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**A. Peretti and D. Günther. The Color Enhancement (E)
of Fancy Sapphires with a New Heat-treatment Technique (Part A):
Inducing Color Zoning by Internal (I) Migration (M)
and Formation of Color Centers
E(IM)**

Message From The Editor's Desk

GRS (GRS Gemresearch Swisslab LTD, Switzerland) is a private gemological research company whose aim is to bring leadership and detailed information on important gemological subjects to the public and the trade.

The activities of GRS are focused on the identification of gemstones from all over the world. These include high-quality gems from newly opened mines and gem imitations and synthetics. Methods are constantly being developed for producing imitations of precious gems, such as rubies, sapphires, diamonds and emeralds. In addition to new synthesis methods, thermal and radiation treatments are being developed to improve the appearance and beauty of gemstones. To find the true nature of a gemstone, and consequently its value, the systematic review of gems from new mines and the research and identification of synthetic and treated gemstones have become increasingly important. Active, in depth research utilizing sophisticated scientific methods is the best insurance for high standards. The GRS gemological reports, documenting authenticity and origin of gemstones are internationally accepted and trusted throughout the world. To show its commitment, GRS invests much of its resources and time on research and continuously publishes the results in leading specialized journals.

GRS aims to become a leader in the field of gemological research. To facilitate this goal, it has developed an in-depth cooperation with scientific partners in Swiss Universities, including the Swiss Federal Institute of Technology (ETH). Travel expeditions and studies of remote gem deposits provide the necessary research materials. Further activities include the visits to highly sophisticated synthetic gem producing laboratories.

The constant monitoring of new gemstone treating technologies allows GRS to identify and distinguish "Synthetic" from "Treated", "Enhanced" and "Un-Enhanced" gemstones.

Continuously documenting and publishing gemological research is indispensable for increasing public confidence in the true value and appreciation of gemstones. To show its contribution to gemology, GRS makes its non-confidential research available through its website (<http://www.gemresearch.ch>) and through its own forthcoming journal "Contributions to Gemology".

This first Issue of "Contributions to Gemology" focuses on the new colored sapphire treatment that produces different colors such as the orangy-pink sapphires (reminiscent of colors commonly known as "Padparadscha"). The acceptance of this new product in the world market is being negatively affected by a lack of knowledge of the exact nature of this treatment.

This article represents a comprehensive scientific study focusing on one of these new gemstone enhancement methods. The conclusions made here are therefore exemplary and applicable to this particular method. A more technically oriented version of this article is presently being prepared for an internationally recognized scientific journal specializing in the latest research of analytical chemistry.

GRS is proud to announce that we are the first research team to successfully measure Beryllium in these newly enhanced colored sapphires using a special technique (LA-ICP-MS). Furthermore, this is the first time that these gemstones have been analyzed by the scientific method of cathodoluminescence.

We here at GRS hope that this gemological research article featured in the first issue of "Contribution to Gemology" will contribute to clear-up the confusion caused by this new color enhancement method.

June 2002, Lucerne, Switzerland



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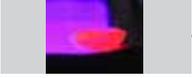
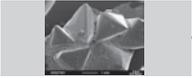
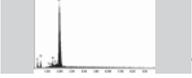
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Abstract

Various colored sapphires have been studied with multiple analytical techniques - including LA-ICP-MS, ED-XRF, SEM-EDS, UV-VIS Absorption Spectroscopy and Cathodoluminescence Analysis - to investigate the origin of color caused by the new treatment method. Beryllium (Be), Magnesium (Mg), Iron (Fe), Titanium (Ti) and Chromium (Cr) concentrations analyzed indicate that the orange contribution to the color is induced by internal migration of trace elements (Mg, Fe, Ti, Cr) and defects, which leads to the formation of color centers.

Keywords:

Corundum, Sapphire, "Padparadscha", Heat treatment, Migration, Diffusion, Excimer Laser Ablation, Defects, Trace Elements, Beryllium, Color Centers

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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 bulk 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, Lit. 1). 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 (Internet Ref 3,4,8 and 13). 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 .

The goal of this report is to contribute to the understanding of the new heat treatment - a treatment which will find a fair place on the market and be distinguishable 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.) New method heat-treated E(IM).
- f.) New method heat-treated, Chantaburi Dec 2001, Table 6, Part A. E(IM1)
- g.) With conventional heat treatment and the additional new heat treatment method, Chantaburi Dec 2001 to Jan 2002, Table 6, Part A. Tested before and after treatment. E(IM1)
- h.) Unheated and conventional heat-treated gemstones, with additional new method heat treatment, Bangkok, Feb 2002, Table 6, Part B. Samples tested before and after treatment E(IM2)

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 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. 2 and 3). 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. 3)). 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 6). 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.

Fig. 1 GRS Color Names for Natural Colored Sapphires and Rubies

Gemological Testing

During routine gemological testing, samples were checked for fluorescence and subjected to a color-stability test procedure (including exposure to UV light as published under www.padparadscha.info). The samples included sapphires of different colors, origin and treatment (N, E, T, E(IM), E(IM1) and E(IM2) and synthetic samples)(See Table 1). Of particular interest are the samples for which the trace element concentration, *Beryllium* in particular, has been analyzed (See Table 6).The samples were first graded for color and saturation according to the GRS Master, and then half-covered with Aluminium Foil. They were than exposed to UV light (Eickhorst lamp, Type Multispec UV-AC) for two days at a distance of 1cm. Two wavelength 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 E(IM)-samples showed a particular reaction (Fig. 6) The E(IM)-samples from Madagascar exhibited intense yellowish-orange fluorescence in long wavelength UV (Fig. 6a.) 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 E(IM)-groups, and absent in the reference samples (E,N). Another group of samples thoroughly examined for *Beryllium* (Sample 1999, Table 6), 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. 2 Dr. A. Peretti selects samples (Chantaburi, 14th December, 2001) enhanced with the new method, sorts the different colors of produced sapphires and non-sapphire crystals (as shown in Fig. 8) 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. 3 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 the new E(IM1) method. 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. 4 Natural Blue and white E(IM1)-enhanced 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. 42 and Fig. 57). The color is found to be unstable. The orange rims are fading after mild exposure to heat.

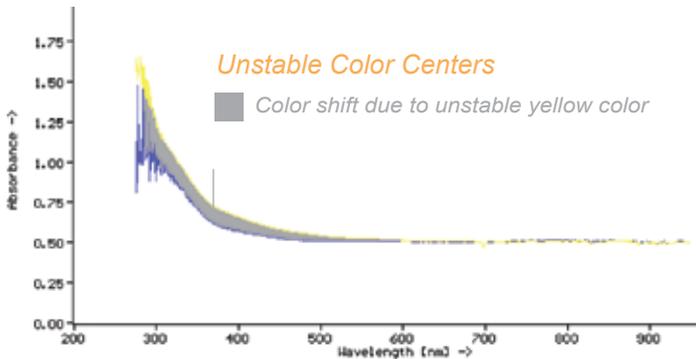


Fig. 5 Polarized UV-VIS-NIR absorption spectra of the E(IM1) enhanced yellow sapphire before and after treatment with UV light. Yellow curve: Spectrum after exposure to UV. Black curve: After fading of yellow sapphire to white color. Note: Shift of the absorption spectrum towards higher absorptions in the blue causes the yellow color in the sapphires due to the presence of color centers.

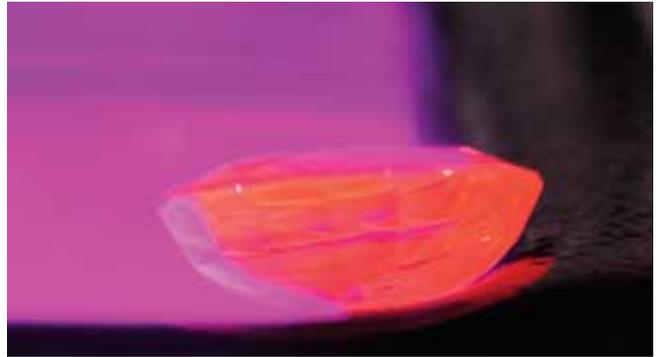
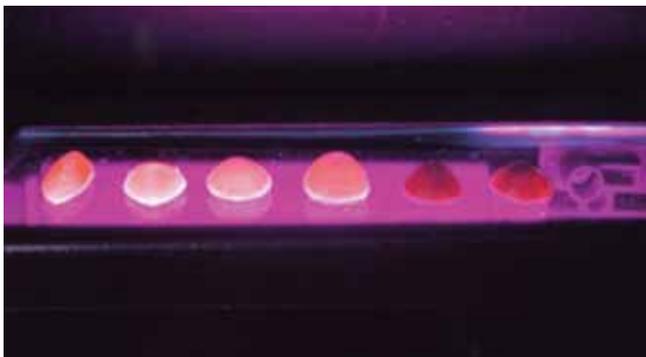


Fig. 6a Fluorescence experiment with Eickhorst UV Lab lamp (long wave 366nm) on faceted sapphires, which had previously been subjected to the new treatment. Left: Orangy-pink sapphires (origin: Madagascar) showing intense orangey fluorescence with more yellowish fluorescence at rim. At right: two samples (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 E(IM) enhanced orangy-pink sapphire (Fig. 6b)

Table 1: UV- Treatment Protocol.

Groups: N = Unheated, E= Conventional Heat Treatment, E(IM1) and E(IM2) = Enhanced with New Method, T = Conventional Surface Diffusion-Treated and Synthetic

GRS No.	Weight	UV Experiments for color change		Color Change YES	Enhancement Group	Origin
		Color: before	Color: after			
12573	0.094	pink	pink		E	Madagascar
12573	0.067	pastel orange	orange	√	E(IM2)	Madagascar
*	0.262	pink	pink		E	Madagascar
*	0.324	orangy-pink	pinkish-orange	√	E(IM2)	Madagascar
12574	0.053	pastel pink	pastel pink		E	Madagascar
12574	0.096	pinkish-orange	orange	√	E(IM2)	Madagascar
12582	0.068	pastel pink	pastel pink		E	Madagascar
12582	0.057	pastel orange	orange	√	E(IM2)	Madagascar
12591	0.044	pastel pink	pastel pink		E	Madagascar
12591	0.091	pastel orange	orange	√	E(IM2)	Madagascar
12580	0.037	pastel pink	pastel pink		E	Madagascar
12580	0.067	Sl.pinkish-orange	pastel orange	√	E(IM2)	Madagascar
12575	0.037	pastel pink	pastel pink		E	Madagascar
12575	0.065	pastel orange	orange		E(IM2)	Madagascar
12737	0.525	brownish-orangy-pink	brownish orangy-pink		N	Madagascar
12737	0.195	pastel orange	orange	√	E(IM2)	Madagascar
12702		purple	purple		N	Madagascar
12702	0.228	pastel orange	orange	√	E(IM2)	Madagascar
1999	0.257	purple	lilac	(√)	N	Madagascar
1999	0.324	pastel orangey-pink	pinkish-orange	√	E(IM2)	Madagascar
GRS 37	0.065	pastel orange	pastel orange		E(IM2)	Madagascar
12567	0.172	pastel orange	orange	√	E(IM2)	Madagascar
12592	0.075	orange	orange		E(IM2)	Madagascar
12570	0.166	orange	intense orange	√	E(IM2)	Madagascar
12611	0.328	golden orange	vivid orange	√	E(IM2)	Madagascar

