and A54. The purpose of the sampling arrangement was to get information on variations in the chemical compositions of the gemstones within steps of 100 micrometers. The profile was positioned in such a way that the variations in chemistry between core and rim on the faceted stones could be studied. The data found is shown in Fig. A36, A37, A38, A41, A42 and also given in Tab. A8, A9, A15.

Concentrations of *Beryllium* (Be), Magnesium (Mg), Titanium (Ti), Vanadium (V), Chromium (Cr), Iron (Fe), and Gallium (Ga) are shown in wt.-ppm (comparison with ED-XRF needs conversion into oxide wt.-%) – Table A5b. Other elements such as Na, Ca, K, and heavy elements, such as Cd and Pb, were found to be unimportant along with other light elements (Lithium and Boron). Two representative samples were checked for additional elements present (Zn, Ge, Ag, Pt, Sn, Pt, Au, Tl and Bi). In all the profiles tested, the dominant elements present were Fe and Cr, followed by minor concentrations of Mg, Ti, V and Ga, as well as Be. All gemstones were enriched with elements in similar areas: Fe, Cr, V, Ti and Mg were depleted in the rim and enriched in an inner rim, while, towards the core, the concentrations decreased, but were less pronounced than towards the outer rim. In contrast,

Beryllium concentrations were highest (maximum concentration approx. 30wt.-ppm) in the outer rim, and penetrated the samples to a depth of about 200-300 micrometers, decreasing within the rim. The highest concentrations of Cr and Fe were not found in the same zones as the *Beryllium* concentrations. The orangy-pink color is concentrated in the inner rim at the positions of the Fe and Cr enrichments. The highest *Beryllium* concentrations were reached in the rim where orange coloration was found (Fig. A38, A41b). Regarding the origin of color, unstable yellow color centers are found in the outer zones of the rim where *Beryllium* concentrations are located (Fig. A26). Regarding the presence of other divalent ions in these zones, it is noted that Magnesium (Mg) is enriched in the zones of higher Cr and Fe. This compositional zoning is confined to the surface of faceted gemstones. The chemical trends with pronounced depletion in the rim were confirmed in total of seven profiles. Details of two other samples of orangy-pink sapphires are given in this report, and a further two samples have been analyzed by both cathodoluminescence, and LA-ICP-MS (Fig. A58). For comparison purposes, further samples unenhanced by heat and pink sapphires were analyzed (Fig. A52). It was found that all the elements were already present in the original material before treatment, with the exception of *Beryllium*, and that the distribution was homogeneous without pronounced rims with Fe and Cr enrichments (Fig. A52). In conclusion, element trends in the treated gemstones are therefore produced by the new Beryllium-treatment – *Beryllium* has been introduced from outside sources, as it is not present in the original material.

Natural White Sapphires Heat-Treated with Beryllium: Results LA-ICP-MS

Although these type sapphires were also subjected to the new heat treatment with Beryllium, almost no change in color did occur. The studied sample was cut in half after the heat treatment experiment and in the subsequently studied with LA-ICP MS (as shown in Fig. A33-A34). Fe concentrations of maximal 700wt.-ppm and more than 100wt.-ppm Mg were achieved by the new treatment in the gemstones more central portions, along with relatively high Ti concentrations (Ti = 100-200wt.-ppm) yet this was not enough to create color in the gemstone, besides a very pale cream. The gemstone's outer rim (where Be concentrations are found) is the location of unstable color centers produced by UV treatment. These faded after exposure to heat (See Fig. A4 and Fig. A5). Only unstable color centers at the rims were detected, obviously related to areas of lowest Ti, Fe and Cr and highest Be-concentrations (Mg/Be-ratio are approx. 10, based on calculation of wt.-ppm values).

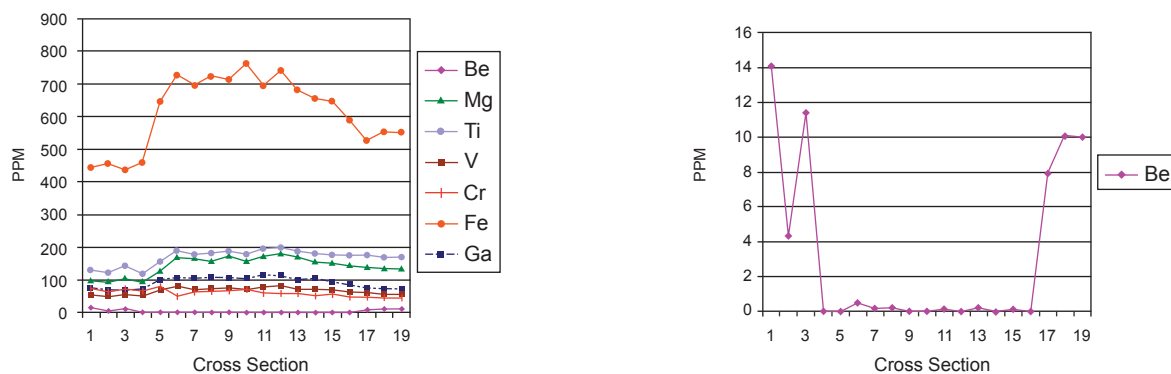


Fig. A33 Chemical compositions in a profile across the white sapphire heat-treated with Beryllium as determined by LA-ICP-MS. Note chemical compositions are dominated by trace element Fe only, while light elements, such as Be and Mg, are subordinate. The Beryllium concentrations are restricted to the outer zone and do not exceed 15wt.-ppm. Note: Decrease of trace elements including Fe and Mg concentrations towards the rim and the increase towards the center of the faceted gemstone, a trend which is confined to the surface of the faceted gemstone. Ti-concentrations are higher than Mg-concentrations (based on calculations of wt.-ppm values).

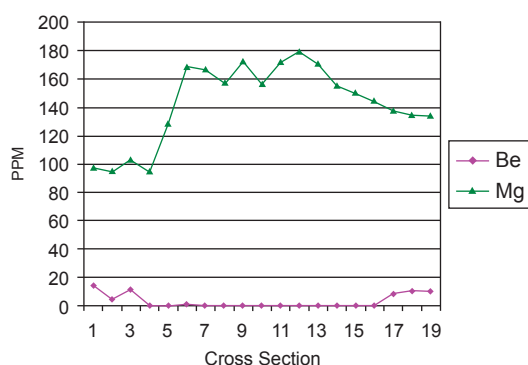
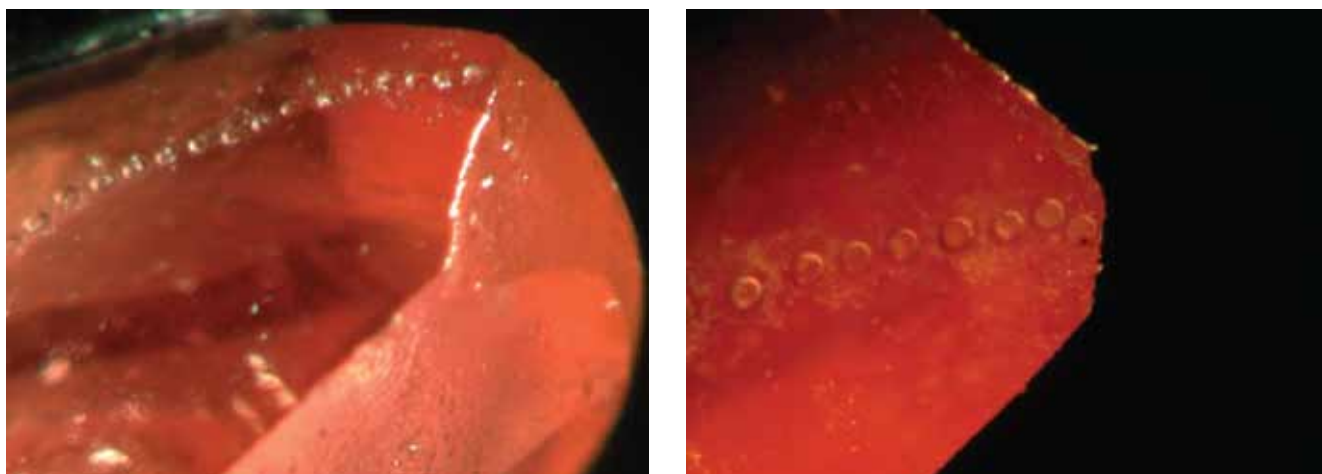


Fig. A34 LA-ICP-MS analysis in a profile across the sample. It is shown that the Beryllium concentrations are restricted to the outer rim outside the observed color zonings. The maximum concentrations are below 15wt.-ppm. It is evident that Be-enrichments occurred outside the zones enriched by Mg.

Table A7: Trace Element Concentrations (in wt.-ppm) of a Natural White Sapphire Heat-Treated with Beryllium. Profile 1-19 across the sample

Sample No. GRS 12922 white

	Be	Mg	Ti	V	Cr	Fe	Ga
1	14.08	97	128	52.1	70.4	443	72
2	4.35	94	121	50.1	64.4	453	69
3	11.41	102	141	53.2	69.1	433	65
4	0	94	119	51.2	67.1	458	70
5	0	127	154	68.8	80.4	645	98
6	0.5	168	188	79.4	50.1	727	104
7	0.18	166	176	71.4	63.3	695	102
8	0.22	156	179	73.0	64.2	720	106
9	0	172	187	76.0	66.6	713	106
10	0	156	175	72.0	71.7	762	102
11	0.12	171	195	77.7	59.2	696	114
12	0.01	179	197	81.6	58.1	740	112
13	0.22	170	185	70.8	57.3	680	98
14	0	154	179	70.6	50.6	655	101
15	0.13	150	174	69.1	55.6	645	91
16	0	143	173	61.9	47.1	589	83
17	7.98	137	174	59.4	46.6	525	73
18	10.11	134	167	56.9	45.7	552	71
19	10.1	133	168	56.9	45.6	551	71



Sample No.GRS 12599

Fig. A35 Faceted orangy-pink sapphire cut in half after Heat-Treatment with Beryllium. A trail of Laser ablation craters is visible (80 micrometer diameter), produced during the measurement of the chemical composition of the gemstones, due to evaporation of test material by applying the Laser. A data point every 100 micrometers could be obtained.

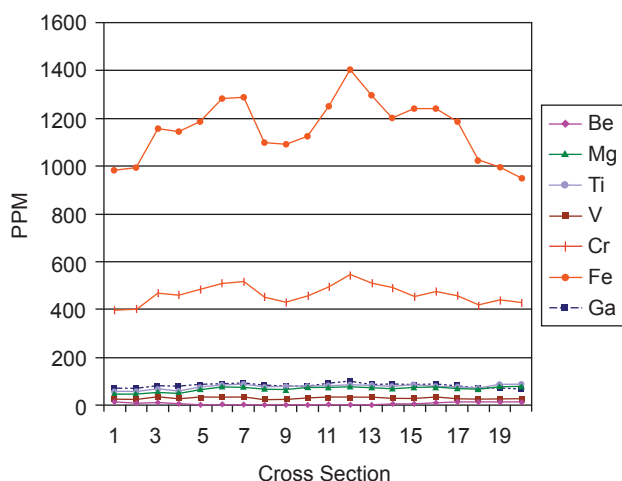


Fig. A36 Chemical variation in a profile through an orangy-pink sapphire heat-treated with Beryllium. All the elements found are shown except Al (in wt.-ppm). Note: Dominant concentrations of Fe and Cr, and the symmetrical variation in composition (depletion of Fe, Cr, Ti, Mg in the outer zone (1-3 and 18-20) and enrichment in points 5-7 and 13-17.).

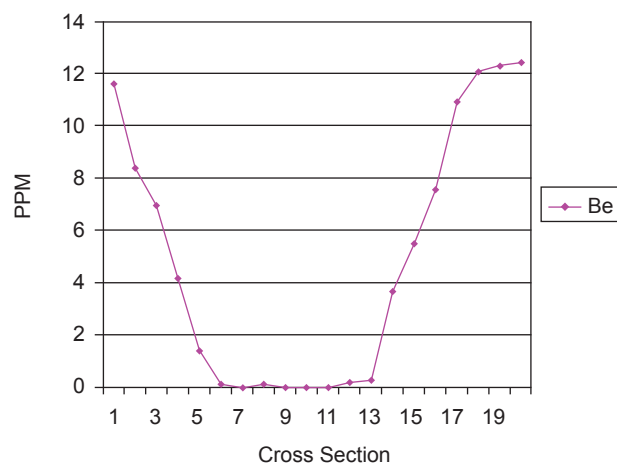


Fig. A37 Same profile as Fig. 44, but only the Beryllium concentrations are shown. Highest Be-concentrations (in wt.-ppm) are found in the rim (points 1-3 and 18-20). The Be-concentrations gradually decrease towards the center (penetration depth into sample approx. 200-300 micrometer)

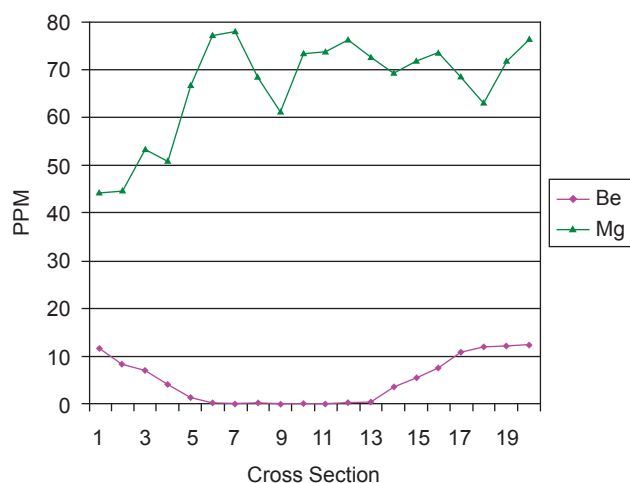


Fig. A38 LA-ICP-MS analysis in a profile across the sample. Comparison of Mg and Be-enriched zones in the enhanced sapphire. The Mg-concentrations (in wt.-ppm) are about 5-10 times higher than the Beryllium concentrations (based on wt.-ppm values) .

Table A8: Trace Element Concentrations (in wt.-ppm) of a Natural Orangy-Pink Sapphire "Padparadscha" Heat-Treated with Beryllium, Profile 1-32 across the sample

Sample No.GRS 12598

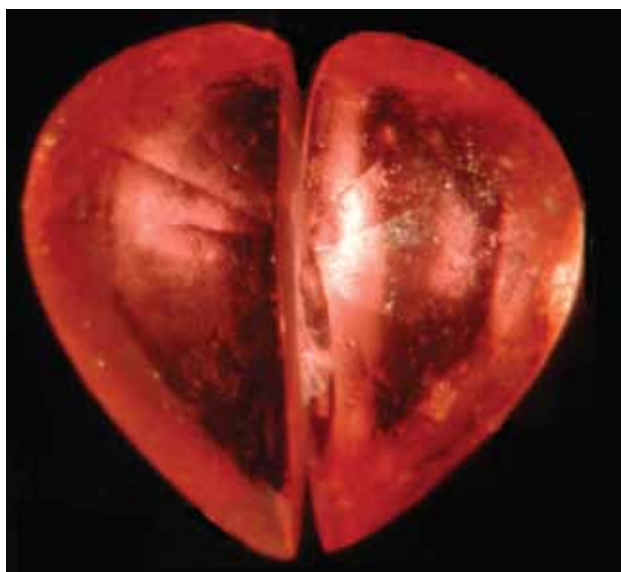
	Be	Mg	Ti	V	Cr	Fe	Ga
1	13.43	46.6	55.5	22.5	320	517	58.6
2	10.94	46.1	57.5	22.8	311	537	58.1
3	9.09	48.3	57.3	23.3	326	533	58.5
4	7.46	49.3	59.6	24.9	341	582	62.4
5	7.5	47.1	58.8	26.1	332	594	64.1
6	7.74	52.3	62.3	27.4	367	605	67.0
7	6.03	63.2	72.9	27.0	378	662	72.0
8	4.75	69.4	84.8	28.3	385	692	73.7
9	3.49	57.1	66.2	26.7	373	656	72.0
10	4.37	61.1	65.6	26.5	380	654	73.2
11	3.33	53.9	60.3	26.5	382	662	73.0
12	4.45	52.4	57.9	27.2	382	677	74.4
13	3.59	49.4	58.8	26.1	377	672	73.8
14	2.64	53.4	58.7	26.8	425	684	74.6
15	0.2	62.3	64.6	29.4	431	734	79.3
16	0.1	57.4	64.6	30.2	426	785	79.3
17	0	64.2	67.3	31.8	435	822	85.0
18	0.41	63.2	64.5	30.5	514	788	82.0
19	0	64.4	69.6	33.9	455	823	85.1
20	0.01	66.4	69.0	31.5	438	780	84.3
21	0	61.8	70.4	31.8	451	768	84.8
22	0	67.4	73.1	32.1	450	781	85.1
23	0	64.6	67.6	30.7	379	761	82.9
24	0.15	64.2	64.0	31.6	443	816	86.8
25	0	62.4	61.3	32.2	436	752	90.2
26	2.58	52.6	59.1	28.3	388	696	79.2
27	5.29	50.0	57.0	26.8	353	654	73.7
28	6.9	45.2	53.8	24.7	335	600	70.1
29	9.5	44.7	52.8	22.7	321	547	62.9
30	11.8	43.5	54.2	23.0	297	532	59.2
31	12.33	45.3	52.5	22.6	301	539	58.3
32	11.79	44.0	52.4	22.4	306	517	58.7

Table A9: Trace Element Concentrations (in wt.-ppm) of a Natural Orangy-Pink Sapphire "Padparadscha" Heat-Treated with Beryllium, Profile 1-20 across the sample

Sample No.GRS 12599

	Be	Mg	Ti	V	Cr	Fe	Ga
1	11.62	44.2	53.7	23.3	396	979	66.6
2	8.39	44.6	54.4	23.7	400	991	65.7
3	6.96	53.2	61.9	29.0	464	1156	77.4
4	4.15	50.8	56.0	26.9	459	1142	76.4
5	1.41	66.7	73.7	28.6	479	1185	79.8
6	0.14	77.1	81.8	29.8	508	1277	85.3
7	0.01	77.8	81.9	30.1	515	1285	86.0
8	0.12	68.4	73.9	24.5	448	1097	78.9
9	0	61.1	72.5	24.1	427	1087	76.1
10	0	73.3	73.5	25.1	453	1122	77.8
11	0	73.7	79.4	28.8	494	1249	88.7
12	0.19	76.1	80.6	31.6	542	1406	93.5
13	0.3	72.6	81.2	29.8	508	1295	85.2
14	3.68	69.2	78.0	27.7	487	1200	83.6
15	5.52	71.8	78.9	28.0	455	1236	82.1
16	7.56	73.4	76.0	29.0	472	1237	83.3
17	10.91	68.5	75.5	27.6	458	1185	79.3
18	12.06	63.0	69.0	24.2	415	1019	68.6
19	12.28	71.8	85.3	23.1	437	993	69.2
20	12.41	76.3	83.2	22.7	427	948	66.2

*LA-ICP-MS Analysis of Natural Orangy-Pink Sapphires ("Padparadscha")
Heat-Treated with Beryllium*



Sample No. GRS 12598

Fig. A39 Heart-shaped pink sapphires were subjected to heat-treatment with Beryllium. On the left, a sample which was heat-treated and subsequently cut in half, while on the right, a half piece from another pink sapphire kept untreated for comparison. Each is about 0.5ct in weight. Note: Color change from pink to orangy-pink due to the Beryllium-Treatment process.

Fig. A40 An orangy-pink sapphire cut in half after treatment. The trail of Laser Ablation craters is also shown. The chemical data obtained allows for conclusions on the chemical composition in the faceted gemstone in profile across the sample.

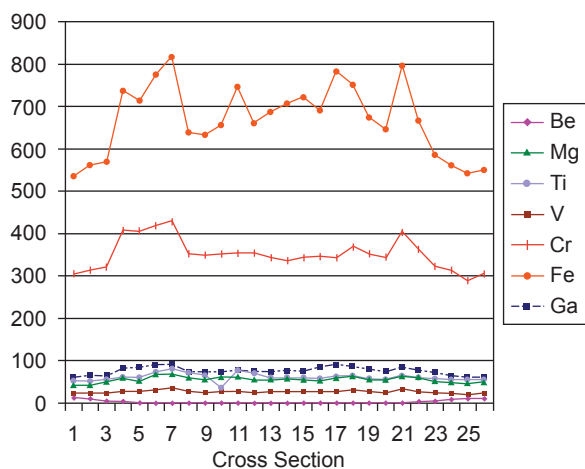


Fig. A41a The chemical variations in a profile across the faceted and Beryllium-Treated orangy-pink sapphire is shown (in wt.-ppm). Note: depletion of trace elements in the rim (including Ti) of the faceted gemstone and enrichment in an inner rim (No. 5-8 and 19-22), including Cr, Fe and Mg. Beryllium is enriched in the outer rim.

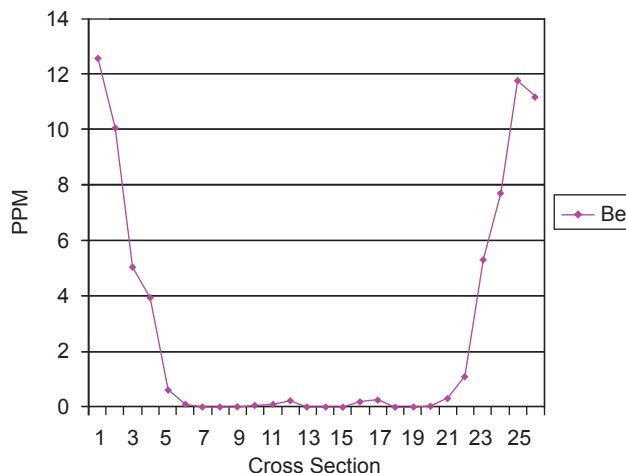


Fig. A41b The distribution of Beryllium in a profile through a faceted orangy-pink sapphire. Note: Be concentrations are found in the outer rim only (max. 14wt.-ppm).

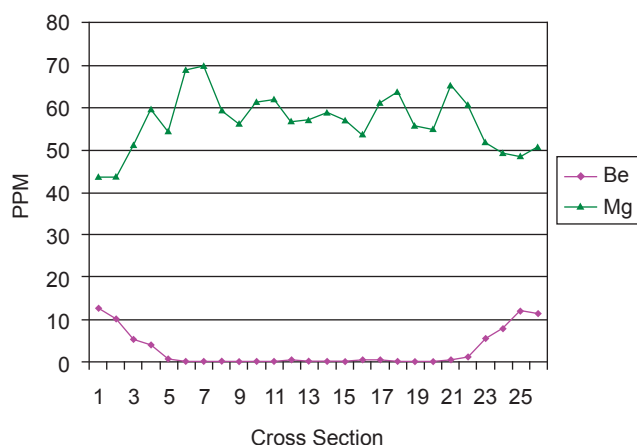


Fig. A42 LA-ICP-MS analysis in a profile across the sample (in wt.-ppm). Mg and Be-enriched concentrations in the enhanced sapphire are shown. The Mg-concentrations are depleted at the outer rim and the Be-concentrations are enriched

Natural Blue Sapphires Heat-Treated with Beryllium: Results LA-ICP-MS

The study of the blue sapphires Beryllium-Treated shows that color zoning in the gemstones is not related to the presence of Beryllium. The color zoning is produced in this sample from a pre-existing whitish band containing titanium. A diffusion of titanium, seen as a blue halo around the white band, occurred. The diffusion of titanium is restricted to about 200 micrometers, and well supported by chemical data. Due to a pre-existing in homogeneous chemical composition in the gemstone, heat-enhancement produced a complicated color zoning pattern with orangy-pink and blue oscillations (Fig. A45). The chemical zoning regarding Fe and Cr is following the faceted surface of the gemstone, with depletion in the rim and enrichments towards the center. Interference with the titanium zoning, at positions of both titanium and Fe-enrichments, has produced a blue color. "Padparadscha" colors were produced at Fe greater than 800wt.-ppm, Cr greater than 200-300 wt.-ppm, Ti lower than 200wt.-ppm, and Mg greater than 80wt.-ppm, while blue colors were produced at Fe greater than 800wt.-ppm and Ti greater than 200wt.-ppm. All the trace elements found in these samples which are responsible for the color can be found in the natural unheated colored sapphires (Fig. A19, A52 and Table 5 and Appendix page 46 and 47). The zones of Beryllium in this sample were found to be concentrated in the outer areas containing unstable color centers (Fig. A4). Therefore orange colors were formed both, in areas with and without Beryllium.

Sample No. GRS 12925.1

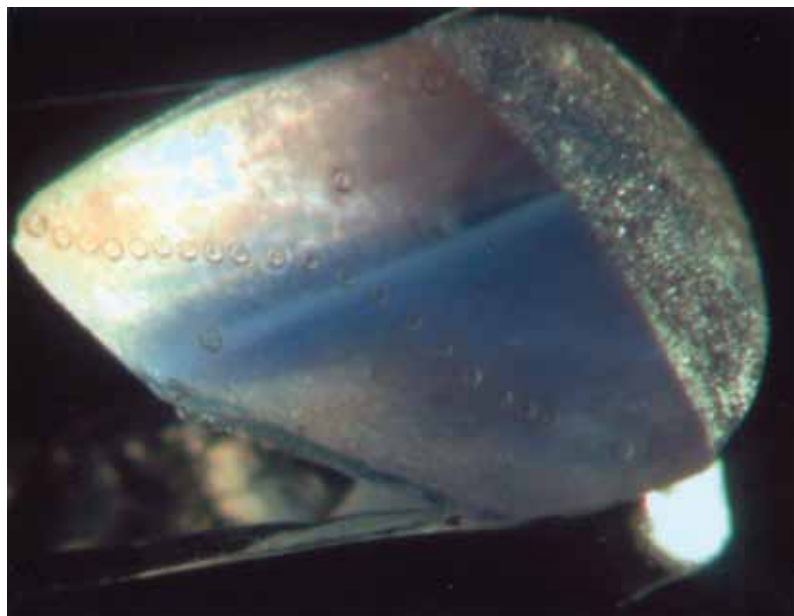


Fig. A43 Microphotograph of a princess cut sapphire heat-treated with Beryllium (second half of the piece shown in Fig. A46). The sample was cut in half after treatment and probed by LA-ICP MS in a profile across the sample. Craters are due to Laser sampling

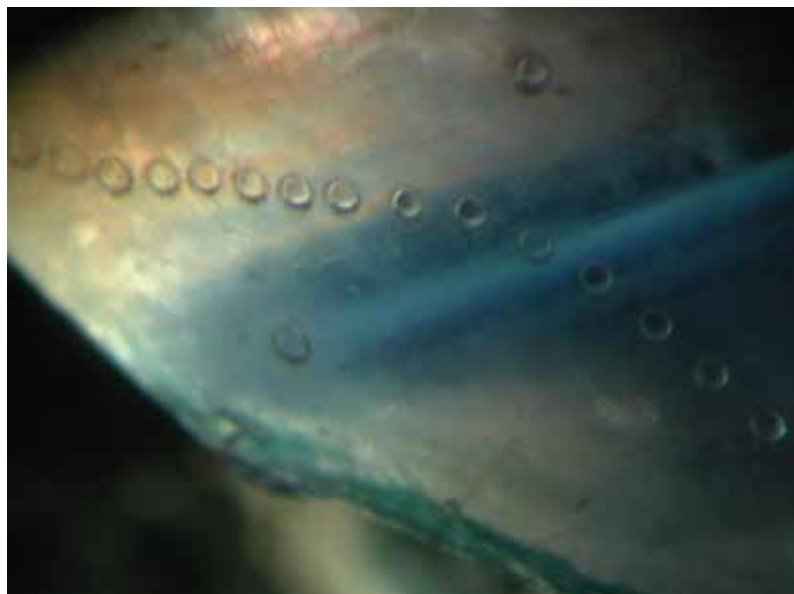


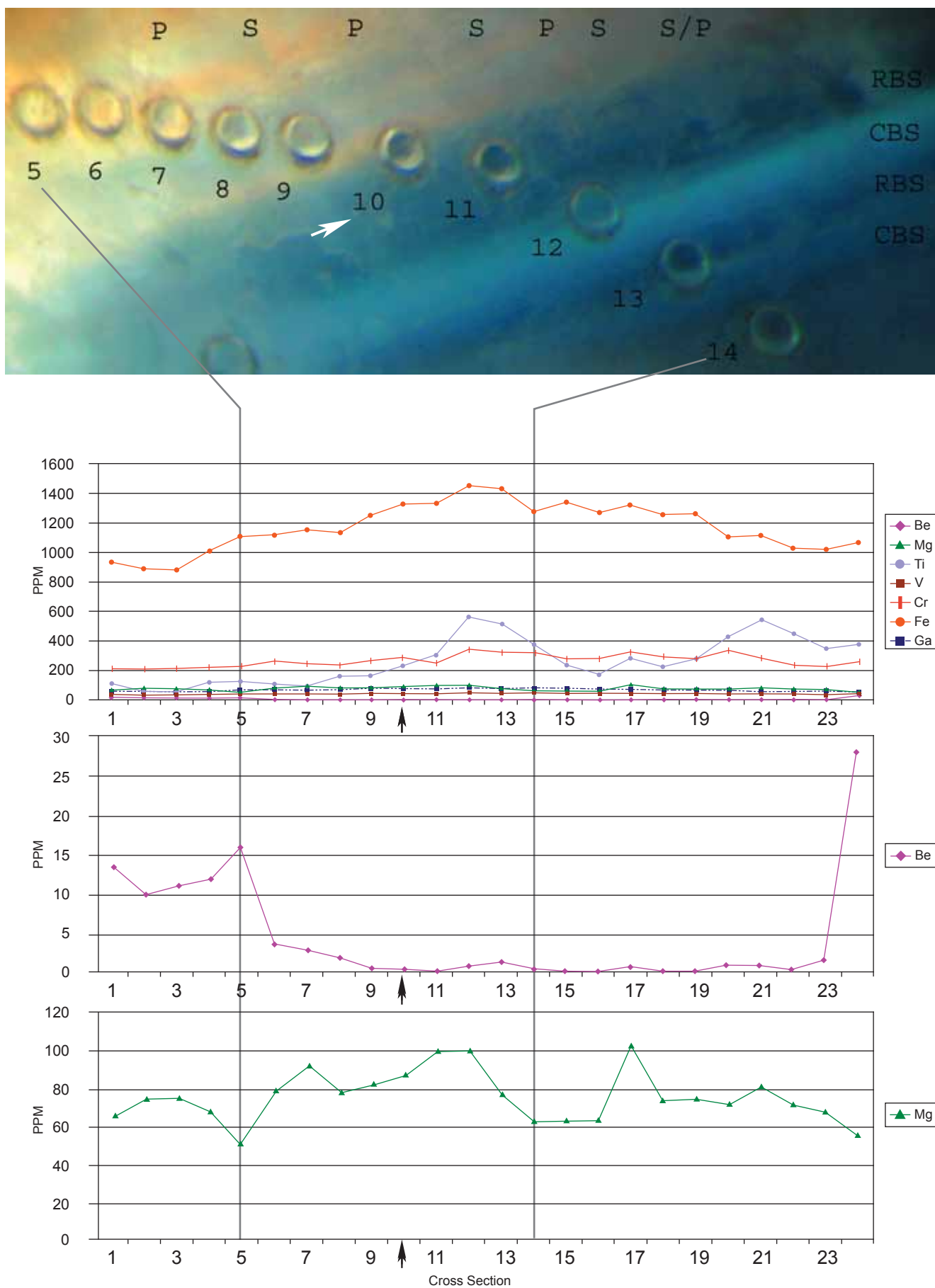
Fig. A44 Extended part of Fig. A43 shows that the sampling is sufficient to collect information on the chemical variations in the gemstone in relation to color zoning present. Note a broad band of blue color on both sides of a whitish-blue band, defining an approximately 200 micron broad blue diffusion zone on each side

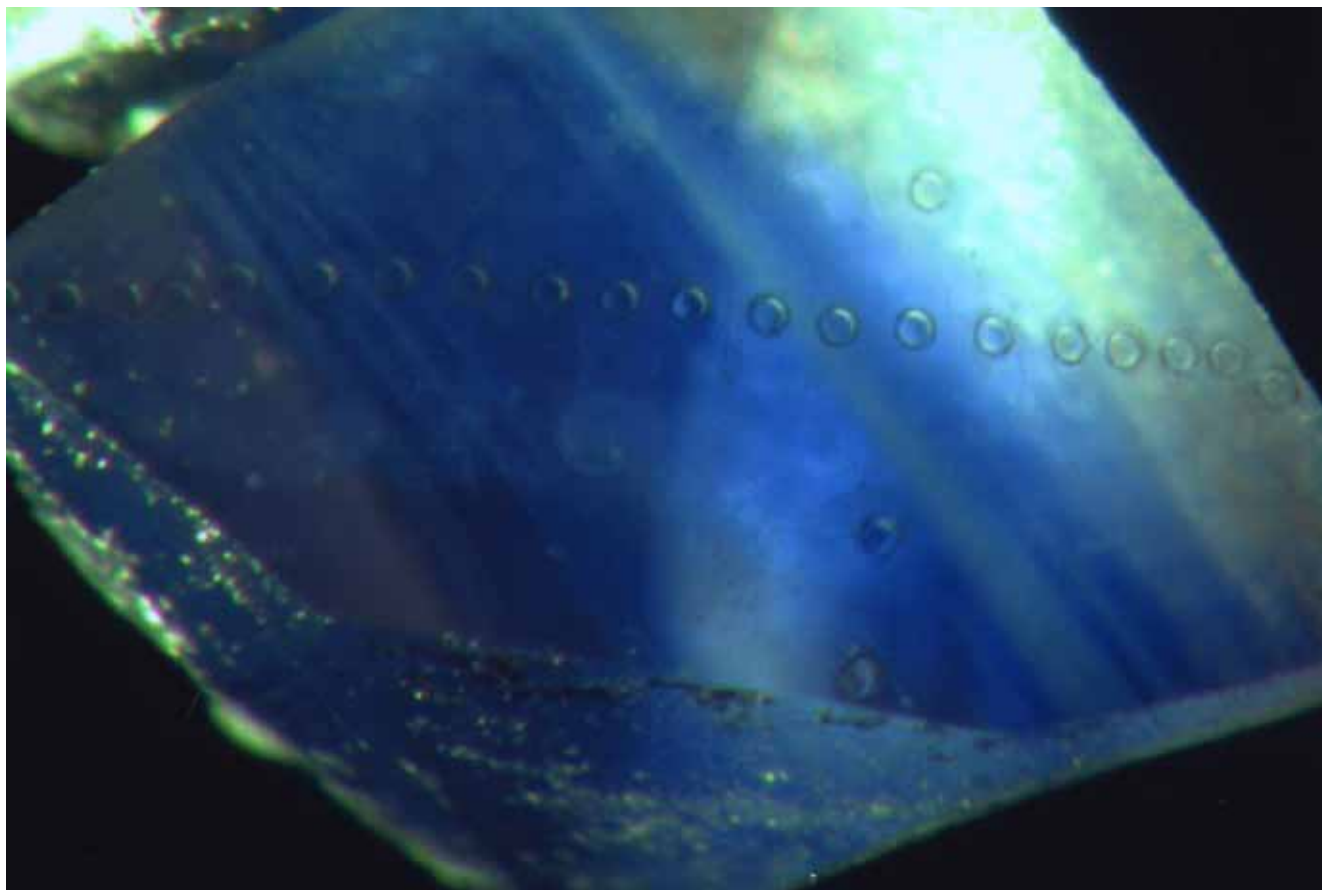
Fig. A45, page 30

The chemical compositions (in wt.-ppm) in a profile across a Beryllium-Treated sapphire as determined by LA-ICP-MS. Note: Chemical compositions are dominated by trace elements Cr, Fe, and Ti - light elements, such as Be and Mg, are subordinate. The Beryllium concentrations are restricted to the outer zone and do not exceed 30wt.-ppm. Magnesium (Mg) is found in the entire profile with concentrations of about 50 to 100wt.-ppm. Note: Zones rich in Mg at the absence of Be are found at points 6 to 10. At Ti below 150wt.-ppm, Cr above 200wt.-ppm and Fe above 1000wt.-ppm "Padparadscha" colors may be formed. This corresponds well to the observed color banding in the gemstone. Note: Point No. 10 (See arrow) is a "Padparadscha" color band containing Fe, Cr, V, Ti and Mg but no Beryllium. Orange color in zones containing Beryllium are found in the outer zone between point 1-5.

LA-ICP-MS Analysis of Natural Blue Sapphires Heat-Treated with Beryllium with Details of Trace Element Concentrations

Fig. A46 Expanded area of Fig. A44 shows details of the color zoning, and the points measured by LA-ICP-MS. The numbers refer to the measured points. color zoning is subdivided into orangy-pink “Padparadscha” (P), pastel blue (S), cornflower blue (CB) and royal blue (RB). Beryllium concentrations are restricted to the zones. (1-5 and 23-24). Element concentrations expressed in wt.-ppm.





Sample No. GRS 12925.2

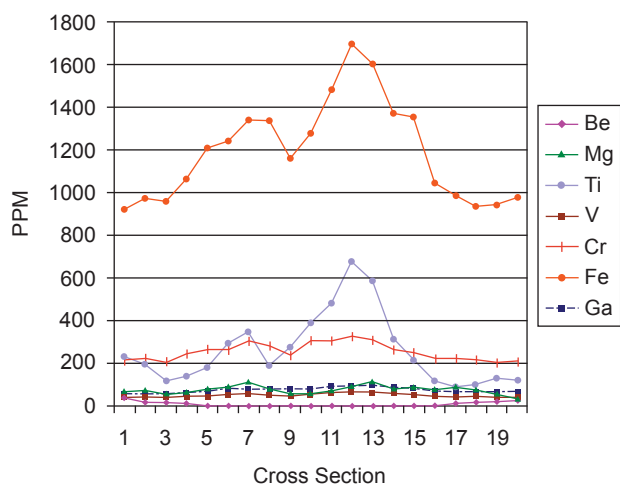


Fig. A46a,b The chemical compositions (in wt.-ppm) in a profile across the blue sapphire (heat-treated with Beryllium) as determined by LA-ICP-MS. Note: Chemical compositions are dominated by trace elements Cr, Fe, and Ti and light elements, such as Be and Mg, are subordinate. The Beryllium concentrations (in wt.-ppm) are restricted to the outer zone and do not exceed 30wt.-ppm. Note: Zones rich in Fe and Ti are found in broader zone at points 5 to 15 with a maximum at point 12. The blue band is confined to the zones enriched in both Fe and Ti. Note: Decrease of Fe concentrations towards the rim and the increase towards the center of the faceted gemstone. Mg concentrations are depleted in the rim and concentrated towards the core (Range between 26 and 106wt.-ppm). At high Ti concentrations no "Padparadscha" colors are formed.

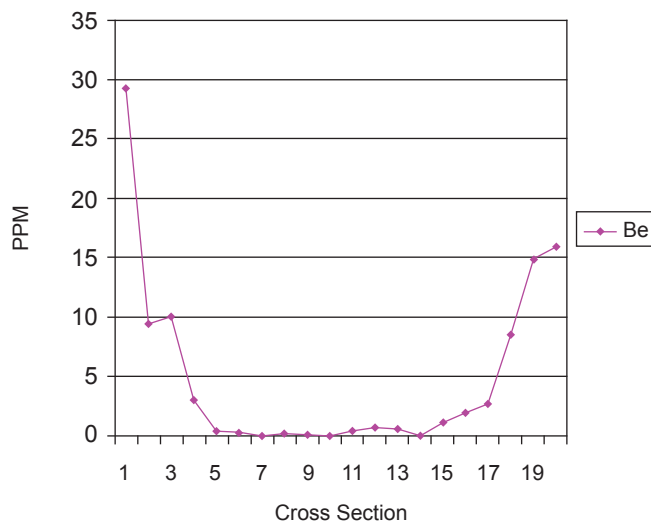
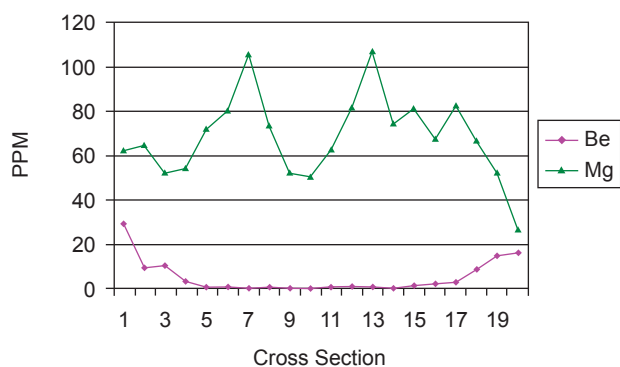


Fig. A47a,b LA-ICP-MS analysis in a profile across the sample. It is shown that the Beryllium concentrations (in wt.-ppm) are restricted to the outer rim outside the observed color zonings. The maximum concentrations are below 30wt.-ppm. In Fig. A47a, it is evident that Beryllium (Be)-enrichments occurred outside the enrichment of Mg.

*LA-ICP-MS Analysis of Natural Blue Sapphires Heat-Treated with Beryllium
with Details on Trace Element Concentrations.*

Table A10: Trace Element Concentrations (in wt.-ppm) of a Natural Blue Sapphire Heat-Treated with Beryllium, Profile 1-20 across the sample

Sample No.GRS 12925.2

	Be	Mg	Ti	V	Cr	Fe	Ga
1	29.25	62	225	34.2	211	916	47.3
2	9.47	64	190	34.7	217	967	49.0
3	10.01	52	105	33.0	198	954	48.3
4	3.01	53	128	37.6	236	1058	53.7
5	0.41	71	170	40.4	256	1206	61.4
6	0.27	80	284	41.7	259	1242	68.5
7	0	105	338	48.6	295	1337	69.6
8	0.2	73	182	42.3	273	1332	70.2
9	0.09	52	268	40.3	233	1159	69.9
10	0	50	384	47.9	295	1273	69.5
11	0.45	62	474	54.8	295	1480	79.9
12	0.71	81	673	60.9	319	1697	84.2
13	0.56	106	582	54.6	302	1600	87.2
14	0	74	307	50.6	259	1370	77.7
15	1.19	81	204	46.6	244	1351	75.3
16	1.94	67	106	37.0	216	1041	60.5
17	2.72	82	83	34.8	217	982	56.9
18	8.52	66	90	33.4	212	931	57.0
19	14.83	51	121	33.6	193	936	55.0
20	15.91	26	111	34.2	204	971	55.6

Table A11: Trace Element Concentrations (in wt.-ppm) of a Natural Blue Sapphire Heat-Treated with Beryllium, Profile 1-24 across the sample

Sample No.GRS 12925.2

	Be	Mg	Ti	V	Cr	Fe	Ga
1	13.53	65.3	105	33.5	212	930	52.5
2	10.02	74.2	59	31.5	206	885	51.8
3	11.16	74.7	55	31.7	209	875	48.9
4	12	67.5	114	35.9	218	1008	55.0
5	15.57	50.9	122	37.7	227	1107	61.7
6	3.35	79.7	105	38.6	259	1114	63.6
7	2.83	91.9	88	37.7	245	1148	63.1
8	1.79	78.5	158	38.4	232	1130	64.4
9	0.2	82.2	161	41.6	263	1249	73.8
10	0.16	86.9	225	43.7	287	1325	71.1
11	0.09	99.2	299	43.5	249	1324	72.6
12	0.75	99.6	557	47.8	340	1448	80.1
13	1.18	76.2	514	46.9	320	1427	74.3
14	0.16	62.2	371	44.1	316	1271	75.7
15	0.08	62.6	234	42.1	274	1336	72.4
16	0.1	62.7	167	40.7	279	1266	70.4
17	0.29	102.8	280	43.1	321	1315	69.6
18	0.08	73.5	219	41.8	291	1250	63.0
19	0	74.6	275	40.4	272	1257	61.7
20	0.51	71.6	426	37.8	333	1100	56.5
21	0.61	81.4	545	39.6	284	1111	54.7
22	0.14	71.4	446	36.7	233	1024	51.9
23	1.51	67.4	345	35.4	225	1014	52.1
24	28.05	55.3	374	37.5	256	1063	55.4

Natural Yellow Sapphires Heat-Treated with Beryllium: Results LA-ICP-MS

The yellow sapphire was produced from a near colorless sapphire by heat-treatment with Beryllium, cut in half, and then the chemical compositions were measured in a profile across the sample (See Table A6). Chemical zoning was found in the gemstone confined to the faceted surface of the sample as shown in Fig. A49 and A50. This zoning was therefore produced by the Beryllium-Treatment.

The dominant trace element in this gemstone is Fe, while all other elements found in the gemstone are below 200wt.-ppm. Beryllium concentrations are restricted to the gemstone's outer zone (15 wt.-ppm maximum), the rim of the gemstone shows a depletion in Fe, and Fe and Mg is enriched towards the center. A large portion of the gemstone reaches levels higher than approx. 800wt.-ppm of Fe-, and Mg concentrations are always greater than Ti-concentrations (based on wt.-ppm values). This seems to be the ideal combination for coloring the sample yellow by the Beryllium-Treatment (such as divalent-cation-trapped hole color-centers) (Lit. 4 and Lit. 24).

The gemstone's outer rim - where Be concentrations are found - is the location of orange colored unstable color centers produced by UV light exposure (See Table A1). These faded after mild exposure to heat.



Sample No. GRS 12540

Fig. A48 Microphotograph of a princess cut yellow sapphire heat-treated with Beryllium. The sample was cut in half after treatment and probed by LA-ICP-MS in a profile across the sample (See craters).

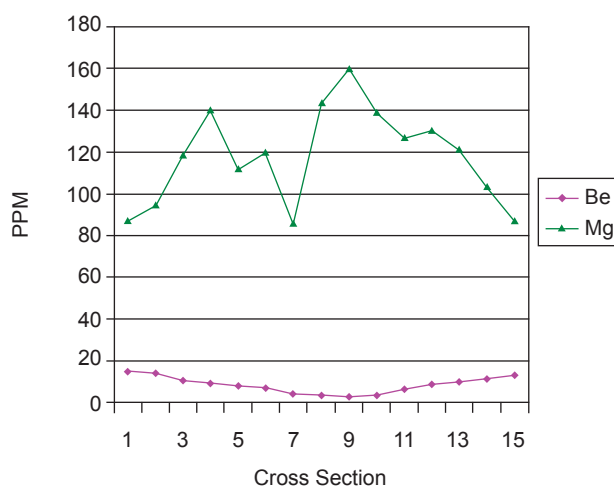


Fig. A49 LA-ICP-MS analysis in a profile across the sample. It is shown that the Beryllium concentrations (in wt.-ppm) are restricted to the outer rim. Mg is enriched in an inner rim. The maximum Beryllium concentrations are below 15wt.-ppm.