12634	0.458	lime Yellow	lime Yellow		E	Sri Lanka
12634	0.516	lime Yellow	lime Yellow		E	Sri Lanka
12642	0.349	golden yellow	golden yellow		E	Sri Lanka
12645	0.687	golden yellow	golden yellow		E	Sri Lanka
12745	0.108	orange	orange		E	Sri Lanka
GRS 20	1.355	modified orange	modified orange		E	Sri Lanka
12740	0.177	Sl.orangy-pink	orange	√	E	Sri Lanka
12561	0.184	pink	pink		E	Madagascar
12569	0.166	pink	pink		E	Madagascar
12588	0.195	pink	pink		E	Madagascar
12593	0.168	pink	pink		E	Madagascar
12563	0.155	pink	pink		E	Madagascar
12584	0.135	pink	pink		E	Madagascar
12559	0.173	pink	pink		E	Madagascar
12583	0.165	pink	pink		E	Madagascar

GRS 11	18.441	colorless	colorless			synthetic
GRS 10	8.988	orange	orange			synthetic
GRS 14	5.874	pastel pink	pastel pink			synthetic
GRS 14b	5.843	pastel pink	pastel pink			synthetic
GRS 13	11.640	pink	Sl. Orangy pink	√		synthetic
GRS 12	6.470	yellow	yellow			synthetic
GRS 19a	0.297	blue	blue			T (surface diffusion)
GRS 19b	0.164	blue	blue			T (surface diffusion)

Table 1 (Continued)

GRS No.	Weight	UV Experiments for color change		Color Change YES	Enhancement Group	Origin
		Color: before	Color: after			
12922	0.113	colorless	pastel yellow	√√	E(IM1)	Madagascar
12922	0.084	colorless	pastel yellow	√√	E(IM1)	Madagascar
12922	0.222	colorless	pastel yellow	√√	E (IM1)	Madagascar
12922	0.091	colorless	pastel yellow	√√	E (IM1)	Madagascar
12922	0.109	colorless	pastel yellow	√√	E (IM1)	Madagascar
12922	0.173	colorless	pastel yellow	√√	E (IM1)	Madagascar
12922	0.165	l.pastel pink	brownish-yellow	√√	E (IM1)	Madagascar
12598	0.281	light orangy-pink	orange	√	E(IM1)	Madagascar
12598	0.298	light orangy-pink	orange	√	E(IM1)	Madagascar
12914	0.350	light orangy-pink	orange	√	E(IM1)	Madagascar
12540	0.098	lime yellow	vivid yellow	√	E(IM1)	Madagascar
12540	0.159	lime yellow	vivid yellow	√	E(IM1)	Madagascar
12536	0.276	orange-yellow	golden orange	√	E(IM1)	Madagascar
12589	0.156	Sl.pinkish-orange	orange	√	E(IM1)	Madagascar
12912	0.415	Sl.pinkish-orange	orange	√	E(IM1), recut	Madagascar
12599	0.260	pinkish-orange	orange	√	E(IM1)	Madagascar
12599	0.241	pinkish-orange	orange	√	E(IM1)	Madagascar
12913	0.239	pinkish-orange	orange	√	E(IM1)	Madagascar
12568	0.178	orange	orange		E(IM1)	Madagascar
12578	0.174	orange	orange		E(IM1)	Madagascar
12586	0.184	orange	orange		E(IM1)	Madagascar
12922	0.292	pastel orangy-pink	orangy-pink	√	E (IM1)	Madagascar
12913	0.237	orangy-pink	orange-pink	√	E(IM1), recut	Madagascar
12922	0.241	V.l.pastel purple	brownish-yellow	√√	E (IM1)	Madagascar
12922	0.179	pastel violet	pastel violet with pastel brown	√	E (IM1)	Madagascar
12922	0.057	violet	violet with vivid orange edge	√	E (IM1)	Madagascar
12925	0.208	blue	blue with orange edge	√√	E (IM1)	Madagascar
12925	0.184	blue	blue with orange edge	√√	E (IM1)	Madagascar
GRS 15	0.142	pastel pink	pink with orange rim	√	E (IM)	Songea,Tanzania
GRS 15b	0.092	pastel pink	pink	√	E (IM)	Songea,Tanzania
GRS 16	0.147	colorless	pastel orangy-pink with orange	√√	E (IM)	Songea,Tanzania
GRS 16b	0.093	colorless	pastel orangy-pink with orange	√√	E (IM)	Songea,Tanzania
GRS 21	0.337	medium orange	orange	√	E(IM)	Songea,Tanzania
GRS 22	0.390	medium orange	orange	√	E(IM)	Songea,Tanzania

12614	1.517	white	light yellow with yellow rim	√√	N	Sri Lanka
12614b	1.231	white	light yellow with yellow rim	√√	N	Sri Lanka
12626	1.219	colorless	yellow		N	Burma
12627	1.152	colorless	yellow	√	N	Burma
12613	4.930	V.light yellow	light yellow	√	N	Sri Lanka
12620	0.758	V.light yellow	V.light yellow		N	Burma
12622	0.816	V.light yellow	V.light yellow		N	Burma
12625	1.226	V.light yellow	V.light yellow		N	Sri Lanka
GRS 43	2.078	V.light yellow	yellow	√	N	Sri Lanka
12624	0.910	light yellow	light yellow		N	Burma
12629	4.099	yellow	yellow		N	Sri Lanka
12619	1.246	light lime yellow	yellow	√	N	Sri Lanka
12606	1.379	pink	pink		N	Burma
12607	0.606	pink	pink		N	Burma
12609	0.749	pink	pink		N	Burma
GRS 34	2.113	pink	pink		N	Madagascar
2132	0.926	purple	lilac	√	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 treated samples from Madagascar E(IM), E(IM1) and E(IM2) reacted differently to all other samples, excluding unheated ones (See Table No.1). Significant changes in the color were seen in samples heated with the new treatment E(IM), and a shift towards more yellow or orange was observed (as shown in the Table 1). A color change from near colorless to yellow was also observed in untreated sapphires of Sri Lankan origin (Table 1). This unheated group of sapphires is known to contain specific color centers (Lit. 19). In E(IM) 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 E(IM1)- heating process developed a thin layer of yellow color during the long term UV exposure (shown in Fig. 4). This observation was also made of E(IM1) enhanced blue sapphires (Fig. 4) 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.

Scanning Electron Microscope Analysis (SEM)

Sampling of colored sapphires enhanced by the new treatment in Chantaburi included the study of faceted gemstones E(IM1) (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. 8). 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. 14). The materials were identified as consistent with glass-aggregates, zircon and Chrysoberyl (Table 2).

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. 16-19), mostly composed of Zr-oxide, plus additional element Silicon (Si), Aluminium (Al), Magnesium (Mg), Calcium (Ca) and Fluorine (F). *Beryllium* could 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. 8) and also by the craters produced at the surface of the sapphires (Fig. 14, 15). 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 is a topic of ongoing international research (Internet Ref. 09, 11, 12, 13). The role of the heavy elements (such as Zr) and, on the other hand, the light elements (such as *Beryllium*) in the heating runs must be further investigated.

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	white	2.78	intr.	not readable	glass
0.366	white	2.78	intr.	not readable	glass
0.424	white	2.60	intr.	not readable	glass
0.481	white	2.60	intr.	not readable	glass

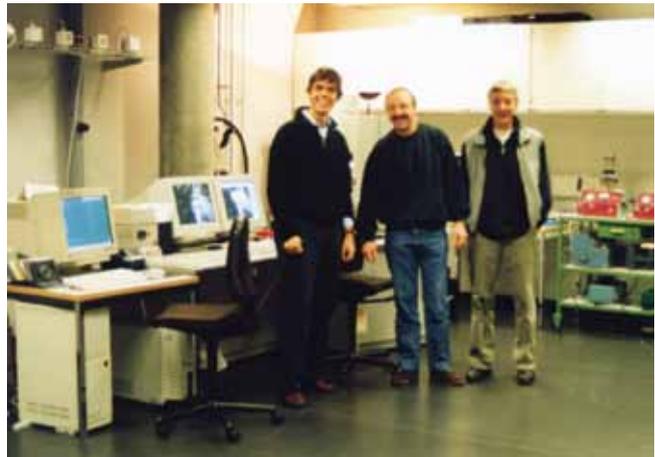


Table 2: Selected representative ID Data on the identified minerals accompanying the sapphires in the new E(IM1)-heat treatment runs. Samples cut in half and polished.

Fig. 7 In February 2002, Chrysoberyl samples were investigated by Scanning Electron Microscopy (SEM) at ZMB laboratory of the University of Basel (Switzerland).

From left to right:
Dr. A. Peretti with laboratory head
M. Duggelin and D. Mathys.



Fig. 8 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. 9. Dr. A. Peretti mounts the Chrysoberyl samples for SEM-EDS analysis in February 2002 at the University of Basel (Switzerland).

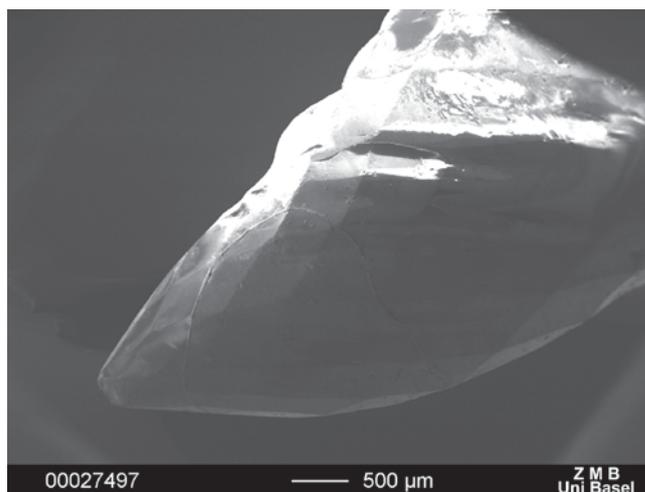


Fig. 10 SEM-SE image of a faceted Chrysoberyl crystal after heat treatment. The crystal has a thin film overgrowth with interference color. Sample not carbon-coated for analysis. Acceleration voltage 20kV



Fig. 11 Macro photograph of glass-aggregate formed by the melting of non-sapphire materials during the new E(IM1)-treatment.