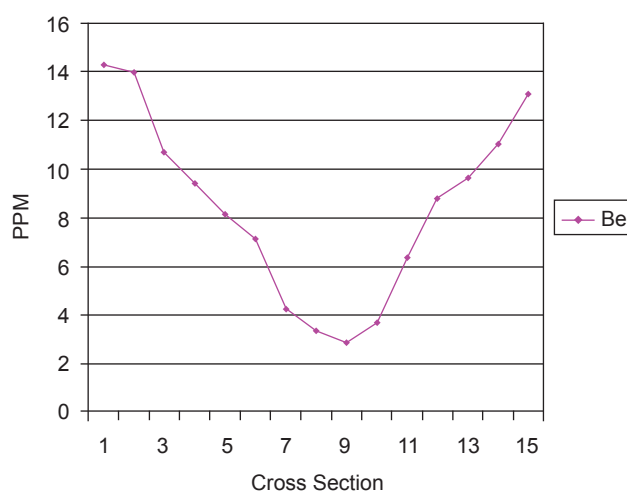
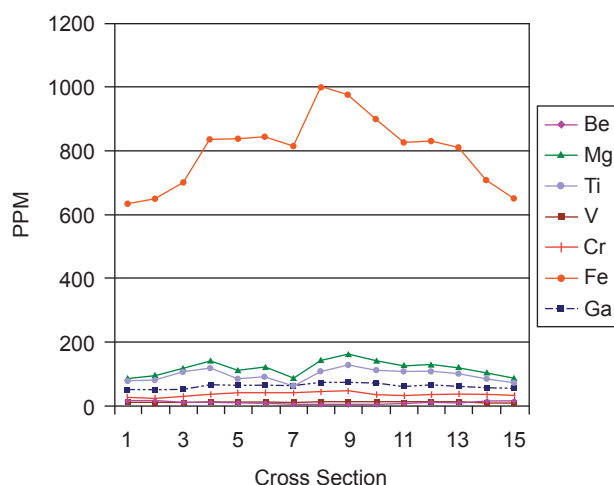


Fig. A50a,b Chemical compositions (in wt.-ppm) in a profile across the yellow sapphire heat-treated with Beryllium as determined by LA-ICP-MS. Note: Chemical compositions are dominated by trace element Fe and Mg compositions, while light elements, such as Beryllium are subordinate (in wt.-ppm). The Beryllium concentrations are restricted to the outer zone and do not exceed 15wt.-ppm. Decrease of Fe and Mg concentrations towards the rim, and the increase towards the center of the faceted gemstone. Mg/Ti-ratio is high (based on wt.-ppm values).

*LA-ICP-MS Analysis of Natural Yellow Sapphires Heat-Treated with Beryllium
with Details on Trace Element Concentrations.*

Table A12: Trace Element concentrations (in wt.-ppm) of a Natural Yellow Sapphire Heat-Treated with Beryllium, Profile 1-15 across the sample

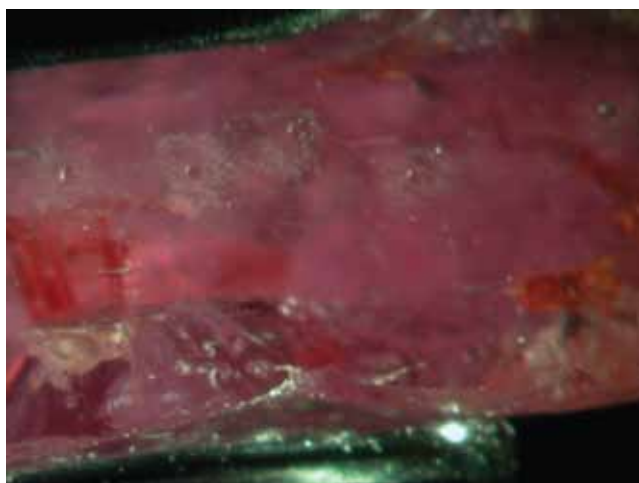
Sample No. GRS 12540

	Be	Mg	Ti	V	Cr	Fe	Ga
1	14.32	87	77	8.11	26.8	634	47.5
2	14.01	94	80	8.41	22.1	650	48.4
3	10.71	118	106	9.18	28.7	699	50.0
4	9.44	140	116	10.77	34.9	835	64.2
5	8.17	112	82	10.68	41.2	835	64.1
6	7.14	119	89	10.65	39.5	844	63.4
7	4.28	86	62	9.46	41.1	814	63.1
8	3.39	143	105	12.29	43.9	999	72.4
9	2.88	160	126	12.52	44.8	976	71.8
10	3.71	139	108	11.79	35.1	900	69.3
11	6.36	126	106	10.83	32.4	823	60.4
12	8.81	130	104	10.70	33.1	829	62.7
13	9.65	120	99	10.55	37.6	810	59.0
14	11.06	103	83	9.15	34.7	707	53.6
15	13.11	86	70	8.14	32.4	651	50.1

Natural Unheated Purple Sapphires Results LA-ICP-MS

This sample is representative for those that can be successfully heat treated using Beryllium (See Fig. A19 (Field LP and P). The same elements are found in the treated samples (Fe, Cr, Ti, V, Mg, Ga), except Be which is missing in the natural sancy sapphires not enhanced by heat. Of particular interest is the ratio of Mg/Ti which in this sample is almost equal to 1 (based on wt.-ppm).

Note: The pronounced chemical zoning (observed in the treated samples) is absent.



Sample No. GRS 1498

Fig. A51 Microphotograph of a purple sapphire unenhanced by heat. LA-ICP MS craters are shown (80 micrometer diameter). Representative for samples that can be successfully heat treated with Beryllium.

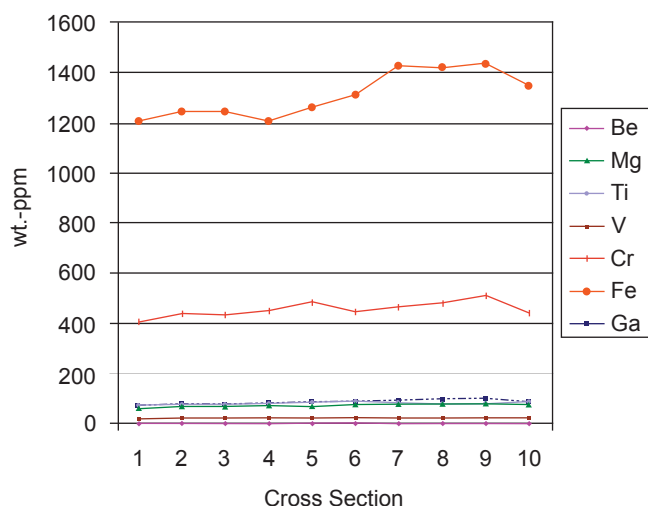


Fig. A52 Profile across the sample of Fig. A51 shows the chemical variations (in wt.-ppm) in the gemstone due to its natural composition. No depletion and no symmetric chemical zonings were present, particularly regarding the lighter elements Mg and Ti. Note: Similar chemical compositions (dominantly Fe, Cr, Ti, V, Mg, Ga) are present as in the enhanced counterparts, with the exception of Beryllium which is absent. Ti concentrations are almost equal to Mg concentrations if expressed in wt.-ppm.

Table 13: Trace Element Concentrations (in wt.-ppm) of a Natural Purple Sapphire Unenhanced by Heat Profile 1-10 across the sample

Sample No. GRS 1498

	Be	Mg	Ti	V	Cr	Fe	Ga
1	0	62.8	71.5	20.97	405	1205	72.5
2	0.19	68.2	75.6	21.57	440	1242	75.0
3	0.07	69.5	77.9	21.5	437	1243	78.4
4	0	73.5	81.8	22.51	453	1206	80.4
5	0.17	69.3	87.0	22.52	484	1261	83.1
6	0	75.6	88.2	22.25	446	1314	89.5
7	0.26	79.5	83.8	21.44	466	1429	91.4
8	0	81.0	81.8	21.41	482	1421	94.7
9	0.3	79.0	80.4	22.65	512	1437	100.0
10	0.01	77.3	87.7	21.64	445	1349	89.5

LA-ICP-MS Analysis of Natural Unheated Violet Sapphires and Beryllium-Treated Orangy-Pink Sapphire with Details of Trace Element Concentrations

Table A14: Trace Element Concentrations (in wt.-ppm) of a Natural Violet Sapphire Unenhanced by Heat (N). Profile 1-17 across the sample

Sample No.GRS 12702

	Be	Mg	Ti	V	Cr	Fe	Ga
1	0	55.7	72.9	25.4	425	1044	69.2
2	0.28	57.2	72.3	26.4	457	1053	71.4
3	- 0.28	58.3	73.9	26.1	469	1080	78.8
4	- 0.08	62.3	73.5	26.2	462	1114	83.7
5	0.1	58.9	76.2	27.0	459	1103	77.5
6	- 0.22	57.1	69.4	26.5	477	1111	84.3
7	0	63.7	70.0	28.4	491	1146	84.6
8	- 0.16	56.0	66.7	27.5	495	1182	88.0
9	0.08	66.1	74.9	32.5	549	1254	95.4
10	0.2	49.1	60.4	25.0	445	973	78.1
11	- 0.18	52.4	63.7	26.4	463	991	79.5
12	0.12	52.9	63.6	25.8	470	989	79.1
13	0.06	52.5	63.7	25.8	469	990	78.7
14	0	69.3	87.8	23.6	423	896	70.7
15	0	73.7	89.4	23.7	418	887	71.1
16	0.04	74.3	85.4	23.3	432	896	70.2
17	0.12	62.7	79.3	23.7	427	841	66.1

Table A15: Trace Element Concentrations (in wt.-ppm) of a Natural Orangy-Pink Sapphire "Padparadscha" Heat-Treated with Beryllium, Profile 1-26 across the sample

Sample No.GRS 12911

	Be	Mg	Ti	V	Cr	Fe	Ga
1	12.57	43.5	53.5	23.0	304	534	59.6
2	10.05	43.3	52.0	23.9	312	560	64.6
3	5.05	50.9	55.5	23.2	320	568	63.4
4	3.98	59.5	61.0	28.8	408	736	81.7
5	0.63	54.3	60.0	27.8	407	714	84.3
6	0.11	68.6	73.0	30.9	418	773	89.8
7	0	69.7	81.6	34.4	430	816	89.5
8	0	59.1	70.1	27.6	352	637	72.9
9	0	56.0	66.7	26.1	351	631	73.2
10	0.07	61.3	37.0	27.3	352	654	73.1
11	0.06	61.6	75.3	28.4	354	745	76.3
12	0.24	56.4	70.7	26.6	353	660	74.7
13	0	56.9	59.6	28.3	343	685	74.0
14	0	58.5	59.9	27.9	338	706	75.9
15	0	56.8	60.2	27.3	344	722	75.6
16	0.2	53.5	59.0	28.1	346	689	83.8
17	0.26	60.8	62.9	28.9	344	781	90.8
18	0	63.6	65.4	29.6	370	749	85.5
19	0	55.5	57.9	27.3	351	671	78.7
20	0.02	54.7	56.8	25.9	343	644	75.5
21	0.33	65.1	65.5	32.2	402	794	83.1
22	1.11	60.4	60.2	27.6	362	665	77.4
23	5.3	51.7	57.6	24.9	321	586	70.5
24	7.69	49.0	56.4	22.6	314	560	65.3
25	11.76	48.2	55.3	22.1	289	541	60.5
26	11.19	50.3	55.6	22.9	306	549	61.2

Comparison of Beryllium-Treated Fancy Sapphires (H(Be)) with Surface Diffusion-Treated Sapphires (T)

Diffusion-treated and fancy sapphires heat with Beryllium the new treatment (pastel colors and vivid colors) can be easily distinguished by both gemological properties (Lit. 14 and Lit. 15) and chemical composition as discussed below. For comparison purposes, we use a blue surface diffusion-treated sapphire. The randomly selected diffusion-treated sample (Fig. A53 and Table A16a) does not contain any *Beryllium*, Ti-concentrations are concentrated at the outer rim, and other chemical elements do not follow Ti-enriched trends. Ti is introduced into the gemstone by diffusion from outside, and only one element is enriched in the rim (Ti concentrations are embedded in a chemistry typical of a natural sapphire, with considerable Fe present, as a natural white sapphire was used for the diffusion treatment). The blue color is interpreted as being produced by Fe²⁺-Ti⁴⁺ pairs (For further discussions See Table A16a-A16c).

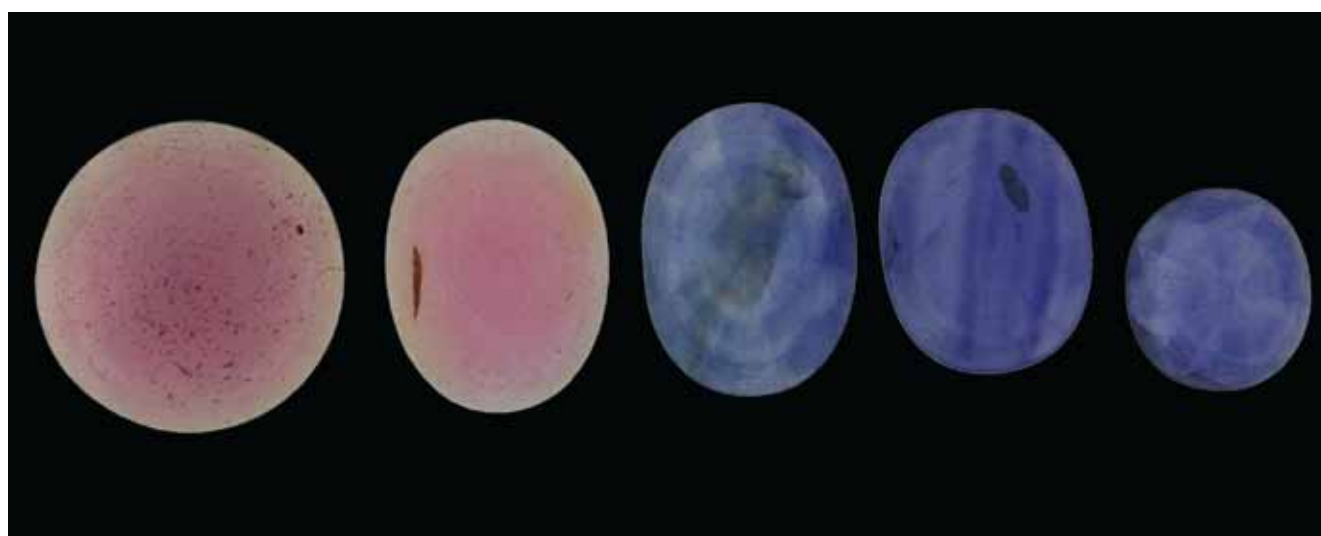


Fig. A53 Two Beryllium-Treated orangy-pink sapphires and three surface diffusion-treated sapphires as seen in Oil immersion. Note the near-surface related blue coloration induced by Ti-diffusion and the more deep penetration of the orange coloration due to Beryllium-Treatment.

Average	Position		Be	Mg	Ti	V	Cr	Fe	Ga	Al
7	Center	Average	0.1	50.1	68.6	6.1	12.0	599	57.1	526604
		Std Dev	0.1	6.8	17.0	0.3	19.9	39.1	4.7	norm
4	Rim	Average	0.1	42.9	540	5.4	1.6	811	46.8	526604
		Std Dev	0.1	2.0	181	0.2	1.9	219	1.6	norm

Table A16a
T - Example: Surface Diffusion-treated Sapphire.

Chemical composition (LA-ICP-MS in wt.-ppm) of a diffusion-treated sapphire (Fig. A53). The rim and the core of the sample were measured to show characteristics of a so-called “surface diffusion-treated” sapphire (T). Note: Increase of Ti only in the rim (with Fe from the sapphires composition) is responsible for the formation of color in these treated sapphires, while the other elements remain unchanged (Alumina “Al” fixed by normalisation to 526604 wt.-ppm).

Average	Position		Be	Mg	Ti	V	Cr	Fe	Ga	Al
7	Center	Average	0.7	93.8	99.5	18.3	562	1686	82.2	526604
		Std Dev	0.8	8	8.9	1.1	58.6	120.5	6.9	norm
4	Rim	Average	6.4	68.5	78.8	13.8	425	1330	65.4	526604
		Std Dev	2	10.3	11.3	0.8	38	74.6	4.5	norm

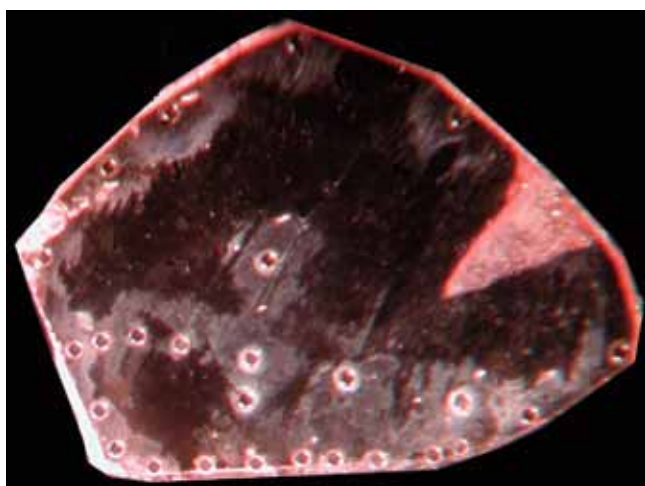


Fig. A54 Sample No.GRS 12910
Natural orangy-pink sapphire heat-treated with Beryllium.
Craters from LA-ICP-MS testing (3 Profiles).

Table A16b
Beryllium-Treated Example: Natural Orangy-Pink Sapphire ("Padparadscha").
Origin: Madagascar

Chemical compositions (LA-ICP-MS in wt.-ppm) of a Madagascar orangy-pink sapphire ("Padparadscha") (Fig. A54) treated with Beryllium with compositional differences in the outer rim and core. Note: Decrease of trace elements in the gemstones' rim and the presence of Beryllium (Be).

Average	Position		Be	Mg	Ti	V	Cr	Fe	Ga	Al
7	Center	Average	5.2	62.1	74.2	12.5	824	8640	59.2	526604
		Std Dev	1.2	18.0	18.3	2.6	159	1056	3.3	norm
7	Rim	Average	7.3	31.1	40.2	10.6	458	6766	42.1	526604
		Std Dev	0.5	14.9	5.8	0.4	83.2	210	2.3	norm

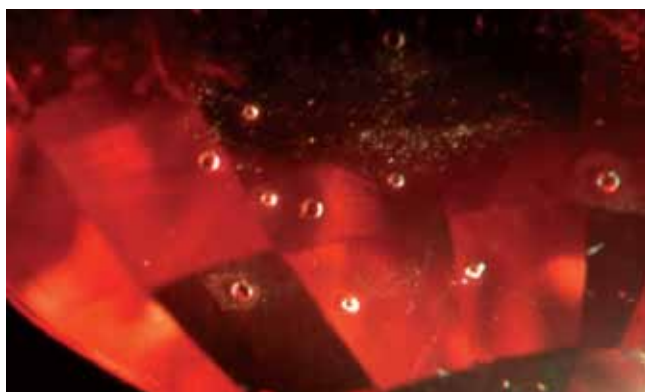


Fig. A55 Sample No.GRS 782
Natural orange-red sapphire from Songea (Tanzania) heat-treated with Beryllium.
Craters from scattered LA-ICP-MS testing.

Table A16c
Beryllium-Treated Example: Natural Orange-Red Sapphire of Songea (Tanzania) Origin.

Chemical composition (LA-ICP-MS in wt.-ppm) of orange-red sapphire from Songea (Tanzania) (Fig. A55) heat-treated with Beryllium. Note: Presence of Cr, Ti and Fe within the gemstone, along with Beryllium of approx 8wt.-ppm. The Beryllium concentrations were found within the entire body of the gemstone, while Fe concentrations are concentrated towards the core – a trend followed by other elements (All are characteristically present in the natural equivalents, except Beryllium).

Cathodoluminescence (CL)

Investigations and contributions to the interpretations were carried out by Prof. K. Ramseyer - karl.ramseyer@geo.unibe.ch - at the University of Berne, Institute of Geological Sciences, Berne (Switzerland) and Dr. J. Mullis, IMP, University of Basel (Switzerland) (See Lit. 19 and lit. 22).

Visual and spectroscopic cathodoluminescence investigations were carried out to characterize the natural orangy-pink sapphires heat-treated Beryllium.

Methods

Natural Beryllium-treated orangy-pink sapphires were prepared as 30 µm thick thin-section and coated with a semi-transparent Al film. An improved cathodoluminescence (CL) microscope (Lit. 25), with an energy of 25 keV, and a source current of 70 µA for photographic recording and 4 µA for spectrographic analyses, was used. The luminescence characteristics were recorded on Ektachrome 400 color slide film and developed at 800 ASA. The CL spectra between 400 and 900nm (10nm resolution) was recorded from a 200 µm spot using a PTI model 01-001 monochromator equipped with a Hamamatsu R928 photomultiplier. The monochromator was linked to the CL microscope by a flexible optic fiber bundle. The CL spectra were not corrected for the spectral response of the instrument.

Results CL

CL clearly documents that the corundum crystal has a homogeneous red luminescing core and a slightly brighter luminescing outer zone of similar thickness (Fig. A58). Between the core and the outer zone, a transitional boundary exists with a lower luminescence intensity than the outer zone (Fig. A56 and Fig. A57). The red CL from both areas contains identical peaks, with peak positions indicative for Cr³⁺-induced luminescence (Fig. A57). LA-ICP-MS data confirms the presence of Cr but also Mg, Fe, Ti, Be and Ga are present (Fig. A56). As shown by LA-ICP-MS, a depletion of the elements Mg, Fe, Ti, Cr, and Ga is found in the outer zone of this sample and Beryllium is enriched. The outer zone was formed after crystallization and reshaping of the crystal and thus represents the result of a treatment.

The results of the CL investigation on two samples are shown in Fig. A58g and A58h. More confirmation is found that the trace element distribution is completely rearranged by the heat-treatment with Beryllium. This was evident by extinction of chemical and structural patterns in the Beryllium-Treated outer rim of the fancy sapphires (Fig. A58h). As shown in Fig. A58g, an additional inner core was detected. This inner core is formed outside the zones enriched in Beryllium.

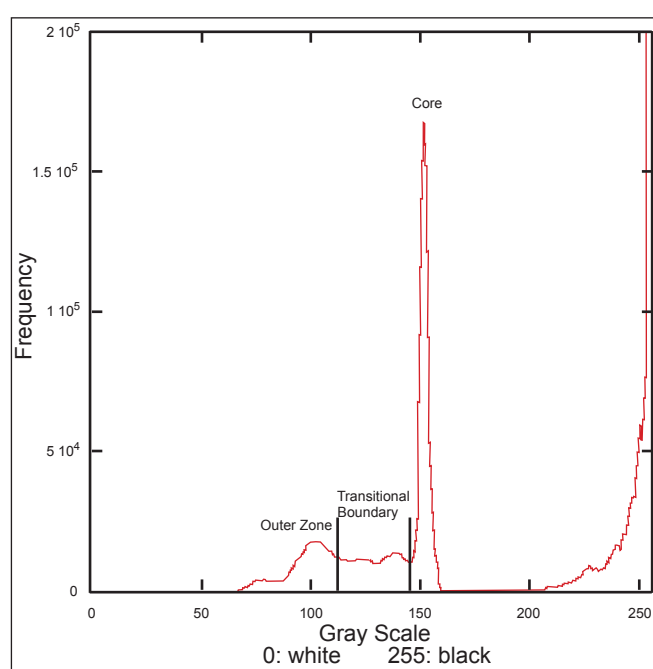


Fig. A56 Luminescence intensity distribution of Fig. A57.

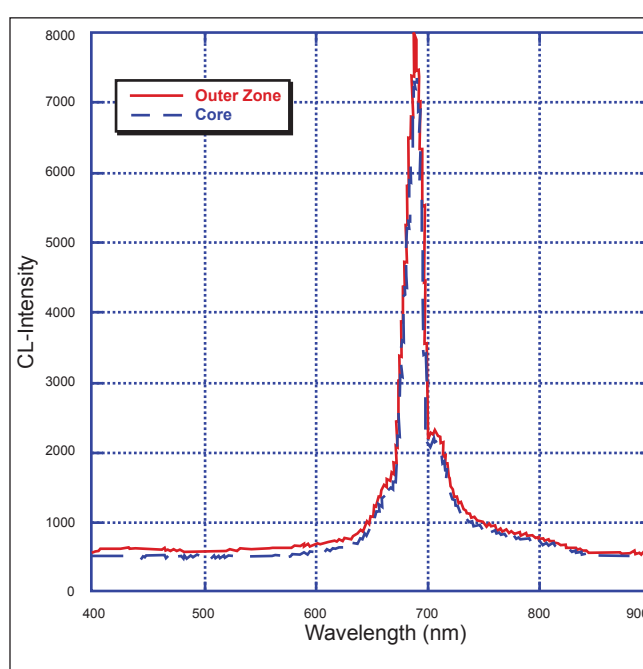


Fig. A57 Representative CL-spectra from the core (blue) and the outer transitional zone (red) of sample Fig. A56.

Correlation of LA-ICP-MS and Cathodoluminescence Analysis of Beryllium-Treated Natural Orangy-Pink Sapphires (“Padparadscha”)

Fig. A58 Cathodoluminescence (CL) microphotographs and projected chemical analysis (in wt.-ppm) as determined by LA-ICP-MS analysis (a-e) in an orangy-pink sapphire heat-treated with Beryllium. Visual color zoning is concentrated in the transitional zone.

Sample No.GRS 12910.1

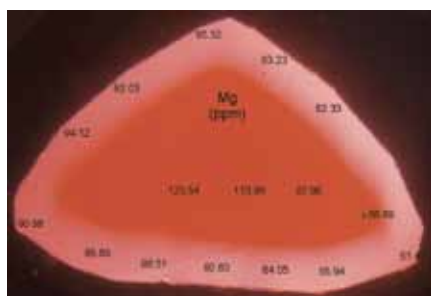


Fig. A58a Magnesium (Mg) – concentrations (in wt.-ppm) depleted in the outer zone.

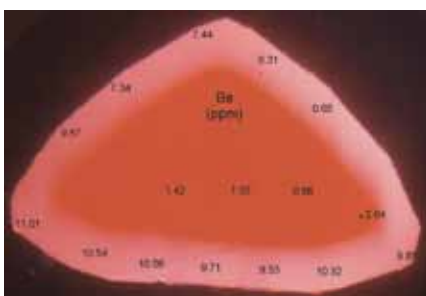


Fig. A58b Beryllium (Be) – concentrations (in wt.-ppm) enriched in the outer zone.

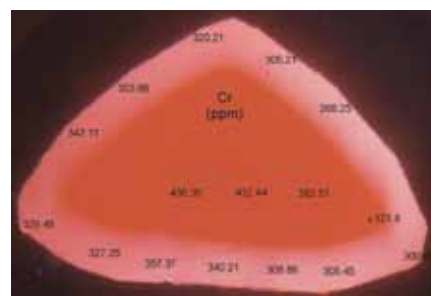


Fig. A58c Chromium (Cr) – concentrations (in wt.-ppm) depleted in the outer zone.

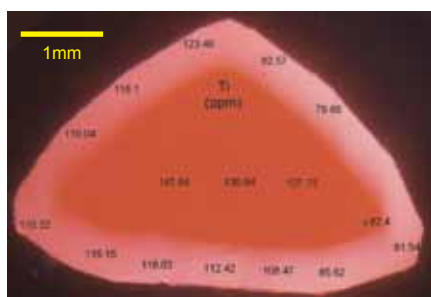


Fig. A58d Titanium (Ti) – concentrations (in wt.-ppm) depleted in the outer zone.

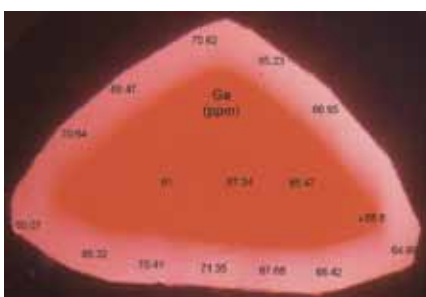


Fig. A58e Gallium (Ga) - concentrations (in wt.-ppm) depleted in the rim.

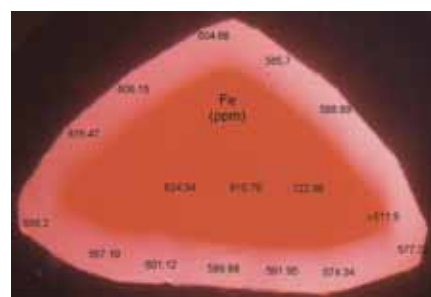


Fig. A58f Iron (Fe) - concentrations (in wt.-ppm) depleted in the rim.

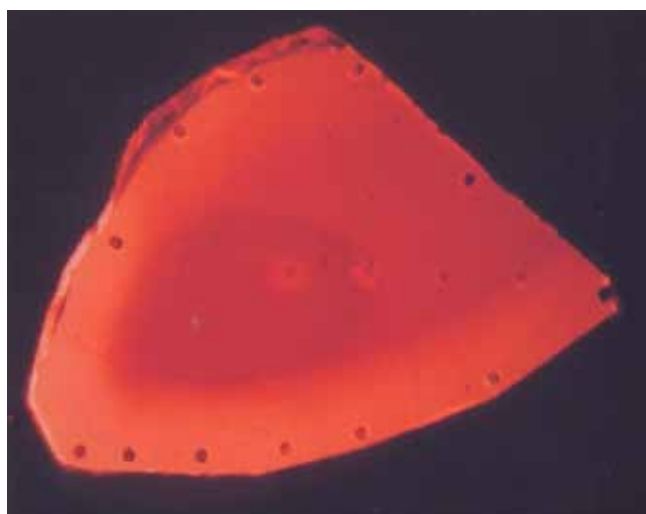


Fig. A58g Cathodoluminescence microphotograph of a Beryllium-treated natural orangy-pink sapphire (by Prof. K. Ramseyer). The Beryllium treatment produces a zoning of chemical and/or structural defect contrasts showing an outer rim, inner rim and an inner core. Craters from LA-ICP-MS (80 micrometers in diameter).

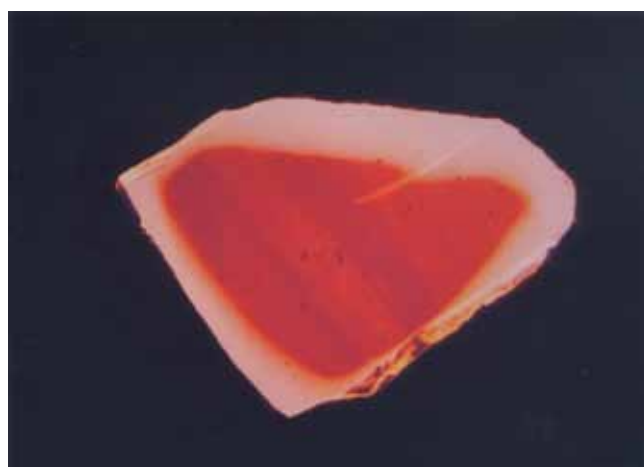


Fig. A58h Cathodoluminescence microphotograph of a Beryllium-treated natural orangy-pink sapphire (by Prof. K. Ramseyer). The picture shows the chemical and/or structural defect contrasts of the natural growth in the centre of a faceted gemstone (diagonal growth lines). The Beryllium treatment resets this contrast in a rim perpendicular to the natural growth zones.

Conclusion Part A

Over the course of the treatment with Beryllium, the following alterations were made to the original sapphire materials.

1.) *Beryllium* is diffused into the surface of the gemstones, either restricted to the rim or penetrating the entire sapphire material (See Fig. A34, A37, A41b, A45, A47b, A50b, A49 and Table A16).

2.) Unstable color centers are formed in the zones containing *Beryllium*. They are interpreted as crystal defects (Fig. A4, A5 and A26) not corresponding to fading color centers caused by irradiation (Lit. 16).

3.) The treatment is characterised by a reaction zone, with indications that the atomic structure of the sapphire is completely rearranged (See Cathodoluminescence analysis (Fig. A58)).

4.) The entire set of cations present in the original sapphire material (Fe, Cr, Ti, V, Ga and Mg) is redistributed in the reaction zone over the course of the treatment. In this case study, the cations are depleted in the rim and enriched in an inner rim (in the Madagascar samples), See Fig. A33, A36, A41a and A49. In the Songea (Tanzania) samples, the entire crystal is involved and the trace elements are enriched at the core (Table A16c). These samples, however, may also show natural chemical zoning.

5.) The color is formed at a particular mix of trace elements, including Fe^{3+} , Cr^{3+} , and with Mg^{2+} and Be^{2+} where crystal defects are present (Fig. A23, A24, A26, A27, A28). In this case study, *Beryllium* concentrations (in wt.-ppm) are ten times lower (*) than the Mg-concentrations (Table A4) and thus their direct contribution to the color needs further research (Part B, this work and Lit 02). The orange color is also formed outside the zone containing *Beryllium* (See Fig. A45) as well as inside. The presence of higher Ti concentrations hampered the formation of these orange color centers (Fig. A45). The nature of these orange color centers are interpreted as trapped-hole type (See Lit. 04 and Lit. 24)(**). Orangy-pink colors "Padparadscha" are formed in the presence of different color causes, such as Fe^{3+} -pairs, Cr^{3+} , Trapped-hole color centers, and at Ti-concentrations below a critical level (Fig. A23, A24, A26, and A27).

6.) The concentrations of Mg and Be are directly correlated in the treated part of the gemstone. As increasing Be-concentrations correlate with decreasing Mg-concentrations (Fig. A42, A45 and A49), this suggests Be replaces Mg positions in the corundum lattice. Profile studies show that the diffusion of Mg towards the core occurred (e.g. Fig. A42 and Fig. A49), however other elements - such as Ti - also diffuse. Titanium-diffusion is best seen when related to pre-existing whitish rutile dust bands (Fig.

A45), or around Ti-oxide minerals (Fig. A61). A very distinct blue halo is formed (Fig. A61), interpreted as color from Fe^{2+} - Ti^{4+} pairs (Ti from diffusion and Fe from the sapphire's composition) (Fig. A45).

The formation of color in the Beryllium-Treated sapphires depends on the chemical differences in the parent sapphire material, while the presence of Ti is found to be the most critical element in preventing the treatment's success (See Fig. A33 and A45). Color zoning is related to the reaction zone of the treatment and can be either confined to the rim or found within the gemstone, depending on the extent of the treatment and the gemstone's chemical composition (See Table A16b and A16c). The use of a high temperature is indicated by the surface melting of the sapphires (Fig. A13 and A14).

Such treatment conditions - including diffusion of elements into the surface, change of oxidation state of Fe, and formation of color centers - can be achieved during heating at a very high temperature near the sapphire's melting point under oxidation conditions (See Lit. 04 and Lit. 24-33).

Identification Test

The identification of this material can be based on gemological tests, including the use of a microscope, particularly in differentiating against other diffusion-treated gemstones. Use of special methods - including the detection of *Beryllium* - are extremely difficult and costly. It uses SIMS (Lit. 24), or LA-ICP-MS (this work)(***). These instruments are commonly unavailable for routine testing. In addition UV-Experiments can be of help (Table A1, Fig. A4 and Fig. A6). This test cannot be used to differentiate against irradiated gemstones or unheated gemstones, but can help to differentiate against other heated gemstones (group E).

(*) If expressed in atomic-ppm (ppma), *Beryllium* to *Magnesium*- ratios are much higher due to corrections by the atomic weight.

(**) Lit. 24-33 appeared after the first version of this Report was published in 2002 (Lit. 01)

(***) Since 2004, GRS developed a LASER based testing technology (UV-LIPS). The analysis produces an extremely small mark (not visible to the naked eye) on the girdle with no damage to the gemstone. (See also Fig. A62)

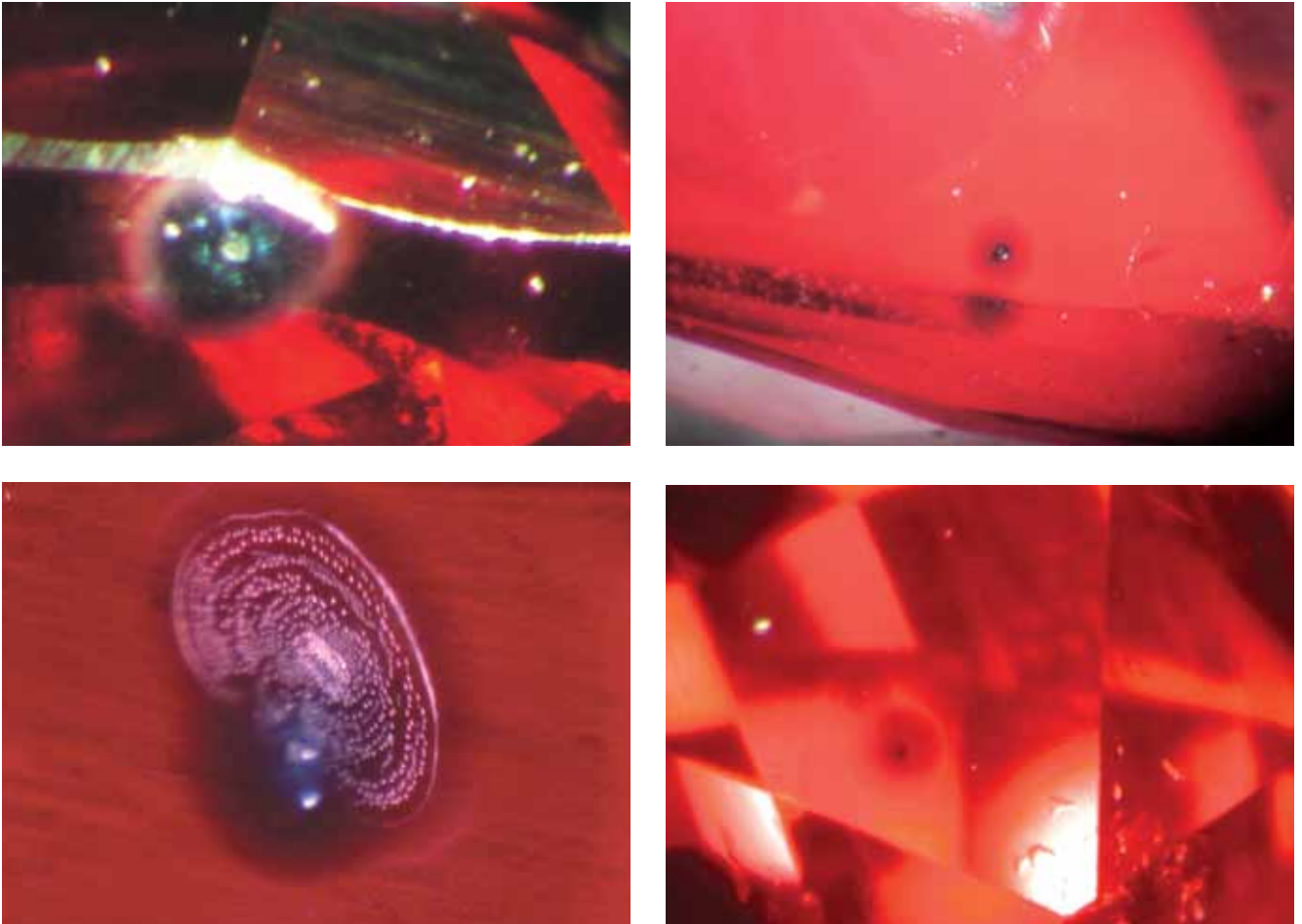


Fig. A61 Microphotographs of inclusions in natural orange-red sapphires from Songea (Tanzania) which have been heat-treated with Beryllium. Round blue halos have been formed around opaque solid inclusions in course of the Beryllium-Treatment. Note: The blue halos around these inclusions are absent in samples unenhanced by heat, but are also been observed previously in other heat-treated corundum materials (J. Koivula, personal communication).



Fig. A62 UV-LIPS at GRS (LIPS = Laser Induced Plasma Spectroscopy) provided non-destructive analyses of Beryllium in corundum since 2004. A similar method has been developed elsewhere, but with major differences in the detection of the Beryllium-Signal as well as in the type of Laser used (Compare with Lit 27). More details on the GRS method will be provided in due course.

The Beryllium-Treatment of Fancy Sapphires with a New Heat-Treatment Technique (Part B).

by Adolf Peretti (*), Detlef Günther(**) and Anne-Liese Graber (**)

(Reprinted with corrections from Contributions to Gemology, No.2, 2003)

(*) GRS Gemresearch Swisslab LTD, Switzerland

(**) Institute of Chemistry, Swiss Federal Institute of Technology, Zurich, Switzerland.

Introduction

The new heat treatment of corundum is a technique that involves extremely high temperatures, oxidation conditions and diffusion of Beryllium into the corundum's surface (Lit 01, Lit 02 and Lit.23 to 33). Part A of this study (Lit 01) concentrated on the interaction of Beryllium with the parent chemistry of natural fancy sapphires and other gemological aspects. It was noticed that only very minor concentrations of Beryllium were present in the treated sapphires. This data was confirmed later (Lit 23). As mentioned earlier, the understanding of the direct contribution of Beryllium to the color of these treated natural sapphires needed additional research (see Lit 01 page 39). As pointed out in a recently published article on this new treatment (Lit 24), the understanding of the new treatment needs more precise data on various trace elements that are not yet available in world literature. In part B of the characterization of the new treatment, we provide extended chemical analyses of natural and synthetic materials, including sapphires, and test the models proposed elsewhere (Lit 24). Further studies appeared after Part B of our study (Lit. 02) was published (Lit. 26-33)

Materials and Methods

The studied materials include synthetic materials from various manufacturers. Colorless synthetic sapphires were from watch glass producers in Switzerland, synthetic pink, orange and yellow Verneuil sapphires were obtained from Djehahirdijan SA (Monthey, Switzerland), and synthetic hydrothermal rubies were from Novosibirsk (Russia). Further natural samples are listed in Tab. A6 and additional samples of rubies and blue sapphires were collected in the market in Bangkok (see Tab. B2 and B3).

The synthetic samples included rough, as well as faceted materials. They were cut in half. One piece was kept untreated for reference ("reference samples"), and one half piece sent for commercial Beryllium-Treatment with the new method to a specialized commercial factory in Chantaburi



Fig. B1 Natural Pink sapphires and brownish pink sapphires were also subjected to the new Beryllium-Treatment.

Note: Color change from pink to orangy-pink due to the treatment.

(Thailand). The heating experiments were reportedly carried out at very high temperature near the melting point of corundum under high oxidation conditions, including Beryllium diffusion. Details of the method remain the intellectual property of the factory. After the Beryllium-Treated samples came back from Chantaburi, untreated and treated samples were compared and color changes investigated (Fig. B1, B26). The treated samples were cut in half for further chemical and spectroscopic analyses (e.g. Fig. B5). Further samples of natural blue sapphires, fancy sapphires and rubies have also been Beryllium-Treated by the same factory as well as by another factory in Bangkok. For comparison, additional natural orange sapphires were investigated which were heated by conventional methods (Tab. B3).



Fig. B2

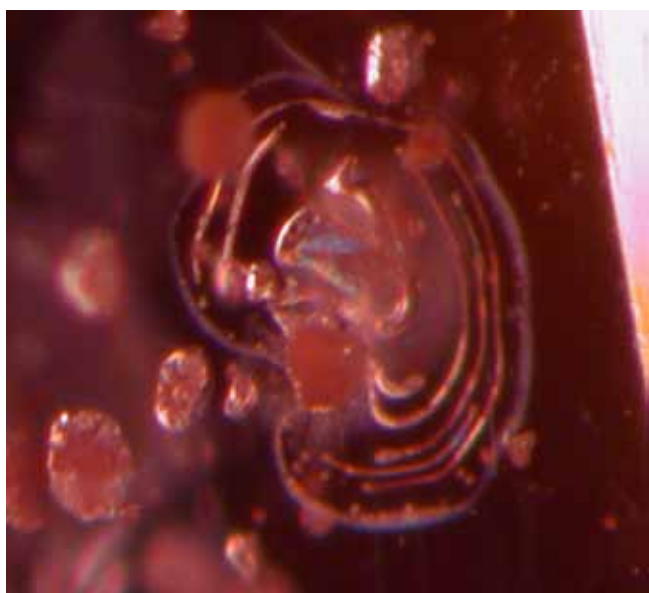


Fig. B3

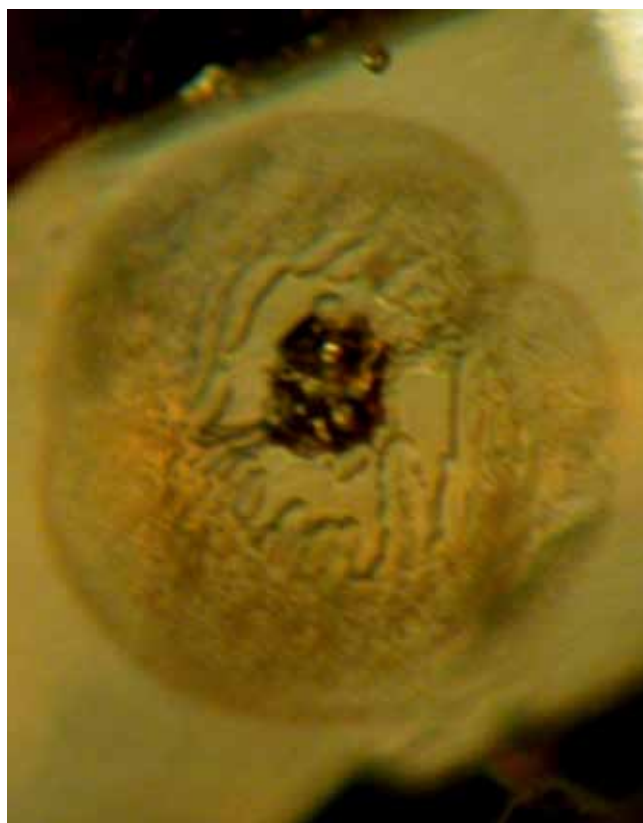


Fig. B4

Fig. B2-4 Microphotograph of inclusions in Beryllium-Treated natural sapphires. Melted inclusions with feathers characteristic for high temperature treatment (See also Lit. 24). These inclusion patterns can not be found in the synthetic counterparts. Magnification in the microscope 60x-80x. Fibre optic illumination. Pictures by John de Jaeger. Copyright GRS.

	Before Be - Treatment			After Be -Treatment			Color Change
	Sample	Color	Doped by	Sample	Color	Doped by	
Synthetic Corundum	GRS 2	colorless	Na, Mg, K, (Si, Fe, Ti, Cu)	GRS 1 <i>(from GRS 2)</i>	light brown	Be, Na, K, (Si, Fe, Ti)	(x)
	GRS 12	light pink	Mg, Ca, Cr, Si (Fe, Na, Ti)	GRS 13 <i>(from GRS 12)</i>	orangy-pink**	Be, Na, Mg, Ca, Cr	(x)
	GRS 4	pink	Na, Cr (Mg, Si)	GRS 5 <i>(from GRS 4)</i>	orange	Be, Cr (Mg, Si)	x
	GRS 8	vivid pink	Na, Cr (Fe)	GRS 9 <i>(from GRS 8)</i>	orange	Be, Cr (Si)	x
	GRS 15	vivid pink	Mg, Si, Ti, Cr, Fe	GRS 16 <i>(from GRS 15)</i>	vivid orange	Be, Na, Mg, Si, K, Ti, Cr	x
	GRS 10	light orange (*)	K, Cr, Si	GRS 11 <i>(from GRS 10)</i>	orange	Be, Cr, Zr	(x)
	GRS 17	orange	Ti, Mg, Si, Cr	GRS 18 <i>(from GRS 17)</i>	orange	Be, Ti, Mg, Si, Cr	
Synthetic Rubv	GRS 19	yellow	Mg, Si, Ni	GRS 20 <i>(from GRS 19)</i>	yellow	Be, Mg, Si, Ni	
	GRS 25	purplish pinkish red	Na, Ti, Cr, Fe, Ni	GRS 26 <i>(from GRS 25)</i>	orange	Be, Ti, Si, Cr, Fe, Ni	x
	GRS 27	red	Mg, Ti, Si, Cr, Fe, Ni	GRS 28 <i>(from GRS 27)</i>	orange-red	Be, Mg, Si, Ti, Cr, Fe, Ni	x
	GRS 29	dark red	Na, Mg, Si, K, Ti, Cr, Fe, Ni	GRS 30 <i>(from GRS 29)</i>	dark orangy-red	Be, Mg, Si, Ti, Cr, Fe, Ni	x

(*) color change from pink to pinkish-orange induced by irradiation treatment

Table B1: Synthetic Rubies and Synthetic Colored Sapphires before and after treatment with Beryllium. Dominant trace elements are in bold. Note: Only Cr-rich samples were reacting to the Beryllium-Treatment. Be = Beryllium, Na = Sodium, Mg = Magnesium, Si = Silica, K= Potassium, Ti = Titanium, Cr = Chromium, Fe = Iron, Ni = Nickel.