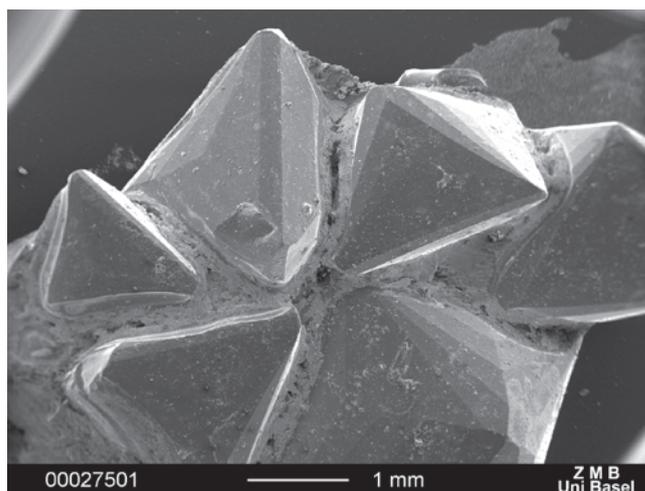


Fig. 12 SEM-SE image of different colored sapphires clustered together in accidental circumstances during the new E(IM1)-heat treatment experiments. Acceleration voltage 15kV.

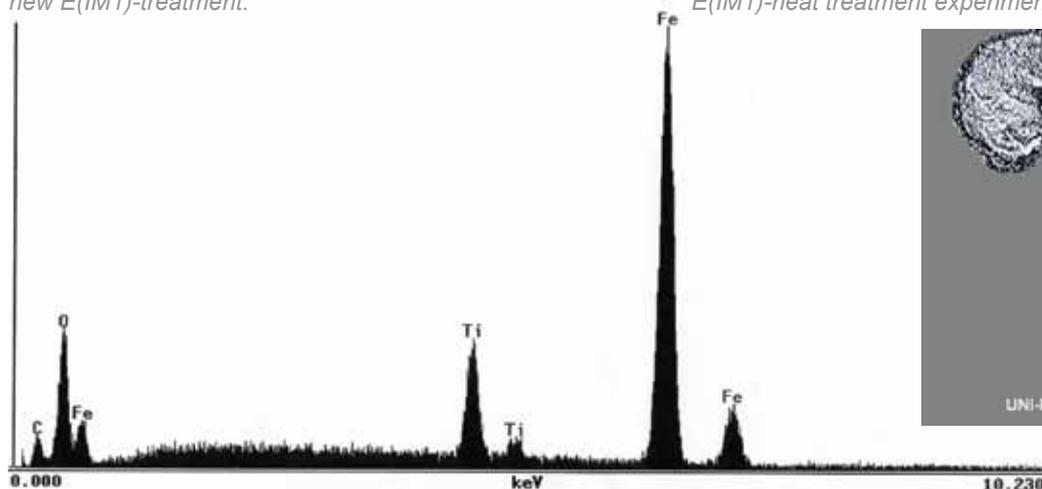


Fig. 13 SEM-BSE image of an inclusion in a fancy sapphire unenhanced by heat (Songea, Tanzania) as determined in 1996 at the SEM laboratory at the University of Basel's Geological Institute. The SEM-EDS spectrum of the white phase in the picture is shown on left (Fe-Ti-oxide, Carbon (C) from coating). The inclusion is composed of an intergrowth of Titanium (Ti)-oxide and Iron (Fe)-Titanium (Ti)-oxide mineral inclusions, approx. 10 micrometers in size.

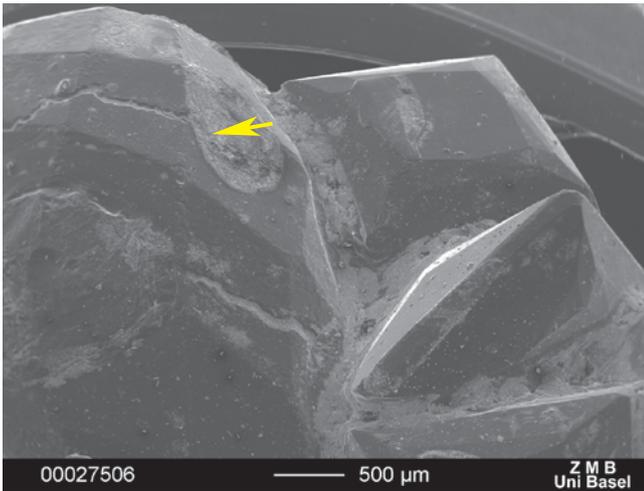


Fig. 14 SEM-SE image of sapphire showing craters due to surface melting of the sapphire material (See arrow). Acceleration voltage 30kV.

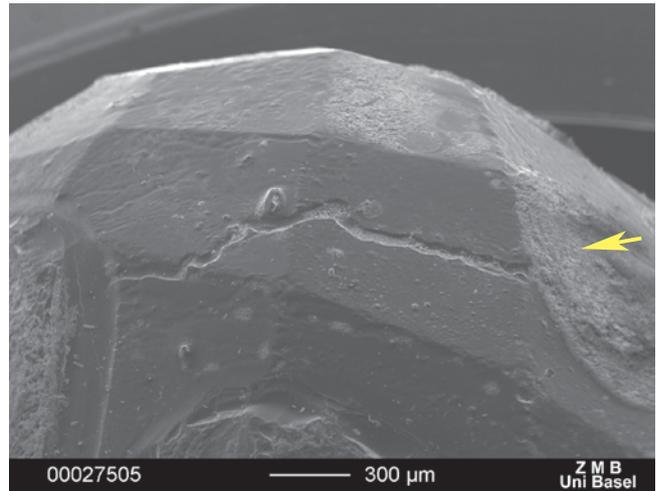


Fig. 15 SEM-BSE image of enlarged area of Fig. 14. The crack is shown as well as a melting crater in the sapphire (arrow) in course of the new E(IM1)-enhancement. Acceleration voltage 30kV.

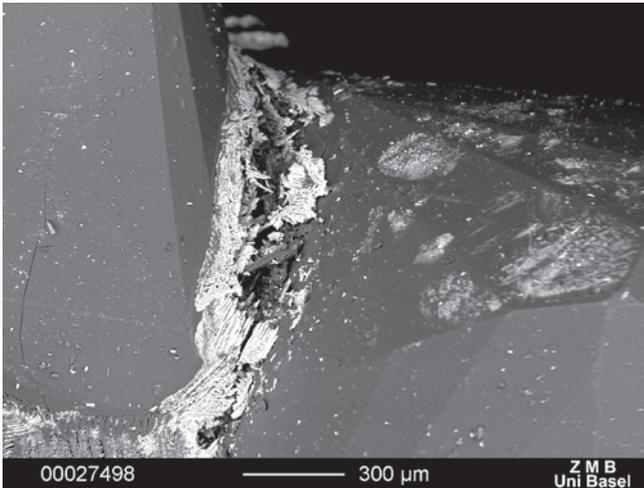


Fig. 16 SEM-BSE image of the matrix between sapphires. Note: Presence of more heavy elements is seen as a white color. These heavy elements are mostly composed of Zirconium (Zr)-oxide of unknown crystal structure (Aluminium (Al) from corundum contamination) as shown by SEM-EDS spectrum on right (Acceleration Voltage 20kV). Note also: Presence of fluorine (F). Samples carbon (C) coated.

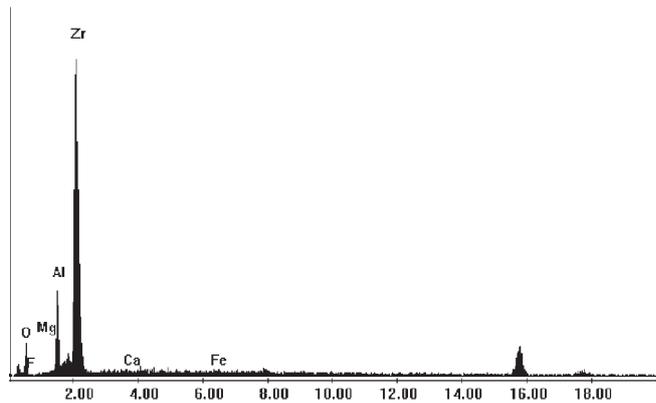
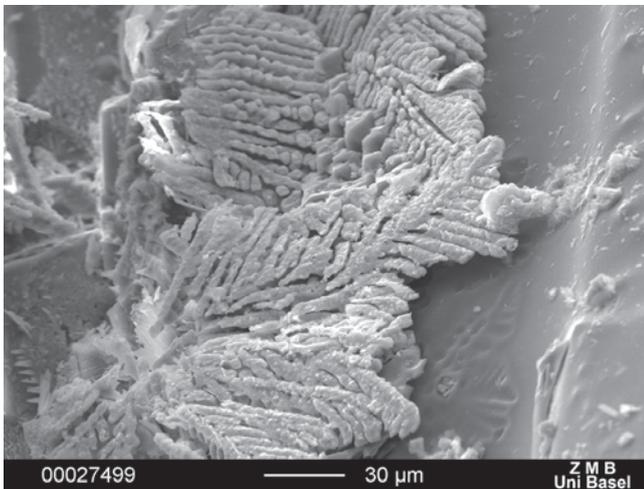
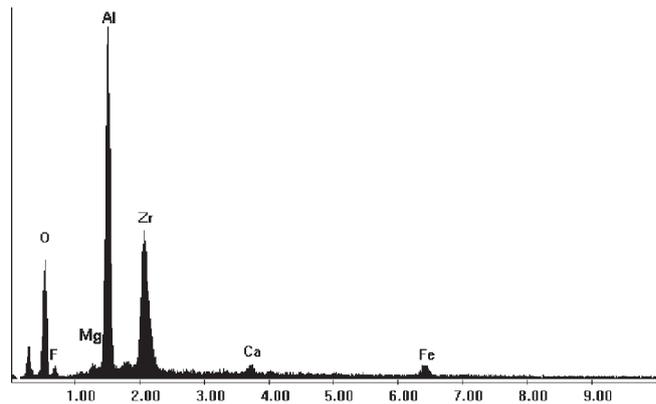


Fig. 17 SEM-SE enlarged portion of the crack shows the growth of dendrites of Zirconium (Zr)-oxide and SEM-EDS spectrum of the same area (Aluminium (Al) from corundum). No high concentrations of iron (Fe), titanium (Ti) or chromium (Cr) were detected as shown by SEM-EDS spectrum on right (Acceleration Voltage 30kV).