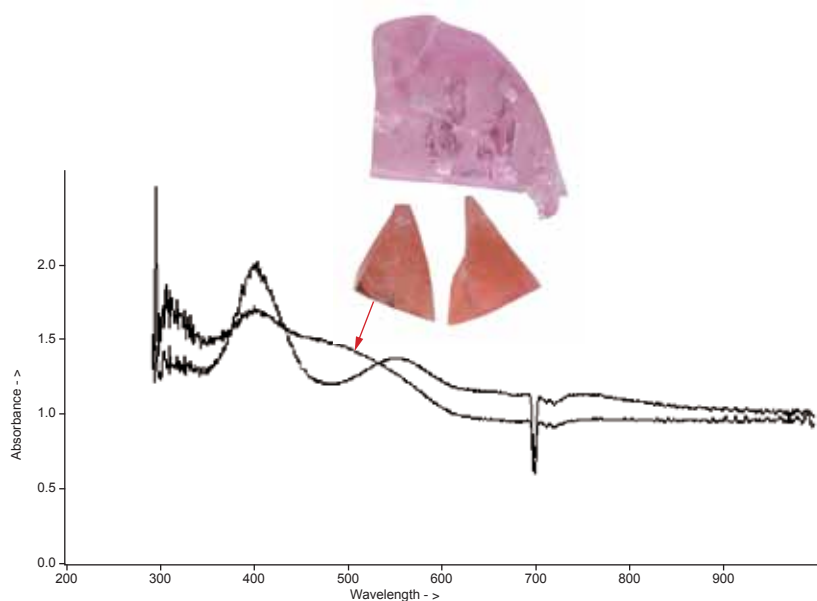


Fig. B5 Polarized UV-VIS-NIR absorption spectra of synthetic pink sapphires (reference sample) and Beryllium-Treatment synthetic orange sapphires. Inserted picture shows the untreated reference (pink) and Beryllium-treated samples (orange) (including fluorescent lines produced by multi-channel spectroscopic measurements). Spectra are recorded in the same crystallographic direction. There is a shift in absorption due to a different sampling volume. Increase in absorption towards the blue region of the spectrum is interpreted as Beryllium (Be)-Chromium (Cr)-color centers superimposed to Cr^{3+} (See also discussion in Lit. 24).

LA-ICP-MS chemical analyses

The LA-ICP-MS measurements were carried out by the Laboratory of Inorganic Chemistry at the Swiss Federal Institute of Technology, Honggerberg Zurich). The details on the methods, data calculation, normalization procedures and error margins see Page 20-21.

An additional set of more than 40 samples has been analyzed including various categories of synthetic, unheated, conventional heated, as well as Beryllium treated samples (see Tab. B1, B2 and B3). Due to detailed series of spots in various profiles on the samples, a total of approx. 1000 chemical data points were collected. Each spot was analyzed for 40 elements. The data shown in Tab. B2 and B3.

Beryllium-Treated Synthetic Pink and other Synthetic Colored Sapphires

The results of Beryllium-Treated Synthetic Sapphires are shown in Fig. B6 to B25 and in Tab. B1, B2 and Fig. B47a. The group of synthetic Pink Sapphires can be subdivided into two different categories depending on the reaction to the Beryllium-Treatment. One group of synthetic sapphires did not color-change after Beryllium-Treatment. The non color-changing category includes synthetic orange and yellow sapphires that contain various elements including Na, Mg, Ni, Sn and Zr (see Tab. B1 and B2). The second group of color-changing samples include synthetic pink sapphires that became more orange with Beryllium-Treatment (Tab. B1 and B2). These samples were dominated by traces of chromium (Cr). Another sample which was doped by Cr and Mg was only partially color-changed. All the Beryllium-Treated samples contain traces of Beryllium, with enriched concentrations at the rim (e.g. Fig. B12). Increasing Cr and Beryllium-concentrations are correlated with

increasing intensity in orange color. Trace element concentrations of many of the elements were heterogeneous (Fig. B8, B12, B16, B22, B19, B25): This is interpreted as chemical zoning in the stones, which is not uncommon in the synthetic Verneuil corundum materials.

Beryllium-Treated Hydrothermal Synthetic Rubies (TAIRUS, Novosibirsk)

After Beryllium-Treatment, synthetic rubies changed to more orange or less dark colors (Tab. B1). The results of the chemical analyses are shown in Fig. B26 to B45). This color change can be correlated with increasing Be-concentrations, independently of the concentrations of Fe (Fig. B47b). A series of other trace elements are present in these synthetic hydrothermal rubies, including Mg, Ti, Si, Cr, Mn, Fe, Ni and minor Sn. They did not prevent the treatment success (Fig. B29, B33, B37, B40 and B46).

Beryllium-Treated Synthetic Colorless Sapphire

White corundum (without Cr-concentrations) slightly color-changed to light brown after the Beryllium-Treatment. Additional traces of Beryllium were detected in the samples (Table B2)

Before Beryllium-Treatment

After Beryllium-Treatment

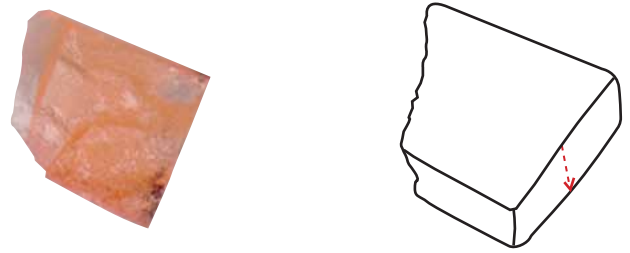
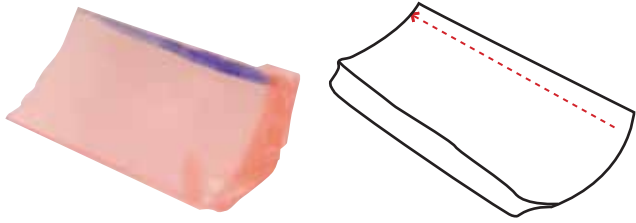


Fig. B6 Microphotograph of GRS 8 (Synthetic light pink sapphire)

Fig. B10 Microphotograph of GRS 9 (synthetic orange sapphire)

Fig. B7 Drawing of GRS 8. Analysis was performed with 61 spots along the broken line (crater diameter : 80 μ m)

Fig. B11 Drawing of GRS 9. Analysis was performed with 12 spots along the broken line (crater diameter : 80 μ m)

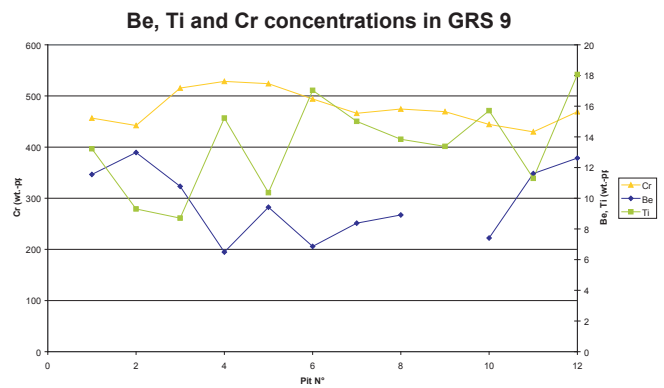
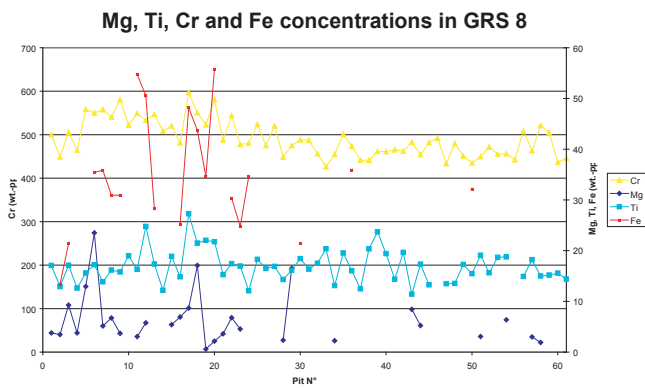


Fig. B8 The chemical variations in a profile across a synthetic pink sapphire (GRS 8) are shown (in wt.-ppm). Complete data see Tab. B2

Fig. B12 The chemical variations in a profile across a Beryllium-Treated synthetic orange sapphire (GRS 9) are shown (in wt.-ppm). Untreated reference sample is GRS 8). For complete data, see Tab. B2.

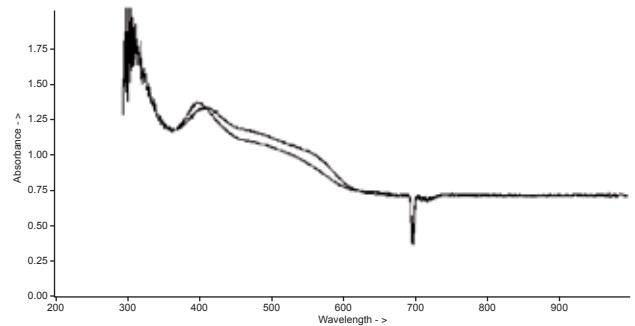
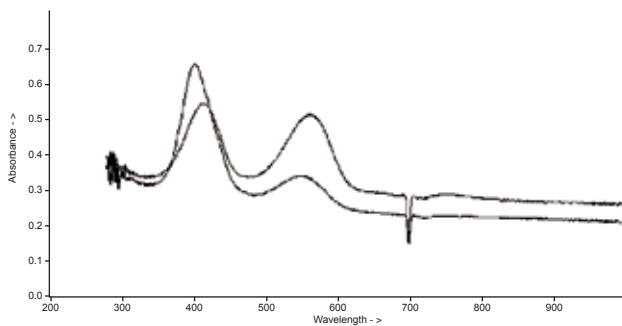


Fig. B9 Polarized UV-VIS-NIR absorption spectra of synthetic pink sapphires (GRS 8) parallel and perpendicular to the c-axis. Absorption characteristics (including fluorescent lines produced by multi-channel spectroscopic measurements) due to Cr^{3+} .

Fig. B13 Polarized UV-VIS-NIR absorption spectra of Beryllium-Treated synthetic orange sapphires parallel and perpendicular to the c-axis. Absorption characteristics (including fluorescent lines produced by multi-channel spectroscopic measurements) due to Cr^{3+} and Cr-Be color centers. The untreated reference sample is GRS 8.

Before Beryllium-Treatment

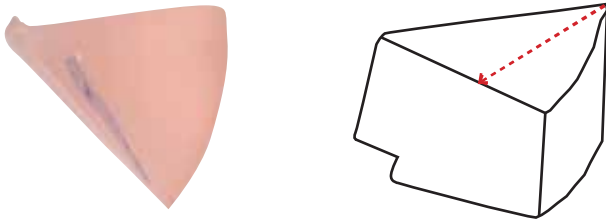


Fig. B14 Microphotograph of GRS 12 (synthetic pink sapphire) **Fig. B15** Drawing of GRS 12. Analysis was performed with 40 spots along the broken line (crater diameter: 80 μm)

Mg, Ti, Cr, Si and Zr concentrations in GRS 12

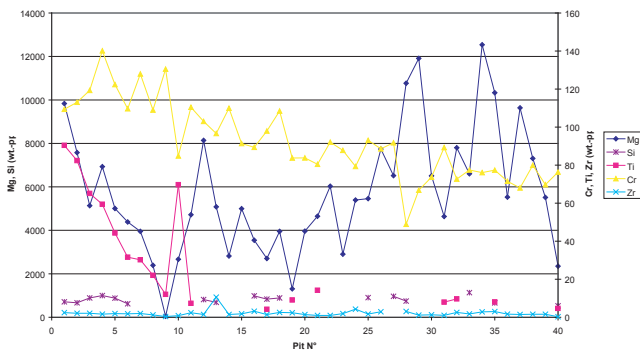


Fig. B16 The chemical variations in a profile across a synthetic pink sapphire are shown (in wt.-ppm). Complete data see Tab. B2.

After Beryllium-Treatment

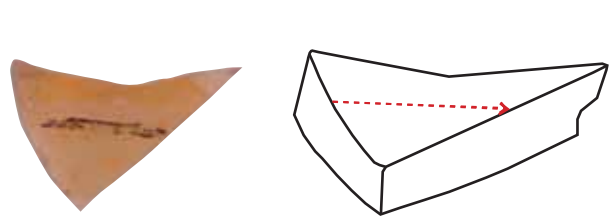


Fig. B20 Microphotograph of GRS 13 (synthetic pink sapphire) **Fig. B21** Drawing of GRS 13. Analysis was performed with 33 spots along the broken line (crater diameter: 80 μm)

Be, Ti, Si and Cr concentrations in GRS 13

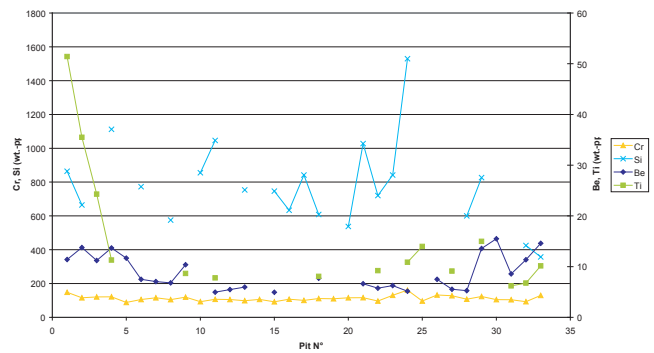


Fig. B22 The chemical variations in a profile across a Beryllium-Treated synthetic orange-pink sapphire (GRS 13) are shown (in wt.-ppm). The untreated corresponding sample is GRS 12. complete data see Tab. B2.

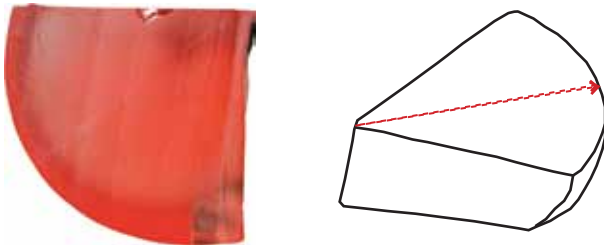


Fig. B17 Microphotograph of GRS 17 (synthetic deep orange sapphire) **Fig. B18** Drawing of GRS 17. Analysis was performed with 80 spots along the broken line (crater diameter: 80 μm)

Mg, Ti, Si, Cr, Ga and Zn concentrations in GRS 17

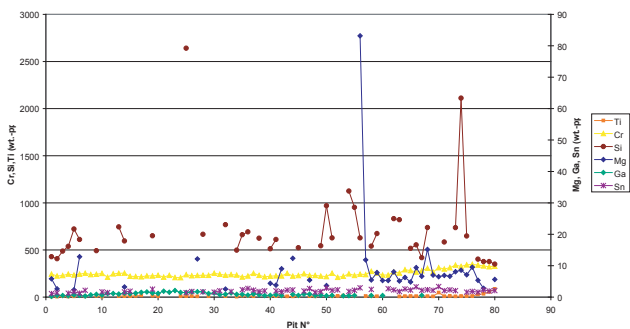


Fig. B19 The chemical variations in a profile across a synthetic deep orange sapphire (GRS 17) are shown (in wt.-ppm). Complete data see Tab. B2

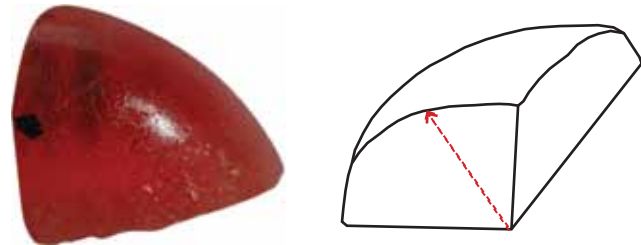


Fig. B23 Microphotograph of GRS 18 (synthetic deep orange sapphire) **Fig. B24** Drawing of GRS 18. Analysis was performed with 35 spots along the broken line (crater diameter: 80 μm)

Be, Ti, Si, Cr and Mo concentrations in GRS 18

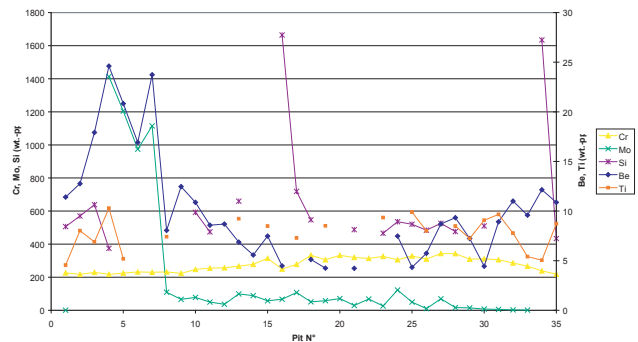


Fig. B25 The chemical variations in a profile across a Beryllium-Treated synthetic deep orange sapphire (GRS 18) (in wt.-ppm). Corresponding untreated sample is GRS 17. For complete data, see Tab. B2

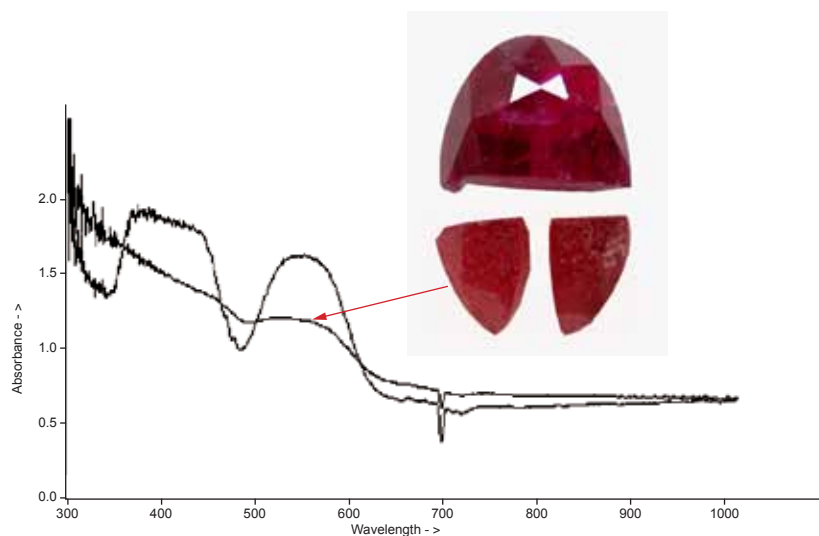


Fig. B26 Polarized UV-VIS-NIR absorption spectra of synthetic hydrothermal rubies (reference sample) and Beryllium-Treated synthetic deep orange sapphires (including fluorescent lines produced by multi-channel spectroscopic measurements). Inserted picture shows the untreated reference (red) and Beryllium-Treated samples (orange). Spectra are recorded in the same crystallographic direction. A shift in absorption is due to a different sampling volume. Increase in absorption towards the blue region of the spectrum is interpreted as color centers involving Beryllium and other trace elements superimposed to Cr^{3+} -absorptions (see Lit. 24).

Chemical Identification Charts for Beryllium-Treated Corundum

For further interpretation of the data, we selected 660 spot analyses from our data bank, which included various samples unheated, enhanced and Beryllium-treated sapphires. A further selection was made for the group of Beryllium-Treated samples, from which we did not take into account the data that were obtained from measurements at or near the surface. In such a way, we eliminated contamination resulting from the treatment experiments which were found at the surface of the samples (high Be, Mg, Cr, Fe, Zr). The data were transformed from wt.-ppm to ppma (a = atomic) and are graphically presented in Fig. B47 and B48.

UV-VIS-NIR Spectroscopic Origin of Color Analyses

Polarized spectra were measured on synthetic corundum, both for untreated and for Beryllium-Treated samples. The results are shown in Figs. B5, B9, B13, B26, B30 and B34. In comparison to the untreated reference samples, it was found that the absorption curves increased towards the blue region of the spectrum. These broad bands in the UV region of the spectrum can be interpreted as proof of the presence of color centers involving Beryllium and other elements (See Lit. 24).

Beryllium-Treated Natural Rubies and Sapphires

The measured samples of natural rubies and sapphires are listed in Tab B3 and shown in Fig. B47c and Fig. B48. Reviewing the data of Tab. B3, it is evident that concentrations of Silica (Si) were found in all samples. Comparing the values with those in Literature (Lit. 24), it was found that much higher Si concentrations were measured in our investigation. They are approx 10 to 20 times higher than the values published (Lit. 24) on similar samples. The distribution of Si in the samples, however, was found to be heterogeneous, e.g. areas that had Si below the detection limit were found in a distance of 50 to 100 microns next to areas of significant Si concentrations. Only minor concentrations of Sn, Ni, Mn, Ca and Li were occasionally also detected in addition to the elements Mg, Ti, V, Cr, and Fe, both in samples before and after Beryllium-Treatment (Tab. B3). Beryllium was found in all Beryllium-Treated samples. The concentration of Beryllium increased towards the rim as previously reported (See Lit. 01).

Before Beryllium-Treatment



Fig. B27 Microphotograph of GRS 25 (synthetic ruby)
Fig. B28 Drawing of GRS 25. Analysis was performed with 18 spots along the broken line.
 (Crater diameter: 80 μm)

After Beryllium-Treatment

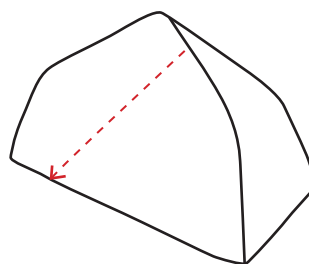


Fig. B31 Microphotograph of GRS 26 (synthetic orange-red sapphire)
Fig. B32 Drawing of GRS 26. Analysis was performed with 16 spots along the broken line
 (crater diameter: 80 μm)

Chemical variations in GRS 25

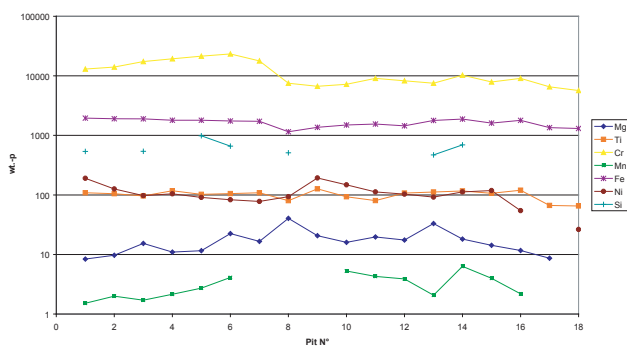


Fig. B29 The chemical variations in a profile across a synthetic hydrothermal ruby are shown (in wt.-ppm). Sample No. GRS 25. complete data see Tab. B2.

Chemical variations in GRS 26

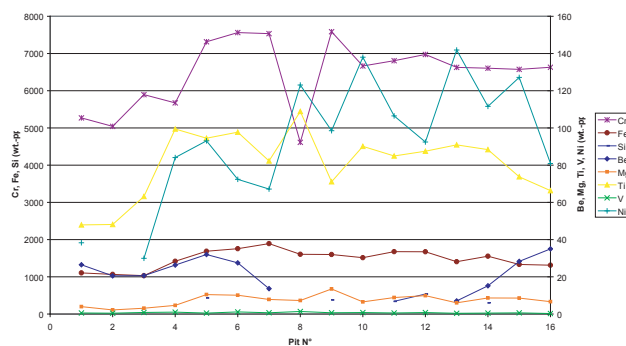


Fig. B33 The chemical variations in a profile across a Beryllium-Treated synthetic orange-red sapphire are shown (in wt.-ppm). Sample No. GRS 26 (untreated reference sample is GRS 25). Silica concentrations out of scale.

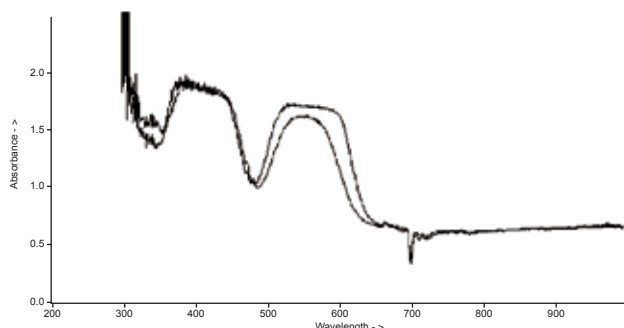


Fig. B30 Polarized UV-VIS-NIR absorption spectra of a synthetic hydrothermal ruby in a direction parallel and perpendicular to the c-axis. Absorption characteristics (inclusive fluorescence lines) due to Cr^{3+} (including fluorescent lines produced by multi-channel spectroscopic measurements).