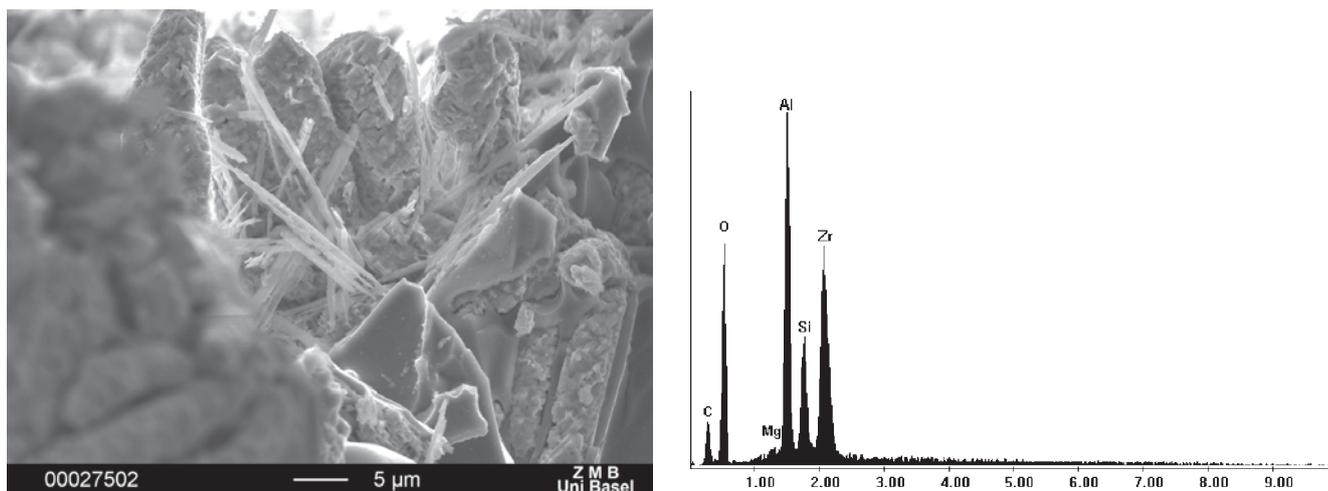


Fig. 18 SEM-SE image of several crystallites of different crystal shapes were detected, mostly composed of Zirconium (Zr)-oxide and Silicon (Si)-oxide phases as shown by the SEM-EDS spectrum. Aluminium (Al) from Corundum. Sample carbon (C) coated. Acceleration voltage 15kV.

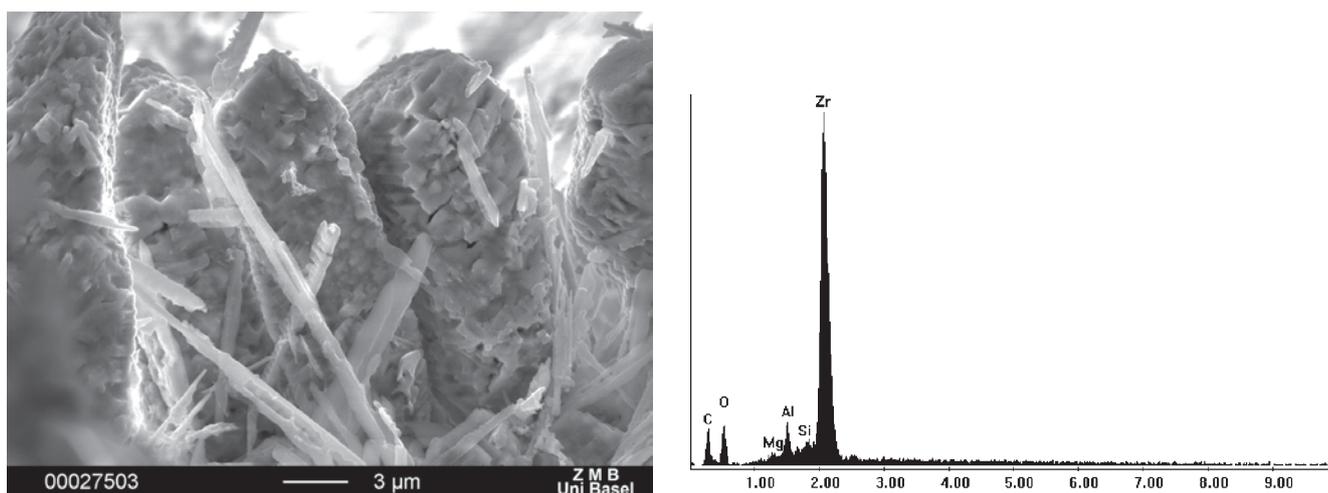


Fig. 19 SEM-SE image of crystallites composed of Zirconium (Zr)-oxide. This crystallite must have been formed over the course of the heating experiments. SEM-EDS spectrum on right (Acceleration voltage 15kV). Sample carbon (C) coated.

Sample	Repeated Measurement		Average 5	Ratio	Repeated Measurement		Average 17	Ratio	Average 15		Ratio
	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
	12914-0.350		12914-0.350		12737-1.25		12737-1.25		12737-Or		12737-Or
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	-
Al2O3	99.648	99.693	99.4997	-	99.183	99.242	99.4997	-	98.972	99.4997	-
K2O	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	11.0950
TiO2	0.024	0.027	0.0164	1.5541	0.020	0.014	0.0149	1.1378	0.069	0.0639	1.0790
V2O5	0.012	ND	0.0032	1.8666	0.003	0.000	0.0031	0.4909	0.009	0.0031	2.9091
Cr2O3	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	-	-
Fe2O3	0.136	0.108	0.1359	0.8974	0.625	0.542	0.7060	0.8265	0.646	0.8121	0.7955
Ga2O3	0.021	0.022	0.0091	2.3654	0.027	0.027	0.0136	1.9879	0.033	0.0140	2.3608

Table 3b 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 3a Averaged LA-ICP-MS Data of Natural Sapphires of Different Colors Enhanced by the New E(IM1)-Method and Unheated Natural (Purple, Violet) Sapphires

Tab.3a Averaged LA-ICP-MS trace element concentration (in ppm) of Natural Sapphires of different colors enhanced by the new heat treatment E(IM1) and two Natural Sapphires unheated (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
	rim analysis		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

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 - analytik@balcab.ch - using a SPECTRACE QuanX 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 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. Using the advantage of the SPECTRACE QuanX system 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. 3b). LA-ICP-MS have already compared to another ED-XRF instrument on a larger scale and found to be compatible (Lit. 8) with the exception of Gallium (Ga), therefore confirming that trace element determinations have been checked for accurate consistency with

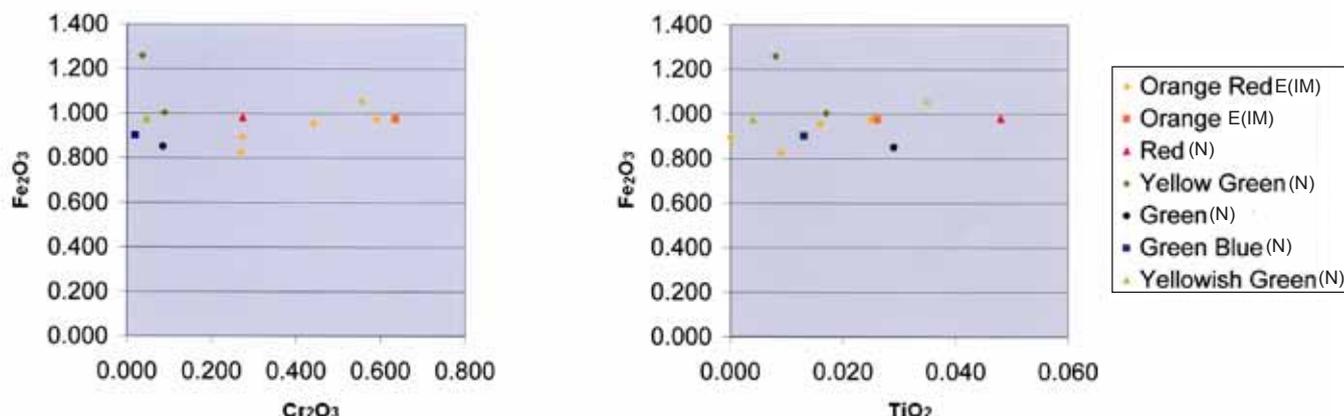


Fig. 20 Representation of ED-XRF data on the dominant trace element concentrations in natural colored sapphires unheated (N) and enhanced by heat with the new E(IM)-method, in oxide wt.-%. These intense saturated colors are found in the sapphires originating from Songea (Tanzania).

other methods as to the best of our possibilities at this stage. The analytical error on the concentrations for TiO_2 is given here as maximal approx. ± 0.01 wt-%, for Cr_2O_3 approx. ± 0.01 wt-%, for Fe_2O_3 approx. ± 0.01 wt-% and for Ga_2O_3 approx. ± 0.002 wt-% and for V_2O_5 approx. ± 0.01 wt-%. These errors are small enough to allow us to interpret the data (See Fig. 23). 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. 5 and shown in Fig.20, 23, 25 and 33. 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.



Fig. 21 The GRS UV-VIS-NIR multi-channel spectrometer used for recording the absorption spectra of the gemstones. A special measuring chamber set-up (To right 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.

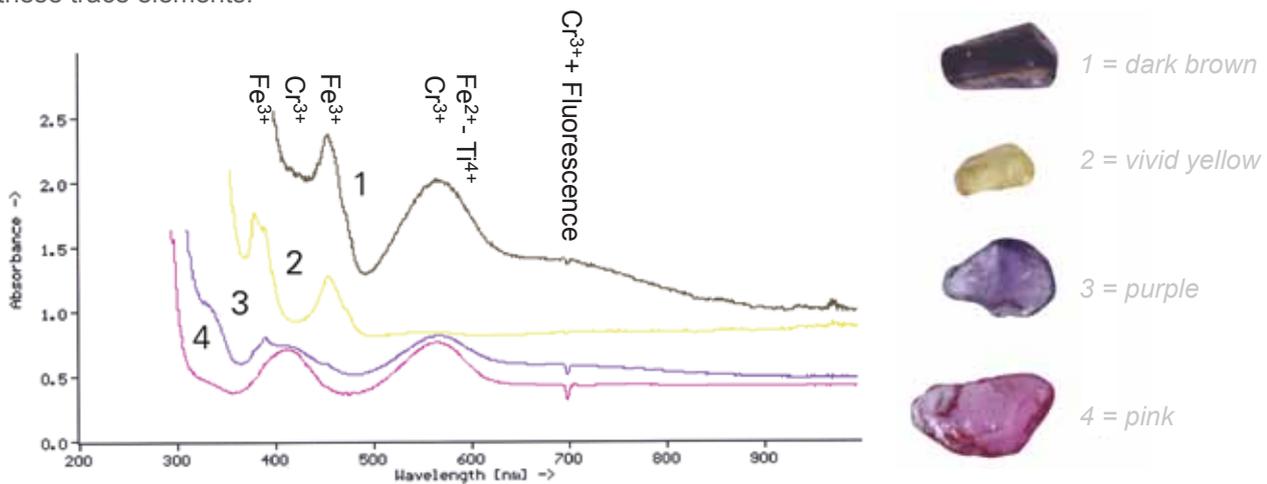


Fig. 22a UV-VIS-NIR non-polarized absorption spectra of natural unheated Fancy Sapphires (origin Madagascar). The observed absorption bands and lines can be explained by variable concentrations in chromium (Cr^{3+}), iron (Fe^{2+} , Fe^{3+}) and titanium (Ti^{4+}) (Trace elements confirmed by ED-XRF analyses). See Fig. 23 and Compare Lit. 28.

Fig. 22b The samples of four different colors of Natural Sapphires spectroscopically measured (Fig 22a).