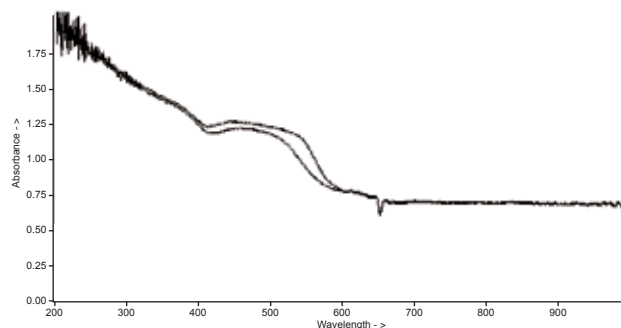


Fig. B34 Polarized UV-VIS-NIR absorption spectra of a Beryllium-Treated synthetic orange-red sapphire (GRS 26) in a direction parallel and perpendicular to the c-axis. Absorption characteristics (including fluorescent lines produced by multi-channel spectroscopic measurements) due to Cr^{3+} and color centers involving Beryllium and other trace elements (General increase in absorption in the blue region of the spectrum). Untreated reference sample is GRS 25.

Before Beryllium-Treatment



Fig. B35 Microphotograph of GRS 27 (synthetic ruby)
Fig. B36 Drawing of GRS 27. Analysis was performed with 16 spots along the broken line (crater diameter: 80 μm)

After Beryllium-Treatment

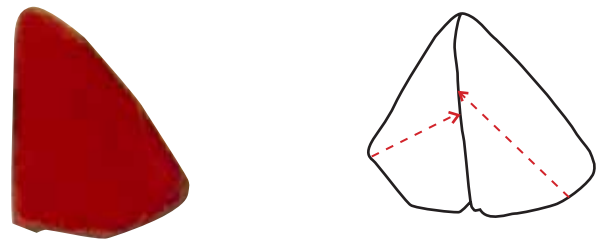


Fig. B41 Microphotograph of GRS 28 (synthetic orange sapphire, Beryllium-Treated sample GRS 27)
Fig. B42 Drawing of GRS 28. Analysis was performed along the two broken lines (crater diameter: 80 μm) Side 1: 23 pits; Side 2: 15 pits

Chemical variations in GRS 27

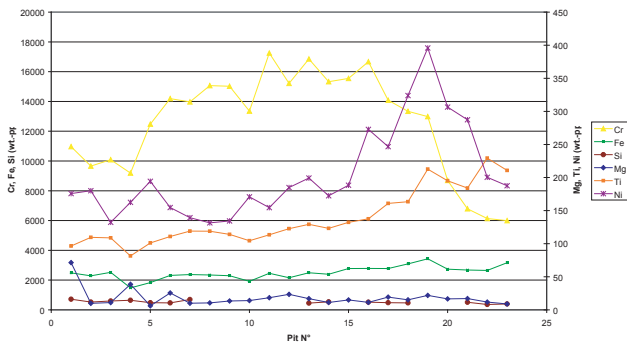


Fig. B37 The chemical variations in a profile across a synthetic hydrothermal ruby (GRS 27) are shown (in wt.-ppm). Complete data see Tab. B2.

Chemical variations in GRS 28

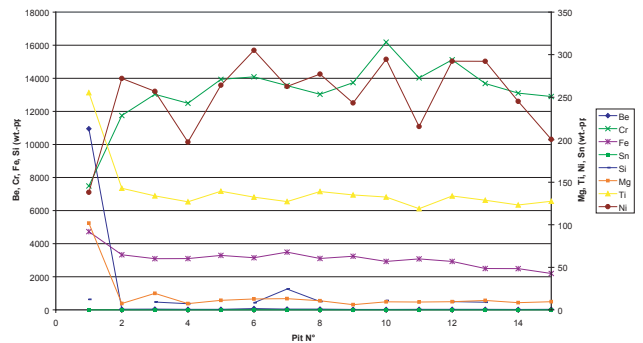


Fig. B43 The chemical variations in a profile across a Beryllium-Treated synthetic orange sapphire (GRS 28) are shown (in wt.-ppm). Untreated reference sample is GRS 27. complete data see Tab. B2.



Fig. B38 Microphotograph of GRS 29 (synthetic ruby)
Fig. B39 Drawing of GRS 29. Analysis was performed with 21 spots along the broken line (crater diameter: 80 μm)

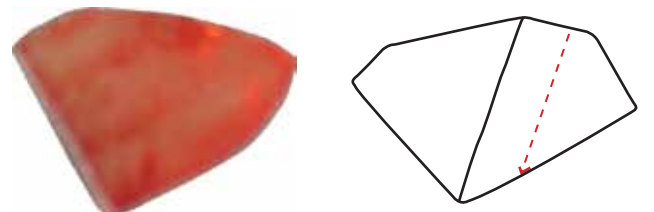


Fig. B44 Microphotograph of GRS 30 (synthetic orange sapphire, Beryllium-treated sample GRS 29)
Fig. B45 Drawing of GRS 30. Analysis was performed with 20 spots along the broken line (crater diameter: 80 μm)

Chemical variations in GRS 29

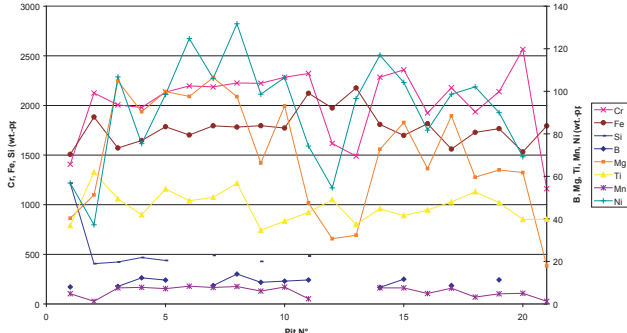


Fig. B40 The chemical variations in a profile across a synthetic hydrothermal ruby (GRS 29) are shown (in wt.-ppm). Complete data see Tab. B2.

Chemical variations in GRS 30

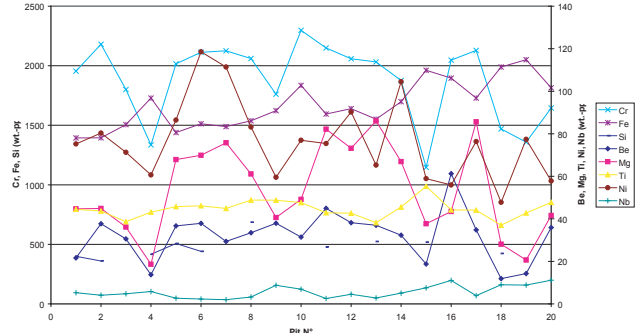
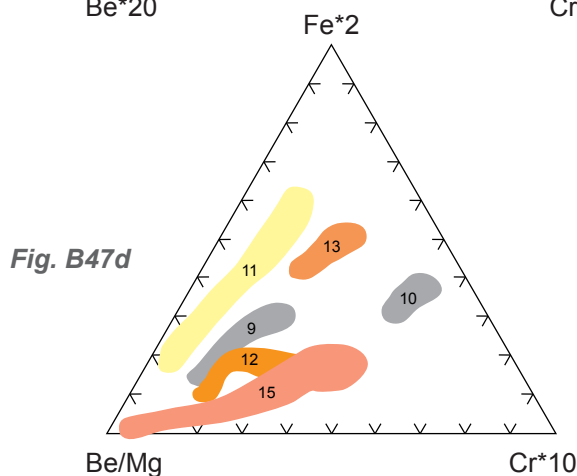
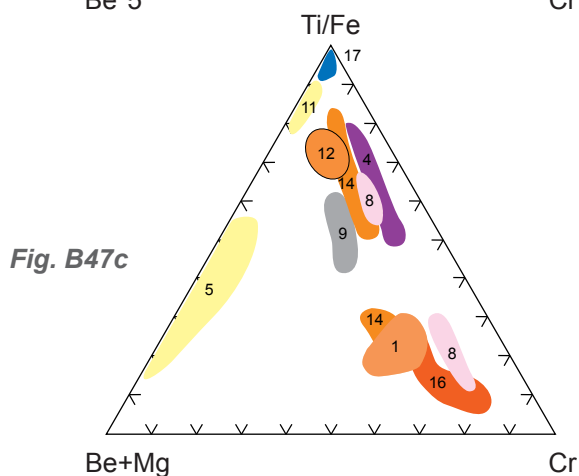
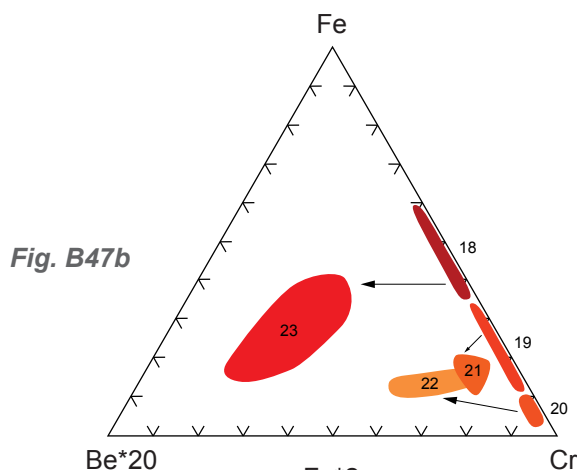
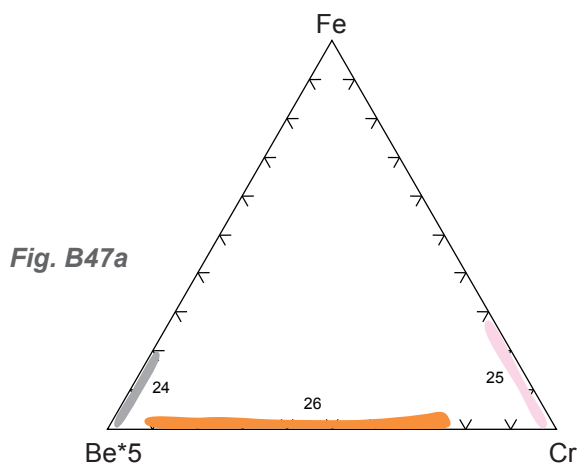


Fig. B46 The chemical variations in a profile across a Beryllium-Treated synthetic orange sapphire (GRS 30) are shown (in wt.-ppm). Untreated reference sample is GRS 29. complete data see Tab. B2.



Legend

1. Natural Padparadscha (N)
2. Natural Violet Sapphire (N)
3. Natural Purple Sapphire (N)
4. Natural Purple to Violet Sapphire (N)
5. Natural Yellow Sapphire (E)
6. Natural Orange Sapphire (E)
7. Natural Padparadscha (E)
8. Natural Pink Sapphire (E)
9. Natural Colorless Sapphire (Beryllium-Treated)
10. Natural White Sapphire (Beryllium-Treated)
11. Natural Yellow Sapphire (Beryllium-Treated)
12. Natural Orange Sapphire (Beryllium-Treated)
13. Natural Padparadscha Pinkish-orange (Beryllium-Treated)
14. Natural Padparadscha (Beryllium-Treated)
15. Natural Padparadscha (Orangy-pink) (Beryllium-Treated)
16. Natural Orangy-red Sapphire (Beryllium-Treated)
17. Natural Sapphire (Beryllium-Treated)
18. Synthetic hydrothermal Ruby GRS 29
19. Synthetic hydrothermal Ruby GRS 27
20. Synthetic hydrothermal Ruby GRS 25
21. Synthetic hydrothermal Ruby (Beryllium-Treated) GRS 28
22. Synthetic hydrothermal Ruby (Beryllium-Treated) GRS 26
23. Synthetic hydrothermal Ruby (Beryllium-Treated) GRS 30
24. Light cream Colorless Synthetic Sapphire (Beryllium-Treated)
25. Synthetic Pink Sapphire
26. Synthetic Orangy-Pink Sapphire (Beryllium-Treated)

Fig. B47 Chemical comparison of Beryllium-Treated and untreated samples (see Legend below). Tab. B2 and B3 (non-averaged complete data set used, see text).

Fig. B47a Beryllium-Treatment produces orange in synthetic pink sapphires caused by an increase in Beryllium (Be) in presence of Chromium (Cr).

Fig. B47b Beryllium-Treatment of synthetic rubies shifts the color to orange, due to an increase in Beryllium in presence of Cr, independent of Iron (Fe)-concentrations.

Fig. B47c Beryllium-Treatment of natural fancy sapphires produces orange with increasing (Mg+Be)-concentration at variable Ti/Fe-ratios and variable Cr-concentrations (Mg = Magnesium, Ti = Titanium)

Fig. B47d Padparadscha color is produced at variable Be/Mg-concentrations with increasing concentrations of Cr

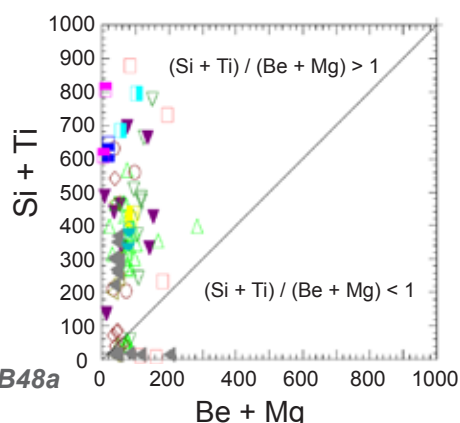


Fig. B48a

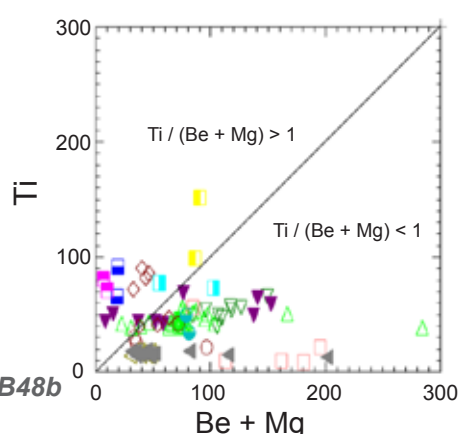


Fig. B48b

Fig. B48 Chemical composition of Si, Ti, Be and Mg in natural corundum heat-treated with conventional methods, and with Beryllium-Treatment. The additional orange color is formed in the field of $Ti/(Be + Mg) < 1$ (Fig. B48b and Legend) and not in the field $(Ti + Si)/(Be + Mg) < 1$. See Lit 24 for further discussion on Si in corundum. Symbols, see Legend below. Ratios are calculated from ppm values.

Legend

Orange Sapphire, Madagascar	GRS 35 S1	◁
Conventional heating		
Orange Sapphire, Madagascar	GRS 35 S2	◁
Conventional heating		
Padparadscha, Madagascar	Rosa 3.59	○
Conventional heating		
Slightly orangy-pink Sapphire	GRS 33	△
Madagascar, New Treatment		
Padparadscha, Madagascar	GRS 34	◇
New Treatment		
Padparadscha, Madagascar	12916	▽
New Treatment (zoned)		
Padparadscha, Madagascar	12916 S2	▽
New Treatment (zoned)		
Ruby, vivid red, Madagascar	Rot 10.69	□
New Treatment		
Natural Sapphire, blue	12132	■
Conventional heating		
Natural Sapphire, dark blue	12344 S1	■
Conventional heating		
Natural Sapphire, dark blue	5.019ct S1	●
Conventional heating		
Natural Sapphire, vivid blue	12133	■
New Treatment		
Natural Sapphire, deep blue	12134	■
New Treatment		

Conclusion Part B

The new Beryllium-Treatment is characterized by the formation of an additional yellow to orange color in Corundum. Chemical and spectroscopic measurements show that the color change can be explained by color centers involving various trace elements including Beryllium (See also page 41). From detailed LA-ICP-MS chemical analyses, it is evident that a large variety of trace elements are present in the Beryllium-Treated Synthetic samples (Fig. B12, B22, B25, B33, B43 and B46). As shown by our experiments with synthetic pink sapphires, Cr and Be alone, at the absence of other trace elements, are sufficient for the formation of orange color centers. From the Beryllium-Treatment of synthetic materials, it is concluded that corundum without Ti and Cr is not changing the color. Other trace element combinations without the presence of Ti, Mg and Be can also form yellow to orange coloration (e.g. Ni see Tab. B1). Synthetic materials, lacking V but with Cr, Ti, Mg, Fe did color change after treatment with Beryllium. This indicates that V does not have to be present for a color change. In more chemically complex natural corundum, increasing relatively lower Ti-concentrations in the presence of other trace elements (such as Beryllium) are favorable for the formation of the orange color. Special attention, however, needs to be paid to the additional presence of detectable concentrations of Si in the treated samples. A model for the explanation of the formation of orange color centers was proposed elsewhere (Lit 24) based on the $(Ti+Si)/(Mg+Be)$ -ratio. As shown by our investigation (Fig. B48a and Fig. B48b), a better correlation is found using the $Ti/(Mg+Be)$ -ratio, without taking into account the Si concentrations. The orange color is formed by the new Beryllium-Treatment in samples with $Ti/(Mg+Be) < 1$ (Fig. B48b). From the distribution of Si in our samples, it seems that Si is heterogeneously distributed in the Beryllium-Treated corundum and may not take part in the reaction with Beryllium. For other trace elements that can theoretically be important to the origin of color in corundum, we found that the concentrations of Co, Cu, Zr, Ba and Pb were present at, or below, the detection limits. Therefore, their role in the treatment is limited as well as unlikely (Tab. B3). Other areas of additional research are necessary to understand the complex re-crystallization process that occurs in connection with this new treatment. Furthermore, it seems to us that modern multi-element cluster analyses (See Lit 21) are preferred for the final understanding of the new treatment with Beryllium.

Identification of Beryllium-Treatment by Inclusion Analyses

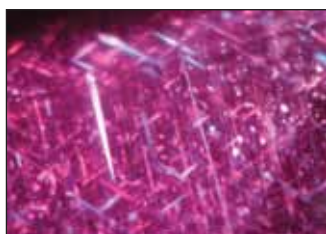
In Part A of our study we elaborated on the melting of zircon and transformation into Zr-Oxide and glass using Scanning Electron Microscope analyses. This melting of minerals other than corundum has been related to the high temperature used for Beryllium-Treatment (Lit. 01 (Fig. A15, A16, A17)). This findings have been recently confirmed (Lit. 24) on studies on zircons included in sapphires, where they found that the Zr-Oxides can be identified as badelleyite. This mineral melting phenomena has become a help in identifying this new treatment (see Fig. B2, B3, B4, C8 - C17). Further valid identification criteria in orange to orange-red sapphires from Songea (Tanzania) turned out to be the blue halos around mineral inclusions (Fig. A61, C11). The very recent appearance of gem quality Beryllium-Treated Blue Sapphires provided a completely new set of inclusion features (Fig. C18 - C22).

Explanation Inclusion Images



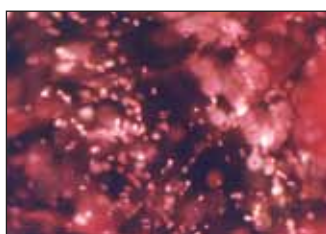
Abundant zircon inclusions in a violetish-blue sapphire from Madagascar. No decompositions and no discoid cracks were detected around the inclusions. This is a good indication that the sapphire are unheated. Heat-treatment at low temperatures may still have been applied (which was not the case in this sample). Inclusion may best be seen at magnifications of 20 to 120times in transmitted light in combination with fibre optic illumination from various directions.

See Figure
C1



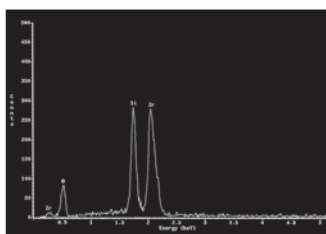
Rutile inclusions in an unheated pinkish-red sapphire from Madagascar. In Beryllium-Treated corundum, no unaltered rutile inclusions have been observed yet. Fibre optic illumination between 30-60x in the microscope.

See Figure
C2, C7



Abundant zircon inclusions in a pink sapphire from Madagascar. The unresorbed zircons and lack of newly formed discoid cracks or feathers around these inclusions is a good indication that no heat-enhancement was applied. Additional attention may be placed on the analyses of fluid feathers and other inclusions than zircon to collect further microscopical indications. Best observed in transmitted or fibre optic illumination. 20-60x magnification.

See Figure
C3



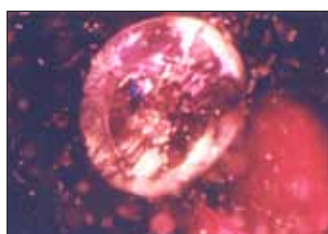
SEM-EDS chemical analysis of a surface reaching zircon crystal (See presence of elements Zr and Si), which was found in an unheated natural pink sapphire from Madagascar.

See Figure
C4



Orange crystal inclusions in an unheated pink sapphire from Madagascar. No signs of melting or decomposition were found. This is indicative that no heat-treatment and no Beryllium-treatment was applied. Magnification 60x in the microscope. Combination of transmitted and fibre optic illumination.

See Figure
C5



Zircon crystal clusters with a discoidal tension crack was found in a pink sapphire from Madagascar which has been heat-treated without the use of Beryllium.

See Figure
C6



Melted zircon inclusions surrounded by "discoid feathers" were found in various natural fancy sapphires from Madagascar which had been treated with Beryllium at high temperatures (see also Lit. 24). These features may also be present in other high-temperature heated corundum which have not been subjected to Beryllium-Diffusion. Transmitted and fiber optic illumination at 40-60x magnification in the microscope.

See Figure
C8, C9, C10
C12-C17



Opaque inclusions in the center of a blue halo was found in this Beryllium-Treated natural yellow sapphire. Combined transmitted and fibre optic illumination. Magnification 120x.

See Figure
C9



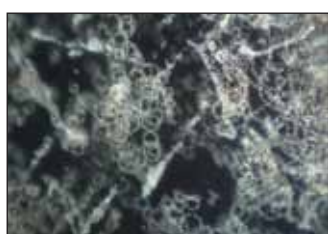
Opaque inclusions associated with blue halos in orange-red Beryllium-Treated sapphire from Songea (Tanzania). Combined transmitted and fibre optic illumination. These features can be seen at various magnifications depending on their size, such as 30-60x.

See Figure
C11



"Incrusted" twinning planes with angular and triangular dense clouds of sub-microscopic whitish particles were found in Beryllium-Treated blue sapphires (origin of sapphires either from Madagascar and Sri Lanka). Magnification 39-50x in the microscope. Fibre optic illumination.

See Figure
C19



Circular, curved and white lines associated to former zones of silk. Magnification 50-100x in the microscope. Fibre optic illumination. This inclusion have so far only been detected in Beryllium-Treated blue sapphires.

See Figure
C18, C20,
C21, C22

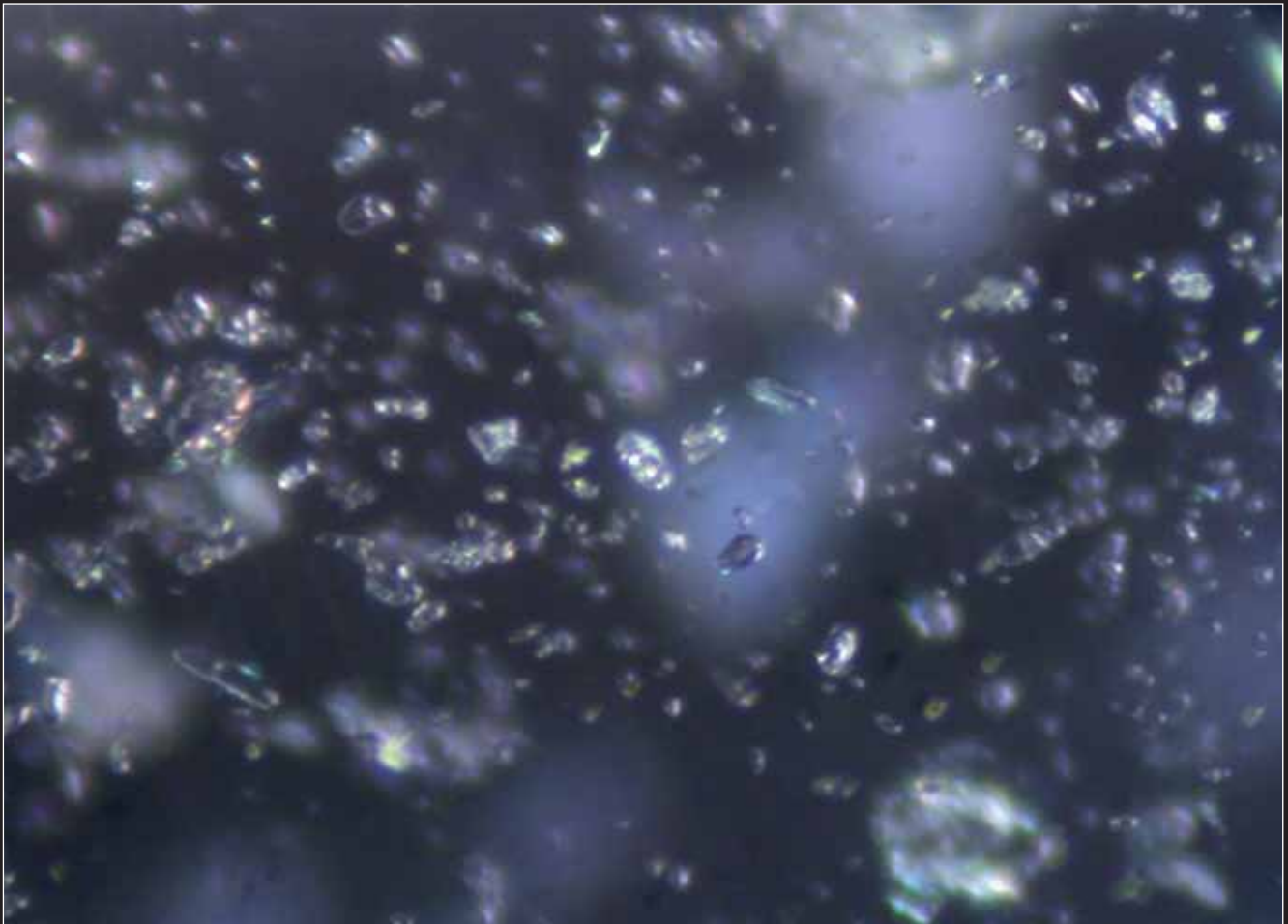


Fig. C1



Fig. C2

Inclusions in Natural Unheated and Heated Pink Sapphires from Madagascar

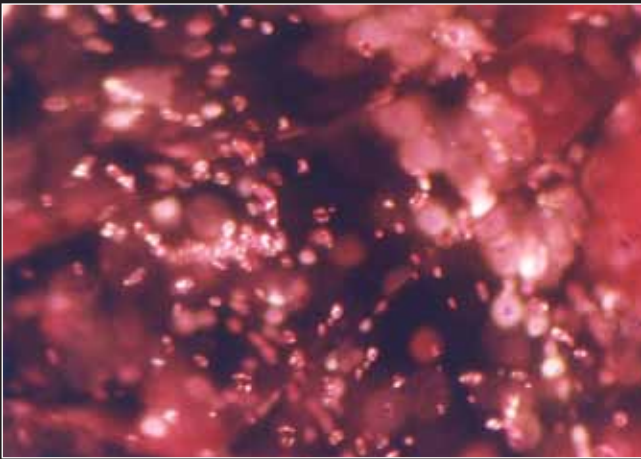


Fig. C3

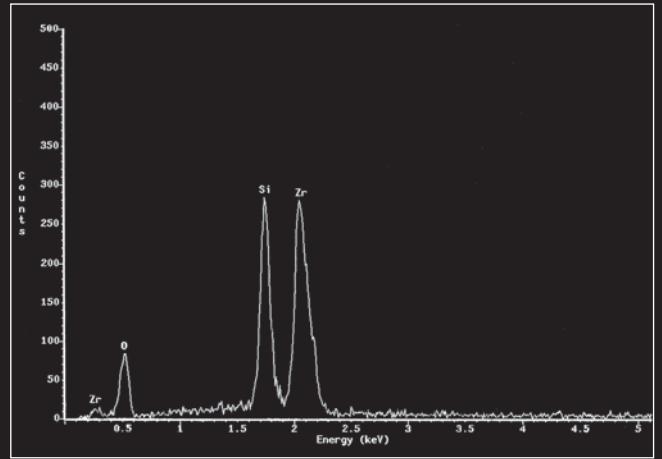


Fig. C4



Fig. C5

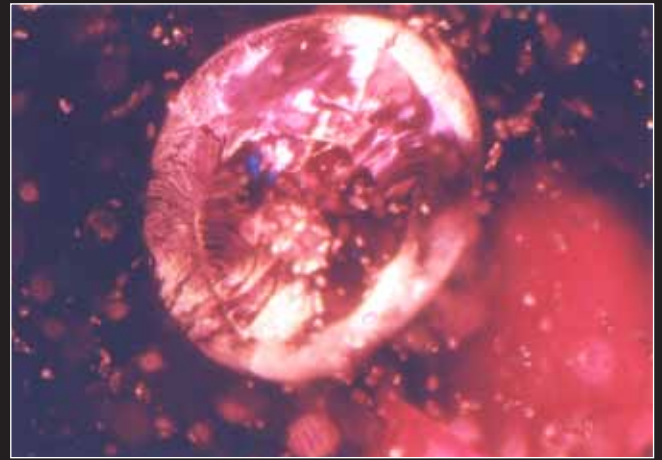


Fig. C6

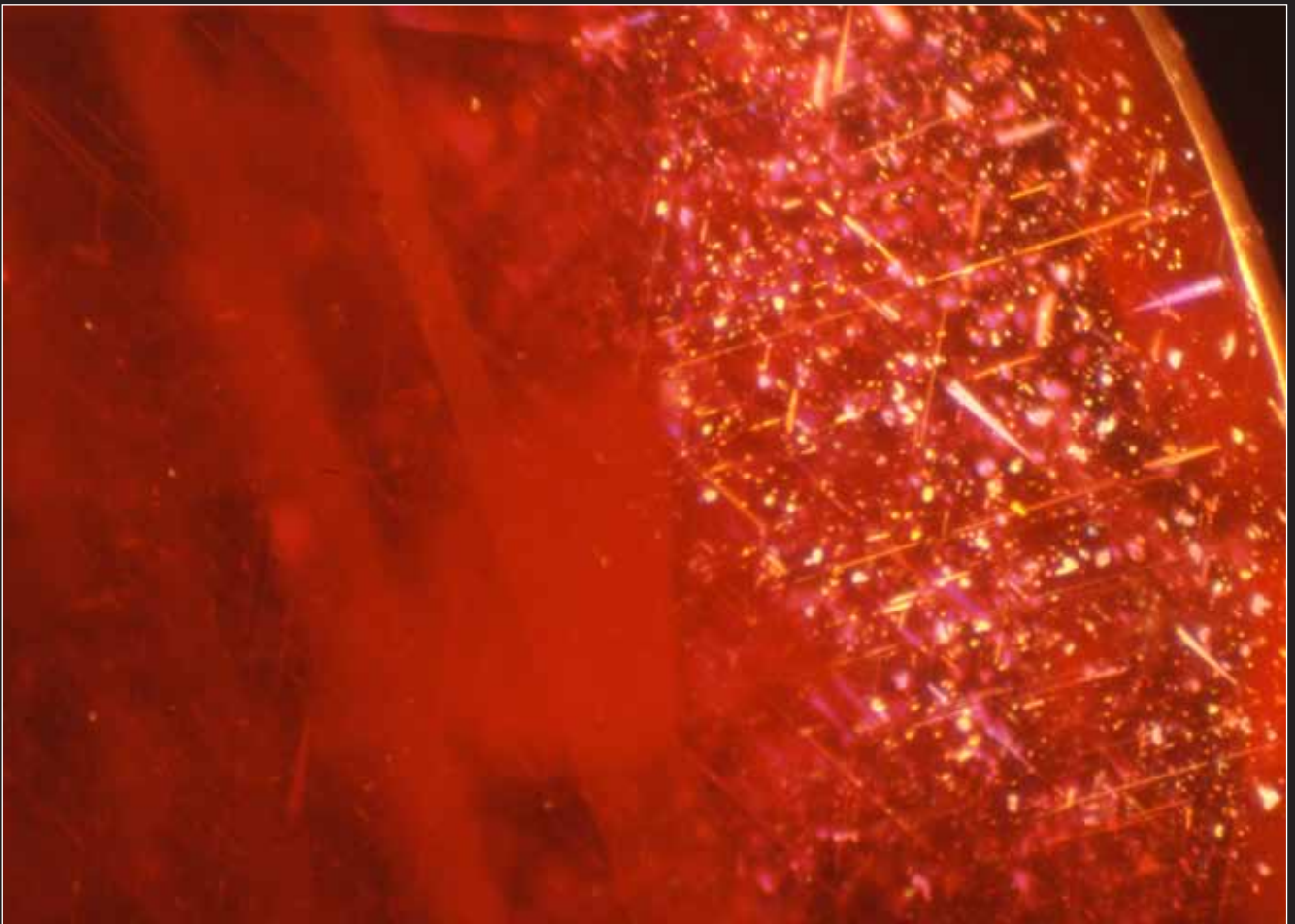


Fig. C7

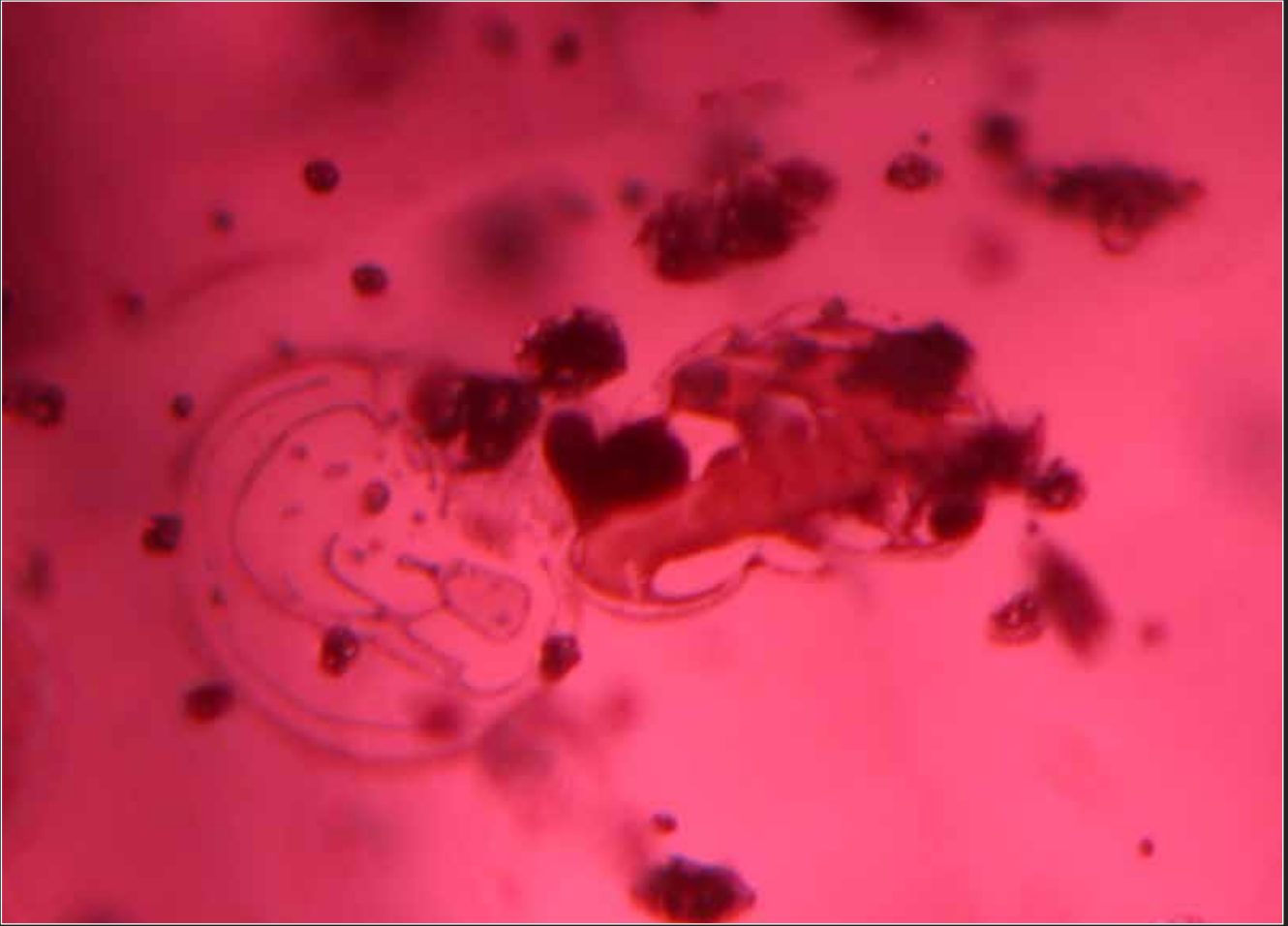


Fig. C8

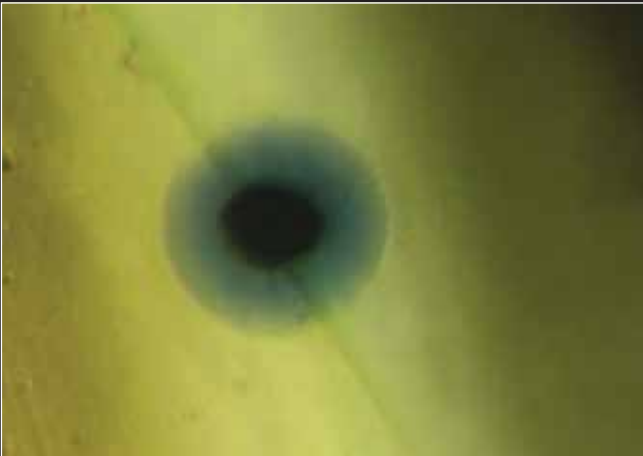


Fig. C9

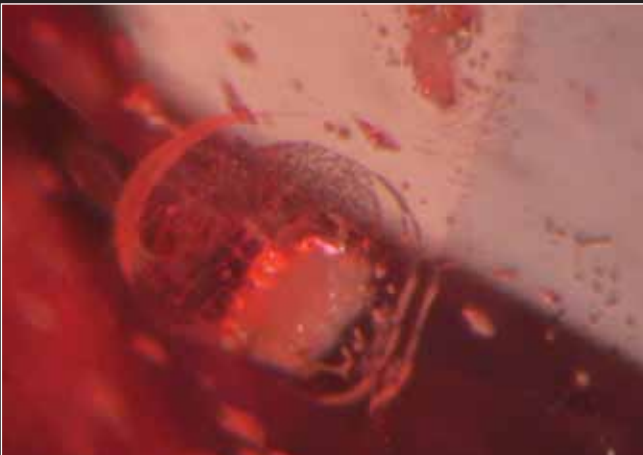


Fig. C10



Fig. C11

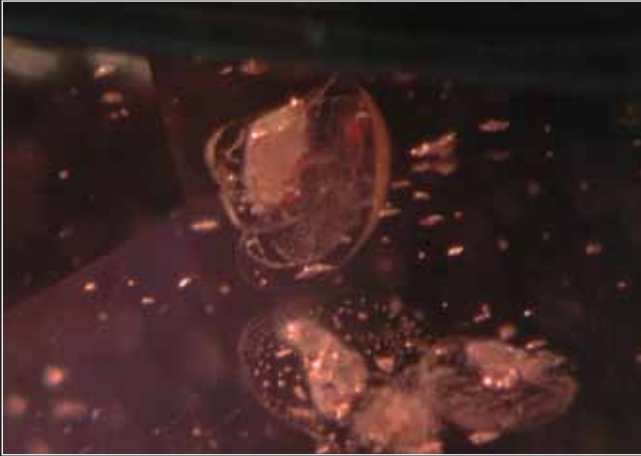


Fig. C12

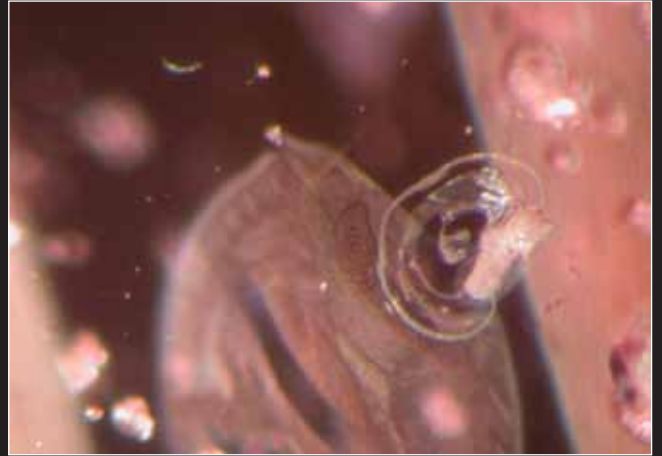


Fig. C13



Fig. C14

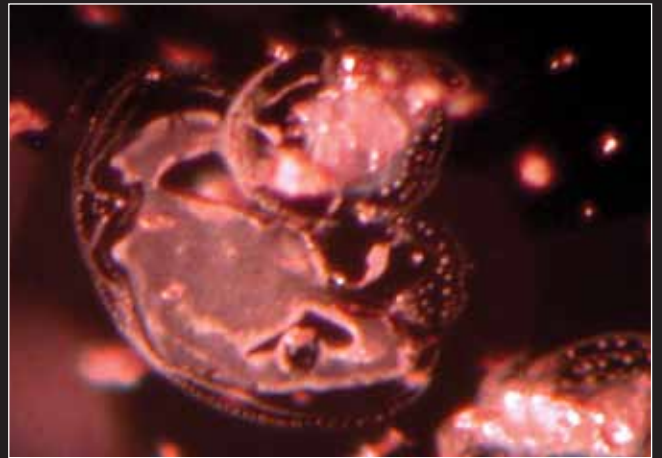


Fig. C15



Fig. C16

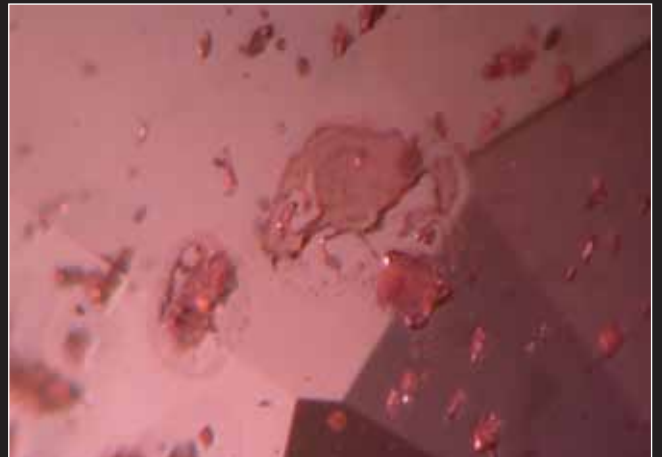


Fig. C17



Fig. C18

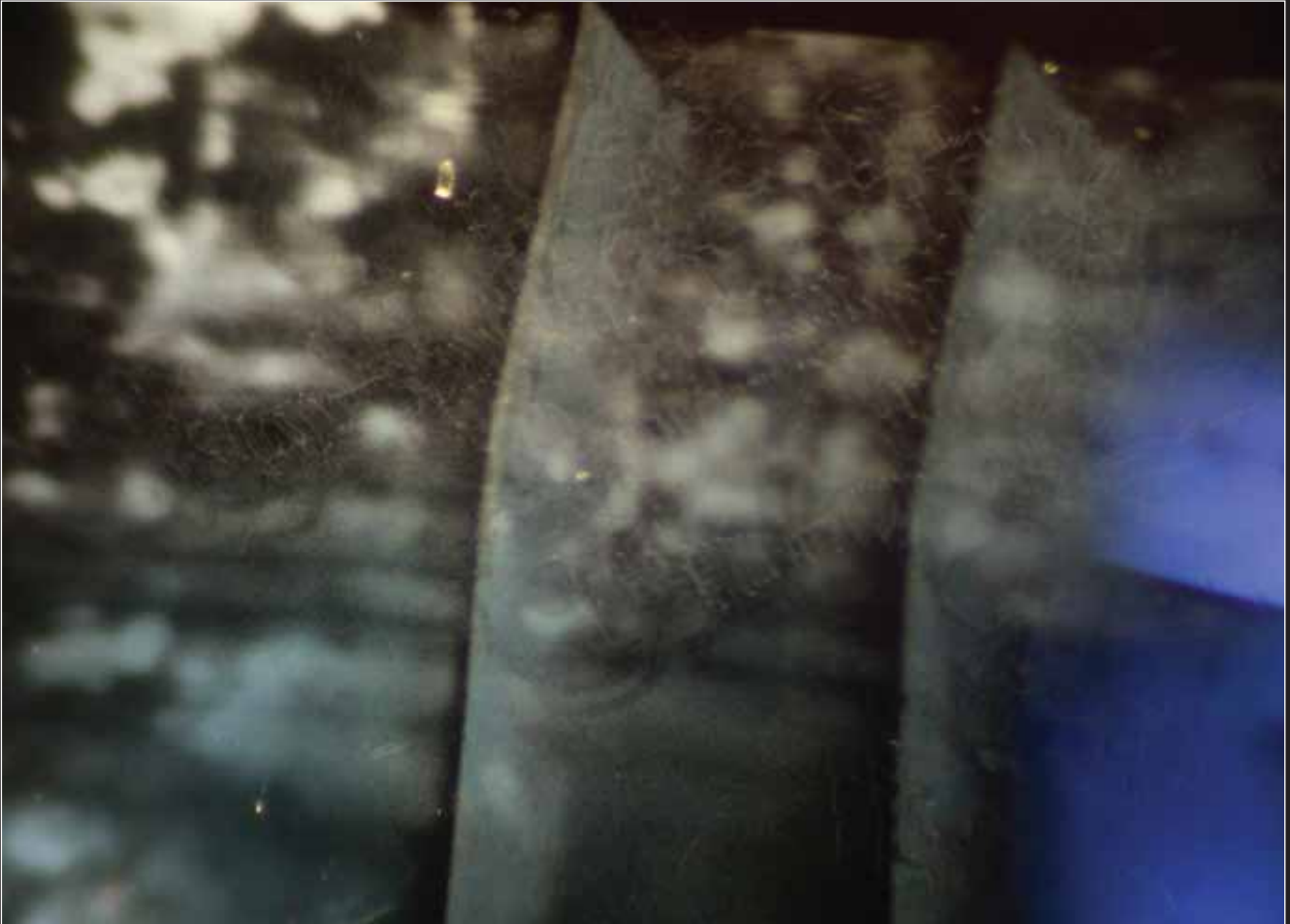


Fig. C19



Fig. C20

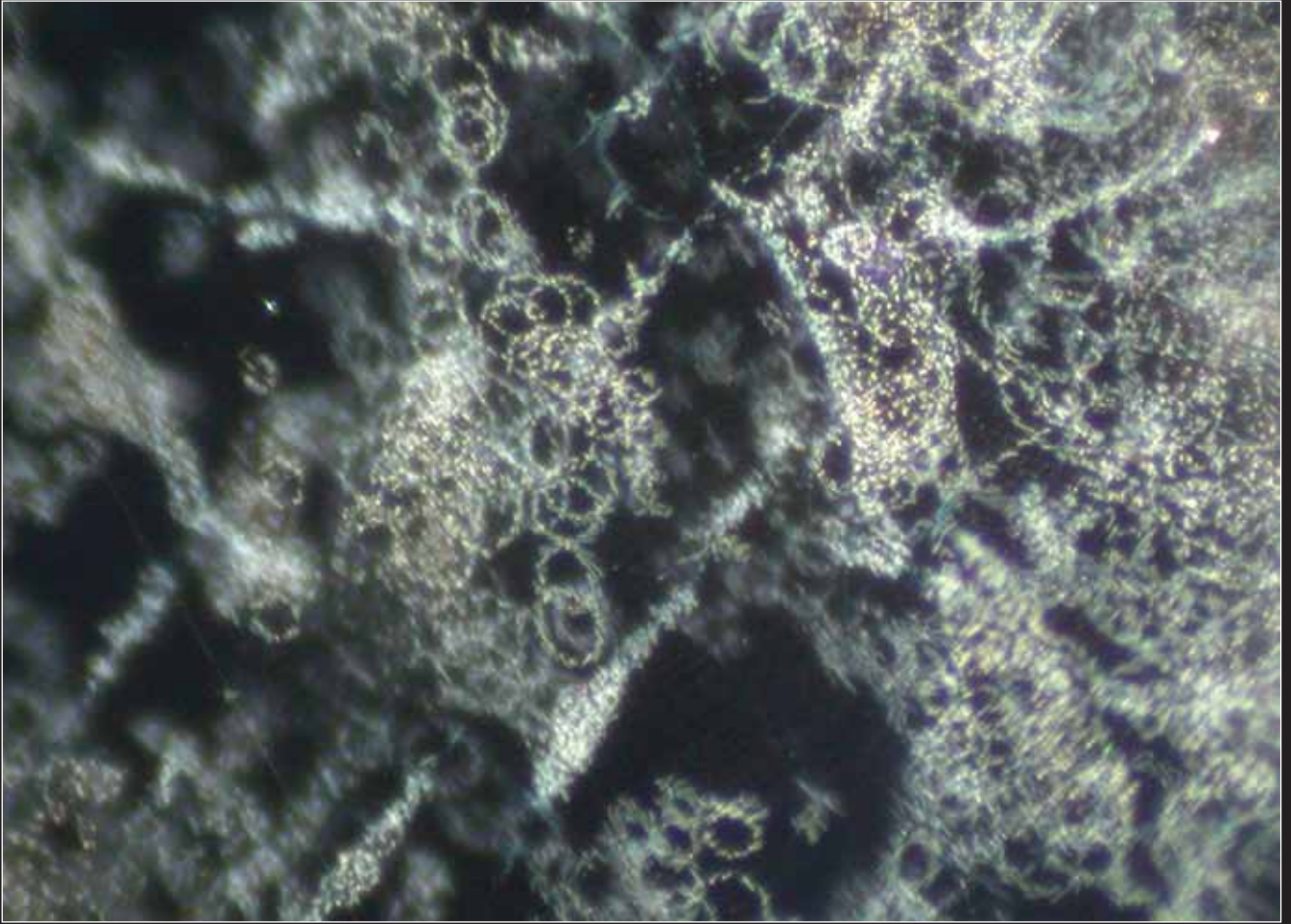


Fig. C21

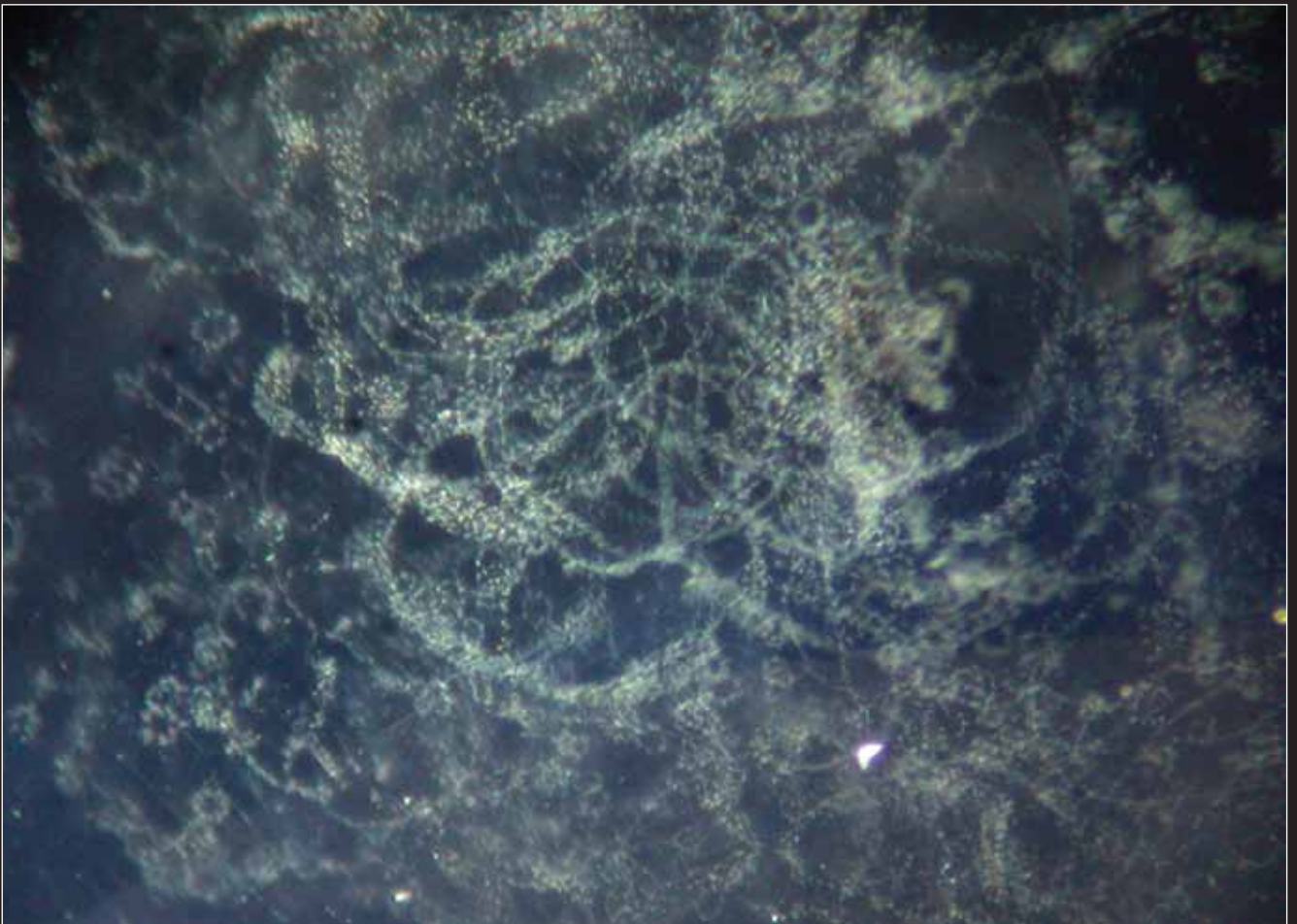


Fig. C22

GRS Table B2 (continued) LA-ICP-MS Analyses (in wt.-ppm) of Beryllium-Treated Synthetic and Natural Corundum

Pit N°	Sample N°	Li	Be	B	Na	Mg	Si	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Ga	Y	Zr	Nb	Mo	Sn	Pb		
		7	9	11	23	25	29	39	42	49	51	53	55	57	59	61	65	69	89	90	93	95	120	208		
		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm		
GRS 25	min.	bd		bd	bd	bd	bd	6.1	bd	65.3	bd	5664	bd	1152	bd	bd	bd	bd	bd	bd	bd			0.93	0.10	
	max.	0.39		7.5	121	40.4	966	30.1	474	127	1.4	23333	6.3	1951	0.35	193	1.7	0.46	0.11	0.95	0.51			3.3	0.88	
Synthetic Ruby	Average	(0.39)	bd	(6.7)	(15.6)	(17.4)	(628)	14.2	(253)	101	(0.67)	11782	(3.2)	1642	(0.20)	(107)	(1.2)	(0.41)	(0.08)	(0.30)	(0.23)			1.8	0.50	
GRS 26	min.	-	bd	-	bd	2.2	bd	bd	bd	47.9	0.30	4615	bd	1031	bd	bd	bd	bd	bd	bd	bd	bd	bd	1.1	bd	
	max.	-	35.0	-	4.5	13.5	538	4.2	-	109	1.4	7587	4.6	1892	0.26	142		0.42						2.5	0.16	
Synthetic Ruby red Be-treated Profile	Average	-	(22.96)	-	(3.8)	7.4	(397)	(2.4)	-	80.9	0.70	6461	(2.2)	1477	(0.20)	(93.7)	(0.32)			(0.19)	0.24			1.7	(0.11)	
GRS 27	min.	-	-	bd	bd	6.0	bd	bd	bd	81.5	bd	5998	bd	1477	bd	131	bd	bd	bd	bd	bd	bd	bd	bd	bd	
	max.	-	-	5.6	16.5	71.4	717	14.5	494	229	0.70	17249	3.3	3429	0.30	396	3.5	0.68	0.16	0.80	0.53			7.3	18.4	
Synthetic Ruby dark red	Average	bd	-	(5.5)	(9.8)	18.2	(525)	(9.3)	(354)	138	(0.55)	12559	(2.3)	2497	(0.25)	204	(1.6)	(0.51)	(0.11)	(0.42)	(0.31)			(3.0)	(1.4)	
GRS 28	min.	bd	bd	bd	bd	5.3	bd	bd	-	86.0	bd	7087	bd	1740	bd	112	bd	bd	bd	bd	bd	bd	bd	1.4	bd	
	max.	0.64	35.6	9.4	5.2	273	608	8.3	-	183	0.83	18300	bd	3292	0.25	474		0.62	0.27	1.0	0.41			7.3	0.41	
Synthetic Ruby dark red Be-treated Profile	Average	(0.38)	(17.95)	(6.8)	(3.5)	20.3	(503)	(4.7)	-	134	(0.61)	14174	bd	2322	(0.17)	243	bd	(0.39)	(0.12)	(0.47)	(0.25)			2.5	(0.15)	
GRS 29	min.	-	-	bd	2.4	17.9	406	3.1	bd	34.7	bd	1161	bd	1508	bd	bd	bd	bd	bd	bd	bd	bd	bd	1.1	bd	
	max.	-	-	14.0	55.6	106	1216	55.5	224	62.0	2.7	2565	8.4	2177	1.6	132	1.9	0.61	0.35	0.19	12.4			3.1	1.1	
Synthetic Ruby pinkish-red	Average	-	-	(10.3)	22.4	70.0	544	21.7	(172)	45.8	(1.3)	2036	(5.9)	1773	(1.0)	(91.5)	(1.3)	(0.45)	(0.20)	(0.09)	5.4			1.9	(0.45)	
GRS 30	min.	-	11.9	bd	-	18.7	bd	bd	-	37.0	bd	1147	bd	1393	bd	47.8	bd	bd	bd	bd	2.0			1.2	bd	
	max.	-	61.2	14.1	-	86.0	686	7.4	-	55.3	3.4	2298	18.3	2051	1.6	119	5.9	0.76	0.31	0.15	11.1			2.9	0.15	
Synthetic Ruby pinkish-red Be-treated Profile	Average	bd	32.0	(10.3)	-	53.7	(475)	(4.0)	-	44.6	(1.6)	1878	(6.5)	1669	(0.93)	76.7	(3.3)	(0.46)	(0.20)	(0.11)	5.6			2.0	(0.10)	
GRS 35	min.	-	-	bd	-	40.1	bd	-	-	32.3	9.2	217	-	5207	-	-	bd	63.1	-	bd	-	-	-	1.2	bd	
	max.	-	-	6.1	-	59.1	622	-	-	45.6	10.9	308	-	5659	-	-	0.95	71.5	-	0.14	-	-	-	1.8	0.22	
Natural orange Sapphire heated (no Be treatment) Surface analysis	Average	bd	bd	(5.9)	bd	48.4	(370)	bd	-	38.8	9.9	280	-	5429	bd	bd	(0.95)	66.7	bd	(0.07)	-	-	bd	1.5	(0.14)	
GRS 35.2	min.	-	-	bd	-	35.6	bd	-	-	32.0	8.8	256	bd	5635	-	-	64.3	-	-	-	bd	-	-	bd	bd	
	max.	-	-	5.8	-	57.4	491	-	-	50.3	11.3	312	3.3	6697	-	-	75.6	-	-	-	0.08	-	-	1.8	0.15	
Natural orange Sapphire heated (no Be treatment) Surface analysis	Average	bd	bd	(5.3)	bd	47.7	(375)	-	-	39.6	10.0	279	(3.3)	6191	bd	bd	70.0	bd	bd	(0.04)	-	-	bd	(1.4)	(0.11)	
GRS 35.3	min.	-	-	bd	-	35.6	bd	-	-	32.0	8.8	256	bd	5635	-	-	64.3	-	-	-	bd	-	-	bd	bd	
	max.	-	-	5.8	-	57.4	491	-	-	50.3	11.3	312	3.3	6697	-	-	75.6	-	-	-	0.08	-	-	1.8	0.15	
Natural orange Sapphire heated (no Be treatment) Surface analysis	Average	bd	bd	(5.3)	bd	47.7	(375)	-	-	39.6	10.0	279	(3.3)	6191	bd	bd	70.0	bd	bd	(0.04)	-	-	bd	(1.4)	(0.11)	
GRS 21	min.	-	bd	bd	bd	bd	bd	bd	bd	72.5	23.6	bd	-	201	-	-	bd	bd	bd	bd	bd	bd	bd	bd	bd	
	max.	-	3.7	5.4	23.9	3.5	1290	18.9	-	281	46.6	14.5	-	635	-	-	28.4	0.60	-	1.4	0.04	-	-	2.1	0.18	
Natural blue Sapphire Be-Treated Profile	Average	-	(2.1)	(4.3)	(11.2)	(2.3)	(620)	(13.3)	-	137	33.3	(9.2)	bd	401	-	-	(9.5)	(0.44)	bd	(0.58)	(0.04)	-	-	bd	(1.5)	(0.15)
GRS 23	min.	-	bd	bd	bd	bd	bd	bd	bd	70.4	24.5	bd	-	510	bd	-	bd	0.95	-	-	-	-	-	bd	bd	
	max.	-	11.2	7.1	115	3.2	2713	7.6	8137	128	45.4	14.8	-	910	5.8	-	1.3	2.2	-	-	-	-	-	1.6	2.5	
Natural blue Sapphire Be-Treated Profile	Average	-	(6.55)	(6.4)	(20.8)	(2.0)	(760)	(5.9)	(8137)	93.1	35.9	(11.0)	-	712	(2.2)	bd	(0.91)	1.4	-	bd	-	-	-	bd	(1.7)	(0.22)