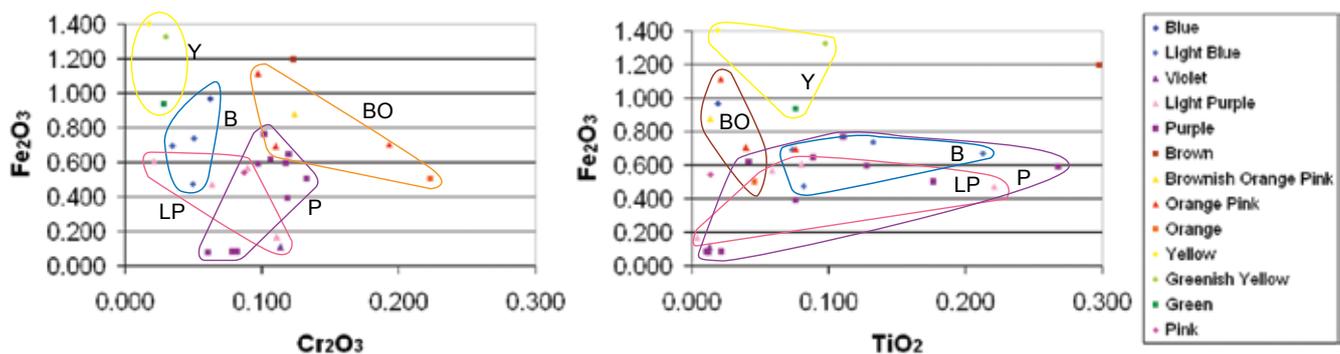


Fig. 23 Representation of ED-XRF data on the dominant trace element concentrations (in oxide wt.-%) in natural colored sapphires unenhanced by heat (N) from Madagascar. Color groups: Y = yellow, greenish yellow, green; BO = brown, orange-pink; B = light blue, blue; LP = light purple and purple; P = purple violet

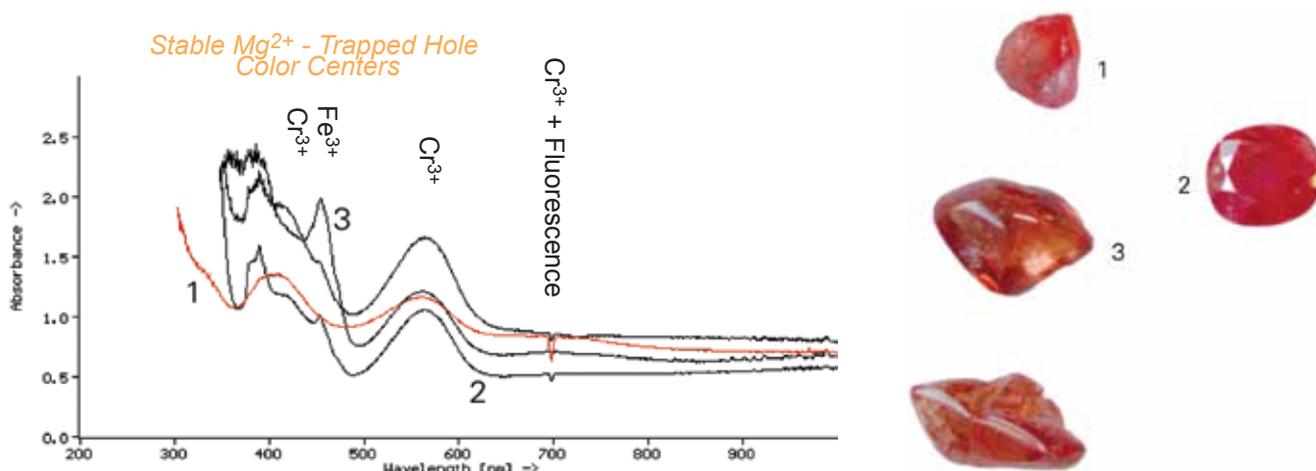


Fig. 24 Representative absorption spectra of natural brownish orangy-pink sapphires from Madagascar unenhanced by heat. Some of the samples are reminiscent of "Padparadscha" colors. Note: Similarity of the absorption spectra of the samples enhanced by heat with those of the new E(IM) method (See Fig. 26). 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. 23), LA-ICP-MS analysis and literature (Lit. 04 and 28). Representative LA-ICP-MS analysis: Mg= 91ppm, Ti= 89ppm, V=21ppm, Cr=521ppm, Fe= 4937ppm, Ga= 101ppm (Average 17 analysis, sample No GRS 12737, LA-ICP-MS, Table 6, Part B).

Fig. 27 UV-VIS-NIR absorption spectra of natural sapphires from Madagascar enhanced with the new E(IM1) method. 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.4 and 5. Effect of unstable color centers to the absorption spectra See Fig. 5 and Fig. 29. Interpretation of color centers based on measured Mg-concentrations and absorption in the blue region of the spectrum (See also Lit. 04).

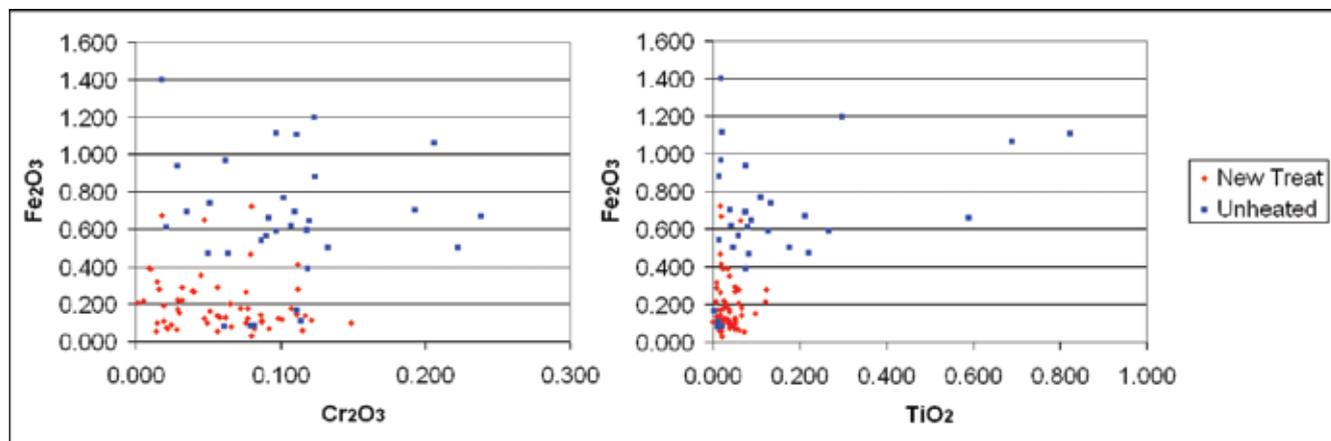


Fig. 25 Iron (Fe), chromium (Cr) and titanium (Ti) concentrations (ED-XRF analysis in oxide wt.-%, See Tab. 5) of natural fancy color sapphires, unheated (blue), and enhanced with the new E(IM1) method (red). Origin: Madagascar. Note: Enhanced E(IM1) sapphires are not enriched in these trace elements (Fe, Cr and Ti) in comparison to those unheated (N).

Origin of Color Analysis of Natural Fancy Sapphires from Madagascar and Tanzania (Songea) Enhanced by the New E(IM1)-Method

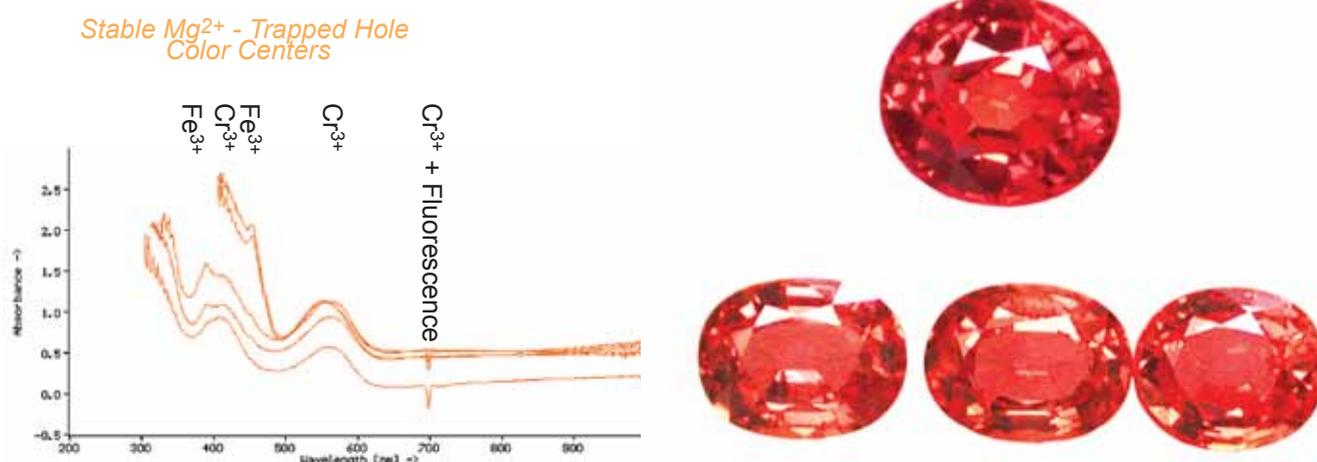
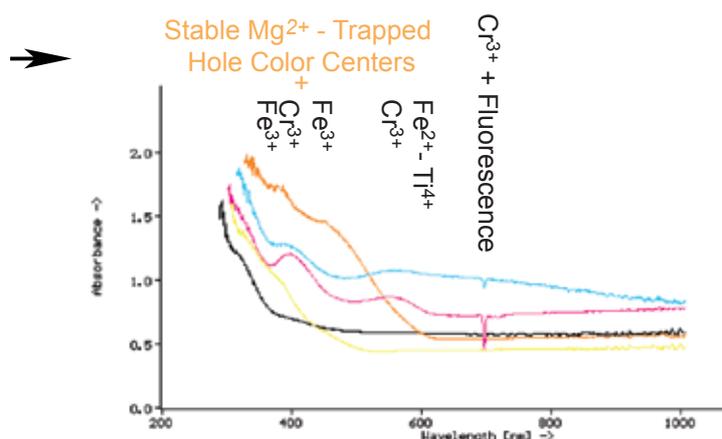


Fig. 26 Polarized UV-VIS-NIR absorption spectra of natural pastel orangy-pink sapphires (Origin: Madagascar) to vivid orange-red sapphires (origin: Songea, Tanzania) enhanced with the new E(IM)-method. Absorption spectra can be interpreted as absorption bands and lines caused by trace elements iron (Fe^{3+} , Fe^{3+} -pairs) and chromium (Cr^{3+}) and magnesium (Mg^{2+} -Trapped Hole Color Centers). Chemical analyses by ED-XRF and LA-ICP-MS (See Fig. 20, 33 and Tables 3, 4 and 7b,c). Increase in intensity of the 450 absorption line can be correlated with increasing Fe-concentrations (Fe^{3+} -pairs) in the gemstones (Images on right).



Corresponding LA-ICP-MS data see sample numbers in Tab.4:

- GRS 12922 (Vivid Orange Sapphire)
- GRS 12925.1 (Blue Sapphire)
- GRS 12598 (Padparadscha)
- GRS 12540 (Yellow Sapphire)
- GRS 12922 (White to Near Colorless Sapphire)

Sample	Color	Average		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
12922	White	19	Average	3.2	129	156	67.8	548
			Std Dev	5	21.8	22.9	15.2	76

Table 4: Averaged chemical compositions (LA-ICP-MS data in ppm) of samples investigated by UV-VIS-NIR absorption spectroscopy (Fig. 27). Detection limits See page 24.