GRS 24	min.	bd	32.6	bd	bd	6.2	bd	bd	bd	80.9	16.9	bd	bd	396	bd	bd	3.7	-	-	3.3	bd	bd	bd	bd	bd	
	max.	0.38	51.0	6.5	7.5	51.9	5608	15.9	800	158	29.4	24.3	2.1	791	0.32	35.1	3.8	19.1	-	5.9	0.16	0.95	3.6	0.71		
Natural blue Sapphire Be-Treated Surface analysis	Average	(0.38)	41.4	(4.7)	(2.6)	22.3	(701)	(7.1)	(331)	103	22.3	(14.6)	(1.8)	568	(0.16)	(17.1)	(1.2)	11.8	bd	4.9	(0.08)	(0.42)	(1.5)	(0.36)		
LOD Be (ppm)		0.35	2.3	3.5	2.3	2.1	334	3.7	124	4.8	0.37	10	1.6	17	0.22	28	0.86	0.24	0.08	0.12			0.72	1.3	0.1	

GRS Table B3 LA-ICP-MS Analysis of Conventional Heated and Beryllium-Treated Natural Colored Sapphires (in wt.-ppm)

		Li	Be	B	Na	Mg	Si	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Ga	Zr	Sn	Ba	Pb
		7	9	11	23	25	29	49	51	53	55	57	59	61	65	69	90	120	138	208
		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
01	Average.	bd	bd	bd	bd	48.45	370.4	38.76	9.94	279.8	bd	5429	bd	bd	bd	66.74	bd	bd	bd	bd
	St.Dev.					5.60	122.2	4	0.4	23.7		149.5				2.6				
02	Average.	bd	bd	bd	bd	47.67	374.7	39.63	10	279	3.32	6191	bd	bd	bd	70.04	bd	bd	bd	bd
	St.Dev.					6.5	63.1	4.5	0.7	15		324.6				2.9				
03	Average.	bd	bd	bd	bd	73.09	847	69.41	10.96	47.91	bd	145.3	bd	bd	bd	104.7	bd	bd	bd	bd
	St.Dev.					9.4	799.8	18	1.5	15.1		29				6.8				
04	Average.	bd	6.40	bd	bd	96.89	448.6	105.4	28.36	656	bd	1031	bd	bd	bd	95.89	1.38	bd	bd	bd
	St.Dev.		1.60			21.1	104.3	11.3	2.3	51.9		62.9				5.3	2.8			
05	Average.	3.95	bd	10.92	78.44	403	1272	225.3	45.64	384.5	5.04	116.3	0.83	bd	50.97	107.5	bd	bd	4.86	3.36
	St.Dev.			3.50	128.8	1005.2	1143	211.2	4.5	81		236.2			86.9	4.6			6.5	4.2
06	Average.	bd	12.67	bd	8.66	98.78	543	123.6	25.7	331.2	bd	333.3	bd	bd	bd	98.79	2.21	bd	bd	bd
	St.Dev.		3.40		15.30	20.1	286.4	16.7	2.2	23.4		46.2				6	3.1			
07	Average.	bd	21.01	bd	bd	96.56	538	122.1	22.22	289.2	bd	515	bd	bd	bd	101.9	22.44	2.29	bd	bd
	St.Dev.		12.3			17.4	232	23.3	2.9	19.7		157.2				5.6	15.2	1		
08	Average.	bd	26.78	bd	bd	46.49	484.1	50.12	53.99	2059	bd	716	bd		bd	132.96	1.03	bd	bd	bd
	St.Dev.		19.90			22.5	539	47.9	5.6	98.2		84.1				3.1	1.3			
09	Average.	bd	bd	bd	5.28	87.89	759	183.8	8.35	bd	bd	947	bd	bd	bd	74.8	bd	7.61	bd	bd
	St.Dev.				6.10	12.8	8.4	43.1	0.9			30.5				1.5		4.6		
10	Average.	bd	bd	bd	bd	22.34	914	176.7	4.2	bd	bd	8187	bd	bd	bd	238.4	bd	bd	bd	bd
	St.Dev.					1.3	112.5	7.4	0.2			79.1				1.7				
11	Average.	bd	min:bd	bd	bd	bd	451.1	98.16	2.89	bd	bd	6559	bd	bd	bd	242.6	bd	5.68	bd	bd
	St.Dev.		max:4.46				58.9	24.6	0.2			44.6				4		1.6		
12	Average.	bd	3.42	bd	bd	48.63	871	177.8	17.91	bd	bd	499	bd	bd	bd	66.34	bd	3.22	bd	0.55
	St.Dev.		1.5			17.2	202	15.4	0.3			33				1.2		0.1		
13	Average.	bd	bd	bd	bd	188.3	417.3	293.8	17.57	17.47	bd	916	bd	bd	bd	44.93	bd	bd	bd	0.28
	St.Dev.					73.1	32.2	87	1.1	22.6		36.1				0.1				0.3
All normalize to 526600																				
LOD (ppm)	0.85	2.6	10.7	4.5	5.8	290	8.5	0.51	14	2.73	29	0.44	40	1.99	0.61	0.4	2.21	0.26	0.24	

LEGEND		
01	GRS 35 S1	Orange Sapphire, Madagascar Conventional Heating
02	GRS 35 S2	Orange Sapphire, Madagascar Conventional Heating
03	Rosa 3.59	Padparadscha, Madagascar Conventional Heating
04	GRS 33	Slightly orangy-pink Sapphire Madagascar, Beryllium-Treated
05	GRS 34	Pink Sapphire, Madagascar Beryllium-Treated
06	12916	Padparadscha, Madagascar Beryllium-Treated (zoned)
07	12916 S2	Padparadscha, Madagascar Beryllium-Treated (zoned)
08	Rot 10.69	Ruby, Vivid red, Madagascar Beryllium-Treated
09	12132	Natural Sapphire, blue Conventional Heating
10	12344 S1	Natural Sapphire, Dark blue Conventional Heating
11	5.019ct S1	Natural Sapphire, Dark blue Conventional Heating
12	12133	Natural Sapphire, Vivid blue Beryllium-Treated
13	12134	Natural Sapphire, Deep blue Beryllium-Treated

Beryllium-Treatment of Commercially Important Blue Sapphires

At the stage of finalizing this report, a new type of commercially important Beryllium-Treated blue sapphires were discovered. The colour of these sapphires matches other types of conventional heated sapphires (low to medium tone, low to medium saturation, not dark, no greenish overtone, good transparency and brilliancy). The identification this material was made during routine Beryllium-Testing at GRS on blue sapphires with unusual inclusion features (see Fig. C18-C22). Testing in immersion did show a slight discoloration from blue to grey in the rim of the sapphires. No orange zone was present. The chemical compositions as determined by ED-XRF was consistent with sapphires originating from Sri Lanka or Madagascar. The spectrum of the sapphires was consistent with those sapphires of low iron-concentrations (see fig. A29). During testing with the UV- LIPS, high Mg-concentrations were found as well as prominent Beryllium-concentrations of approx. 20-50ppm. No further light elements such as Li and B were detected. Further research is currently conducted.

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This summary report has been compiled (second edition) from the following publications.

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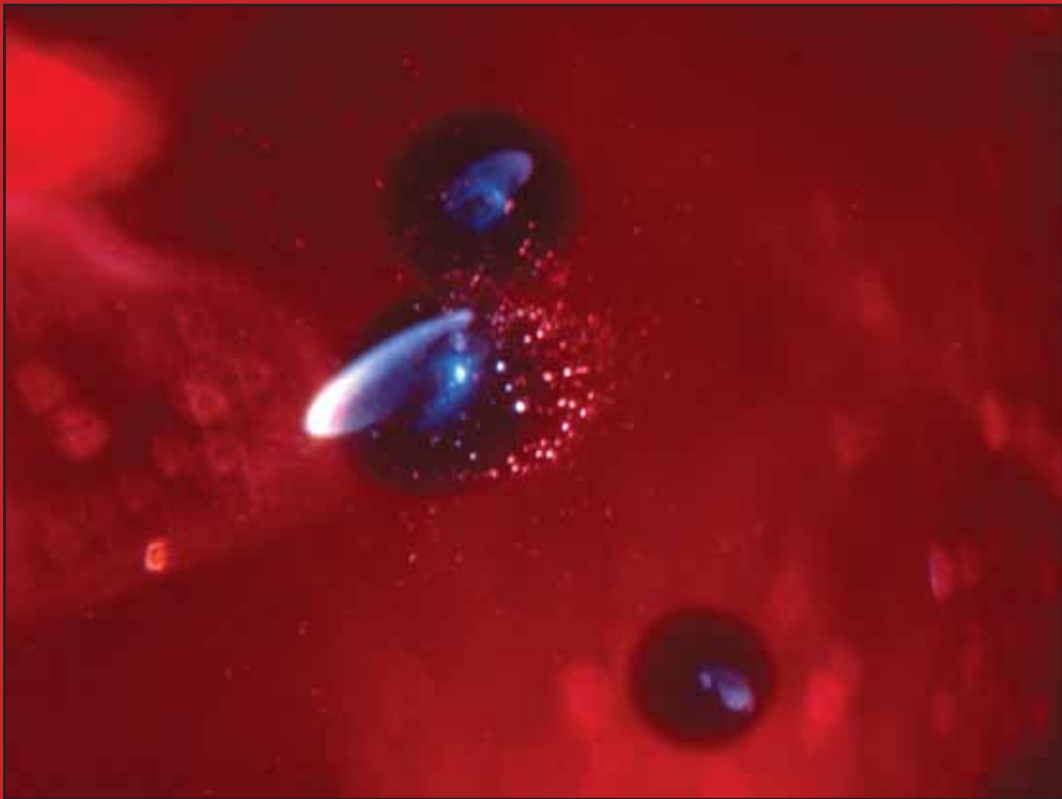
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Inclusion Feature in a Beryllium-Treated Orange Sapphire.
Blue Halos are found around Solid Inclusions.