BOX: Methods UV-VIS-NIR Absorption Spectroscopy

Spectroscopic analysis was carried out with a multi-channel spectrometer with 1024 diode arrays and an 80Watt Xenon lamp from J&M GmbH in Aalen, Germany. 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 (TIDAS).

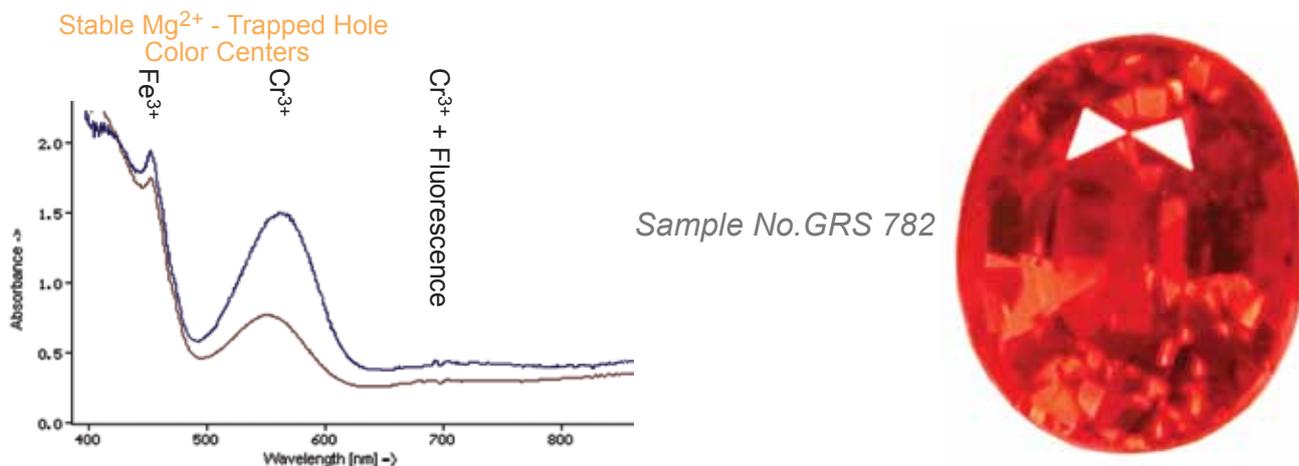


Fig. 28 Polarized UV-VIS-NIR absorption spectra of a vivid orange sapphire enhanced with the new method E(IM). Absorption parallel and perpendicular to the c-axis are shown, responsible for yellow-orange to orange-red dichroism in the gemstone. Note: Strong effect of pleochroism to the development of the 550nm band and the presence of a prominent 450nm line (Due to higher Fe $^{3+}$ -concentrations) in the spectra. Chemical composition for Mg, Be, Cr, Fe see Table 7c. (Mg- concentrations 10x higher than Be-concentrations).

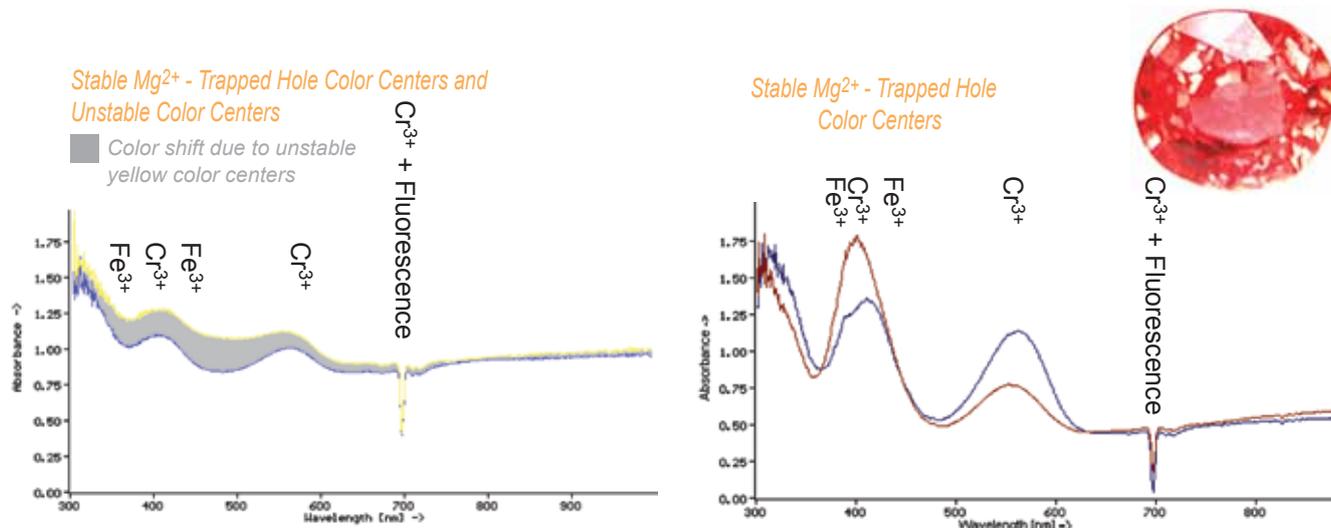


Fig. 29 Polarized UV-VIS-NIR absorption spectra of a pastel orange-pink sapphire enhanced with the new E(IM1) method. Absorption parallel and perpendicular to the c-axis are shown, responsible for orange-pink to pink pleochroism in the gemstones. Note that the 388nm absorption line and weak 450nm line is visible in the direction of the optical axis. 450nm line (due to Fe $^{3+}$ -pairs) was not present in many samples before the treatment experiment. LA-ICP-MS data see sample GRS 12598 (Table 4). 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. Mg^{2+} -trapped hole color centers are interpreted as stable (See blue curve at lower absorptions) (Compare Lit. 04).

UV-VIS-NIR Absorption Spectroscopy of Natural Yellow Sapphires and Blue Sapphires Enhanced by the New E(IM)-Method and Surface Diffusion-treated (T) Sapphires.

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 spectroscope) will also appear in an absorption spectrum as a negative peak towards lower absorptions. Multi channel spectroscopy can be used for the color measurement of gemstones (Lit 21). Polarized absorption spectra were found to be well

suitable for testing rubies and sapphires in the GRS laboratory ("finger-printing").

Results of these analyses are given in Fig. 5, 22a, 24, 26, 27, 28, 29, 30, 31, 34 and 35.

Stable Mg^{2+} - Trapped Hole Color Centers

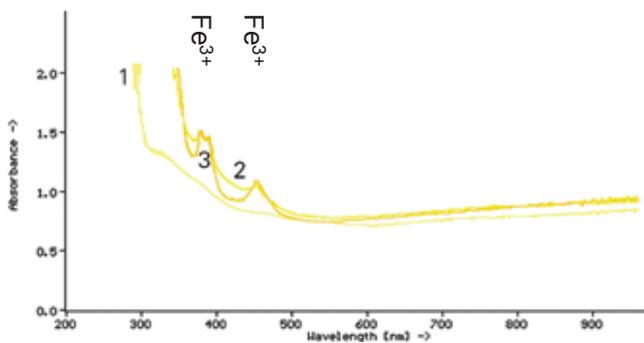
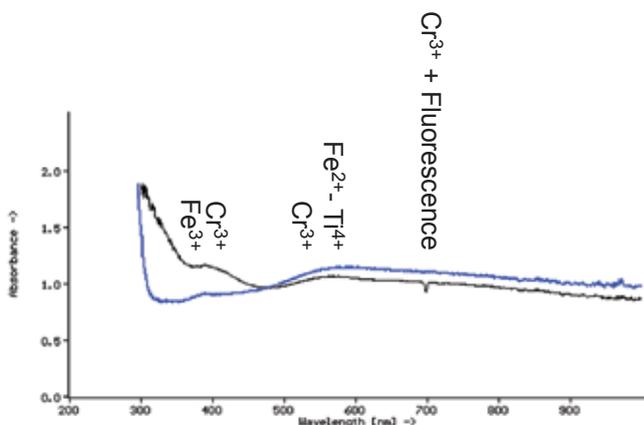


Fig. 30 Polarized UV-VIS-NIR absorption spectra in the direction of the c-axis of yellow sapphires with increasing saturation produced by the new method E(IM1). The spectra is dominated by iron (Fe^{3+} and Fe^{3+} -pairs) for spectrum No. 3. Increase of Fe-concentrations (from 1 to 3) as determined by ED-XRF analyses. Presence of color centers based on spectral curve (absorption in the blue region of the spectrum) and Mg-concentrations (See LA-ICP-MS Data Table 4). Compare also with Lit. 04.



Sample No. GRS 12925



Sample No. GRS T-Blue

Fig. 31 Polarized UV-VIS-NIR absorption spectra of a diffusion-treated blue sapphire (T) (See blue line), and blue sapphire produced by enhancement with the new technique E(IM1). 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.

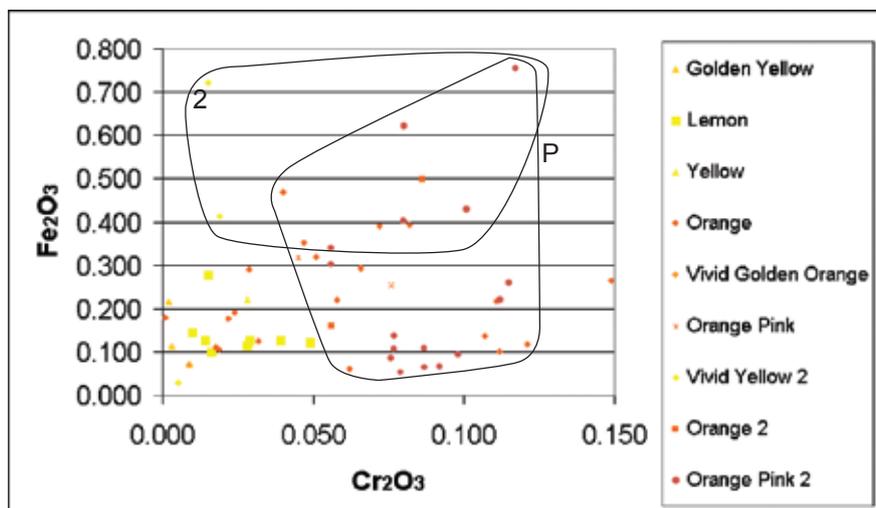
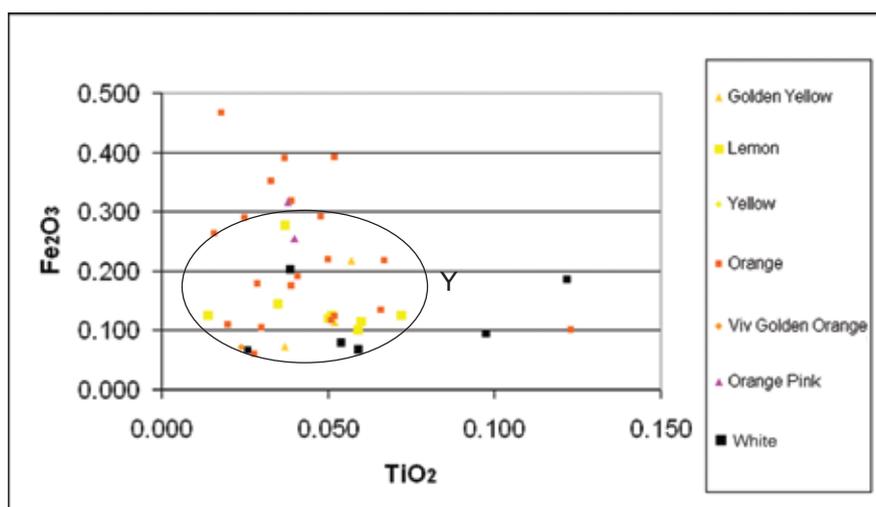
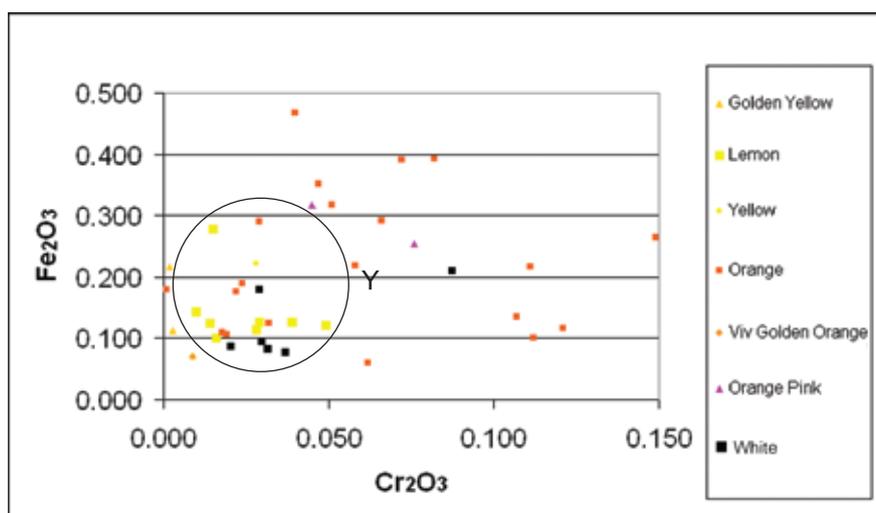


Fig. 33a, b ED-XRF chemical analyses (in oxide wt.-%) of different natural colored sapphires enhanced with the new method. The samples from the first two graphs originate from the same heat treatment run of pastel colored sapphires from Madagascar (See materials f.). The group of colors indicated via 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-enhancement with the new E(IM1) method. Compare P (these figures) with Fig. 23. BO and the field designated as Y. It can be noted that the chemical compositions (as determined at the surface of the gemstones by ED-XRF analysis, See Fig. 33) are much lower than the natural unenhanced counterparts with the same color (compare Fig. 23).

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 enhanced by heat with the new E(IM) method (Compare Fig. 23, 25, 33a). Comparing the quantitative data, (e.g. focusing on the concentration of trace elements between enhanced E(IM) and unenhanced (N) sapphires of the same color, and the intensity of the absorption lines, Compare Fig. 22a, 24 with Fig. 26 and 27), the following major differences were noticed:

For the large group of E(IM1) enhanced sapphires tested it was

Origin of Color: Natural Unheated (N) Violet-Blue Sapphires and Orange Sapphires Produced with the New E(IM)-Method

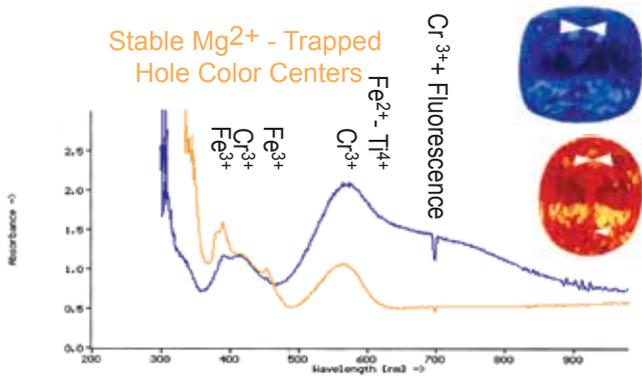


Fig. 34 Polarized UV-VIS-NIR absorption spectra of two sapphires with different colors measured in direction of the c-axis. An orange-red sapphire enhanced by the new E(IM) method, and a violet-blue sapphire unenhanced by heat (N). For comparison: Both stones have iron (Fe), chromium (Cr), and titanium (Ti) concentrations, but the violet-blue colors are dominated by $Fe^{2+} - Ti^{4+}$ charge transfer and Cr^{3+} - absorptions (broad band 500 to 700nm), while the orange-red colors are dominated by Fe^{3+} -pairs and Cr^{3+} absorptions (band centered at 560nm to 580nm and absorption at 450 and 388nm) as well as color centers (general absorption in the blue region of the spectrum).

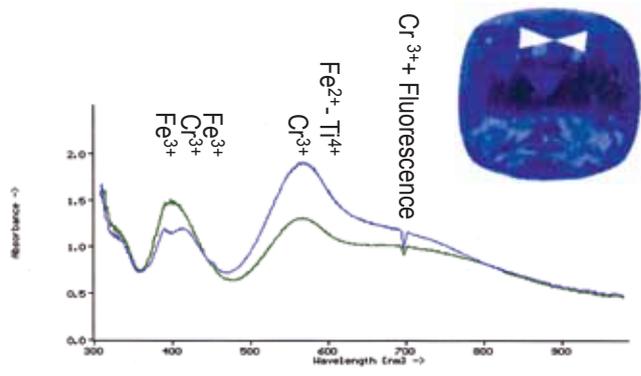


Fig. 35 Polarized UV-VIS-NIR absorption spectra of a violet-blue sapphire (color-changing). The spectra were recorded parallel (blue) and perpendicular to the c-axis (black). The spectra can be interpreted in terms of iron (Fe^{3+} -pairs), titanium ($Fe^{2+} - Ti^{4+}$ charge transfer) and chromium (Cr^{3+})-concentrations. Note: Appearance of the 450nm line (Fe^{3+} -pairs) in the spectrum recorded in the direction of the c-axis. The dominant $Fe^{2+} - Ti^{4+}$ charge transfer absorptions in the red region of the spectrum are responsible for the blue component of the color.

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. 26 and 27).

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) (Compare Lit. 04).

- 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 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 6) and extensive measurements by LA-ICP-MS as shown in the following pages.

Table: 5 ED-XRF Chemical Analysis of Natural Sapphires of Different Colors Unheated (N), Enhanced by Heat (E) and with the New E(IM)-Method Origin: Madagascar and Africa (in oxide wt-%, Al₂O₃ by 100% difference)

Origin Madagascar								
SAMPLE	Color	Treated	TiO2	V2O5	CR2O3	MNO	FE2O3	GA2O3
VIOLET1-0.179	blue	E(IM)	0.088	0.061	0.096	0.020	0.106	0.023
BROWN2-0.166	brown	E(IM)	0.132	0.000	0.088	0.010	0.278	0.033
BROWN3-0.214	brown	E(IM)	0.109	0.000	0.079	0.018	0.099	0.032
BROWN4-0.203	brown	E(IM)	0.060	0.000	0.016	0.014	0.098	0.019
BROWN5-0.126	brown	E(IM)	0.079	0.000	0.107	0.002	0.269	0.030
BROWN6-0.146	brown	E(IM)	0.139	0.020	0.088	0.000	0.153	0.026
YELLOW1-0.326	golden-yellow	E(IM)	0.037	0.000	0.009	0.000	0.072	0.027
YELLOW3-0.170	golden-yellow	E(IM)	0.052	0.000	0.003	0.000	0.113	0.015
YELLOW4-0.142	golden-yellow	E(IM)	0.057	0.029	0.002	0.000	0.217	0.016
LAVEND1-0.268	Lavendar	E(IM)	0.025	0.002	0.068	0.000	0.071	0.019
LAVEND3-0.289	Lavendar	E(IM)	0.029	0.000	0.072	0.000	0.056	0.023
LAVEN10-0.239	Lavendar	E(IM)	0.074	0.000	0.045	0.000	0.063	0.021
LAVEN12-0.137	Lavendar	E(IM)	0.081	0.056	0.045	0.007	0.170	0.029
LAVEN11-0.093	Lavendar	E(IM)	0.110	0.014	0.147	0.000	0.203	0.026
LEMON1	lemon	E(IM)	0.072	0.003	0.014	0.008	0.125	0.025
LEMON2	lemon	E(IM)	0.060	0.009	0.028	0.004	0.114	0.016
LEMON3	lemon	E(IM)	0.014	0.006	0.029	0.000	0.126	0.016
LEMON4	lemon	E(IM)	0.059	0.000	0.016	0.005	0.100	0.036
LEMON5	lemon	E(IM)	0.050	0.014	0.049	0.002	0.121	0.032
LEMON6	lemon	E(IM)	0.037	0.031	0.015	0.001	0.278	0.025
LEMON7	lemon	E(IM)	0.051	0.002	0.039	0.003	0.126	0.019
12548-0.255	lime yellow	E(IM)	0.035	0.014	0.010	0.000	0.144	0.021
ORANGE1	orange	E(IM)	0.051	0.038	0.121	0.000	0.116	0.014
ORANGE2	orange	E(IM)	0.028	0.009	0.062	0.000	0.060	0.019
ORANGE3	orange	E(IM)	0.016	0.000	0.149	0.001	0.264	0.017
ORANGE4	orange	E(IM)	0.033	0.000	0.047	0.001	0.352	0.022
ORANGE5	orange	E(IM)	0.123	0.000	0.112	0.000	0.100	0.017
ORANGE6	orange	E(IM)	0.050	0.000	0.058	0.000	0.219	0.024
ORANGE7	orange	E(IM)	0.041	0.000	0.024	0.003	0.190	0.017
ORANGE8	orange	E(IM)	0.048	0.001	0.066	0.000	0.292	0.029
ORANGE9	orange	E(IM)	0.052	0.006	0.082	0.007	0.392	0.028
ORANGE10	orange	E(IM)	0.029	0.023	0.001	0.000	0.179	0.005
ORANGE11	orange	E(IM)	0.037	0.013	0.072	0.000	0.390	0.025
ORANGE12	orange	E(IM)	0.067	0.038	0.111	0.000	0.217	0.027
ORANGE13	orange	E(IM)	0.039	0.000	0.051	0.000	0.318	0.020
ORANGE15	orange	E(IM)	0.020	0.000	0.018	0.000	0.109	0.012
ORANGE16	orange	E(IM)	0.018	0.008	0.040	0.000	0.467	0.024
ORANGE17	orange	E(IM)	0.039	0.000	0.022	0.003	0.175	0.016
12586-0.184	orange	E(IM)	0.066	0.000	0.107	ND	0.135	0.031
12527-0.93	orange-pink	E(IM)	0.038	0.017	0.045	0.000	0.317	0.016
12528-0.667	orange-pink	E(IM)	0.040	0.004	0.076	0.000	0.254	0.029
12538-0.314	Vivid golden orange	E(IM)	0.024	0.006	0.009	0.001	0.070	0.026
WHITE1	white	E(IM)	0.097	0.001	0.030	0.000	0.089	0.014
WHITE2	white	E(IM)	0.054	0.021	0.021	0.000	0.080	0.020
WHITE3	white	E(IM)	0.025	0.008	0.032	0.000	0.070	0.019
WHITE4	white	E(IM)	0.039	0.028	0.087	0.000	0.207	0.039
WHITE5	white	E(IM)	0.059	0.062	0.038	0.004	0.062	0.069
WHITE6	white	E(IM)	0.122	0.000	0.030	0.006	0.178	0.025
MIX4-0.291	white	E(IM)	0.055	0.000	0.067	0.008	0.670	0.068
MIX3-0.112	white-blue	E(IM)	0.063	0.036	0.047	0.000	0.163	0.056
YELLOW2-0.286	yellow	E(IM)	0.050	0.011	0.028	0.005	0.221	0.022
MIX5-0.159	yellowish-blue	E(IM)	0.126	0.021	0.117	0.017	0.263	0.011
01994-0.494	orange	E(IM)	0.014	0.004	0.056	0.005	0.158	0.017
01994-0.476	orange	E(IM)	0.016	0.008	0.086	0.002	0.499	0.018
01994-0.834	orange-pink	E(IM)	0.000	0.018	0.087	0.004	0.106	0.023
01994-0.621	orange-pink	E(IM)	0.021	0.000	0.098	0.000	0.093	0.022
01994-0.552	orange-pink	E(IM)	0.019	0.000	0.092	0.000	0.064	0.017
01994-1.885	orange-pink	E(IM)	0.009	0.000	0.056	0.001	0.302	0.015
01995-1.213	orange-pink	E(IM)	0.022	0.007	0.080	0.000	0.622	0.021
01995-1.265	orange-pink	E(IM)	0.018	0.008	0.080	0.002	0.401	0.015
01995-0.556	orange-pink	E(IM)	0.019	0.000	0.112	0.000	0.219	0.021
01995-0.574	orange-pink	E(IM)	0.051	0.010	2.068	0.000	0.327	0.027
01995-1.562	orange-pink	E(IM)	0.019	0.003	0.056	0.001	0.339	0.030
01995-1.240	orange-pink	E(IM)	0.009	0.011	0.117	0.000	0.754	0.021
01995-0.689	orange-pink	E(IM)	0.023	0.009	0.087	0.003	0.064	0.020
01995-1.478	orange-pink	E(IM)	0.009	0.005	0.101	0.000	0.427	0.018
01995-0.706	orange-pink	E(IM)	0.016	0.000	0.076	0.000	0.086	0.020
12912-0.414	orange-pink	E(IM)	0.018	0.011	0.079	0.000	0.052	0.017
12914-0.350	orange-pink	E(IM)	0.024	0.012	0.077	0.002	0.136	0.021
12914-0.350	orange-pink	E(IM)	0.027	ND	0.077	0.004	0.108	0.022
01994-0.607	vivid yellow	E(IM)	0.007	0.009	0.005	0.001	0.029	0.019
01994-0.658	vivid yellow	E(IM)	0.008	0.006	0.015	0.000	0.721	0.020
01994-0.597	vivid yellow	E(IM)	0.036	0.000	0.019	0.001	0.413	0.015
Origin Tunduru								
SAMPLE	Color	Treated	TiO2	V2O5	CR2O3	MNO	FE2O3	GA2O3
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 5 (Continued)

Origin Madagascar								
SAMPLE	Color	Treated	TiO2	V2O5	CR2O3	MNO	FE2O3	GA2O3
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	0.000	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
12675-0.143	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	0.036	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	0.022	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	0.024
12737-PINK	pink	N	0.014	0.000	0.087	0.005	0.542	0.027
Origin Songea								
SAMPLE	Color	Treated	TiO2	V2O5	CR2O3	MNO	FE2O3	GA2O3
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	0.000	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	0.088	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	E(IM)	0.009	0.004	0.269	0.005	0.826	0.011
TU-0.24	orange red	E(IM)	0.025	0.003	0.589	0.002	0.975	0.015
TU-0.26	orange red	E(IM)	0.035	0.002	0.555	0.009	1.053	0.020
TU-0.32	orange red	E(IM)	0.000	0.004	0.272	0.001	0.895	0.010
TU-0.40	orange red	E(IM)	0.016	0.000	0.440	0.000	0.955	0.007
121002-0.824	orange red	E(IM)	0.000	0.000	0.190	0.004	0.941	0.010
TU-0.37	orange red	E(IM)	0.026	0.008	0.634	0.000	0.976	0.014
SONG1-0.26	orange red	E(IM)	0.016	0.022	0.162	0.000	1.177	0.013
SONG4-0.31	orange red	E(IM)	0.015	0.001	0.071	0.000	0.518	0.010

LA-ICP-MS: Methods

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. 10], excimer [Lit. 11]), homogenization optics, increased mass spectrometer sensitivity, accompanied by an increased linear dynamic range, has led to a large number of new applications (Lit. 08).

In this work, an ArF excimer laser (193nm; Compex 110I, Lambda Physik, Goettingen, Germany), coupled with a quadrupole mass spectrometer (Elan 6100 DRC Perkin Elmer/Siex, Toronto, Canada), was used. 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.



Fig. 36 Special Analyses were carried out at the Swiss Federal Institute of Technology (SFIT), Department of Chemistry, Laboratory of Inorganic Chemistry, Zurich (Switzerland).

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 through 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)



Fig. 37 LASER ABLATION ICP-MS Analyses in the Laboratory of Inorganic Chemistry. Prof. D. Günther and Dr. A. Peretti discuss measuring strategies.

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.

The detection limits for the following elements are:

Be = 0.3 to 0.5ppm

Mg = 0.2 to 0.5ppm

Ti = 1ppm

Cr = 2ppm

V = 0.1 - 0.2ppm

Fe = 3ppm

Ga = 0.06 to 0.12ppm

(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. (e.g. See Fig. 40) Blank level determinations were placed randomly across the sample (e.g. See Fig. 67) to determine differences between enhanced (E), unheated (N) and samples enhanced with the new E(IM)-method.



Fig. 38 Detailed image of the microscope, sample chamber (above) and Mass-spectrometer (below) used for LA-ICP-MS analysis. Applications - See: Guillong M. and Günther, D. (2001): 'Quasi "non-destructive" Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry Fingerprinting of Sapphires. *Spectrochimica Acta Part B*, 56, p 1219-1231.

Fig. 39 Prof. D. Günther and Dr. A. Peretti evaluating data gained on "Padparadscha" sapphires with special attention to Magnesium and Beryllium concentrations. Details - See Günther D. And Peretti A. (2002): *Color Enhancement of Fancy Sapphires with a New Heat Treatment Technique: Inducing color zoning by Internal Migration and formation of color centers. Journal of Analytical and Bioanalytical Chemistry (in preparation).*





Sample No.GRS 12922 white

Fig. 40 . Microphotograph of a princess cut white sapphire enhanced by the new E(IM1)-method (second half shown on right). The sample was cut in half after treatment and probed by LA-ICP MS in a profile across the sample. Craters indicate Laser sampling sites.

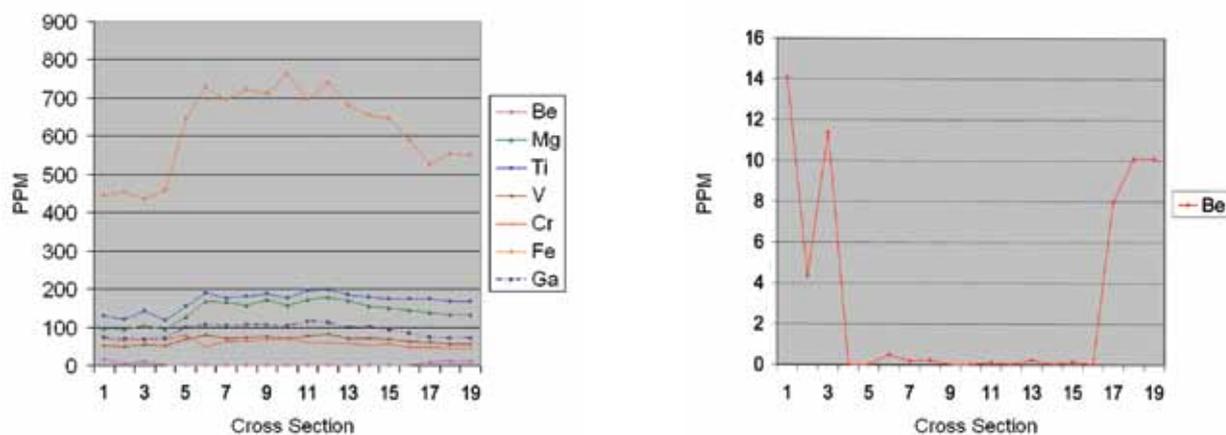


Fig. 41. Chemical compositions in a profile across the white sapphire enhanced with the new E(IM1)-method as determined by LA-ICP-MS. Note chemical compositions are dominated by trace element Fe only, while light elements, such as Be and Mg, are subordinate. The Beryllium concentrations are restricted to the outer zone and do not exceed 15ppm. 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 and produced by the new E(IM1) enhancement. Ti-concentrations are higher than Mg-concentrations.

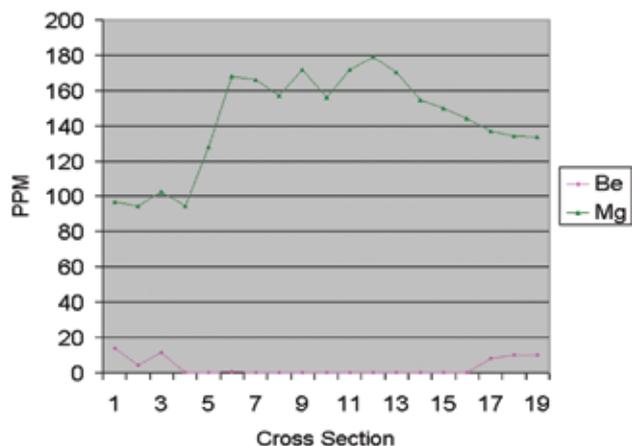


Fig 42: LA-ICP-MS analysis in a profile across the sample. It is shown that the Beryllium concentrations (9 in ppm) are restricted to the outer rim outside the observed color zonings. The maximum concentrations are below 15ppm. It is evident that Be-enrichments occurred outside the zones enriched by Mg.

Results LA-ICP-MS

The different colors analyzed (Tab. 2, Part A) are discussed below, including orangy-pink, white, blue, and yellow sapphires enhanced with the new E(IM1) method. Details of sampling strategy and preparation are summarized in Table 2, and discussed in more details below. The results are given in Tab. 3a, 3b, 4, 7 and presented in page 26-37 in more details.

Natural Orangy-Pink Sapphires E(IM1) Results LA-ICP-MS

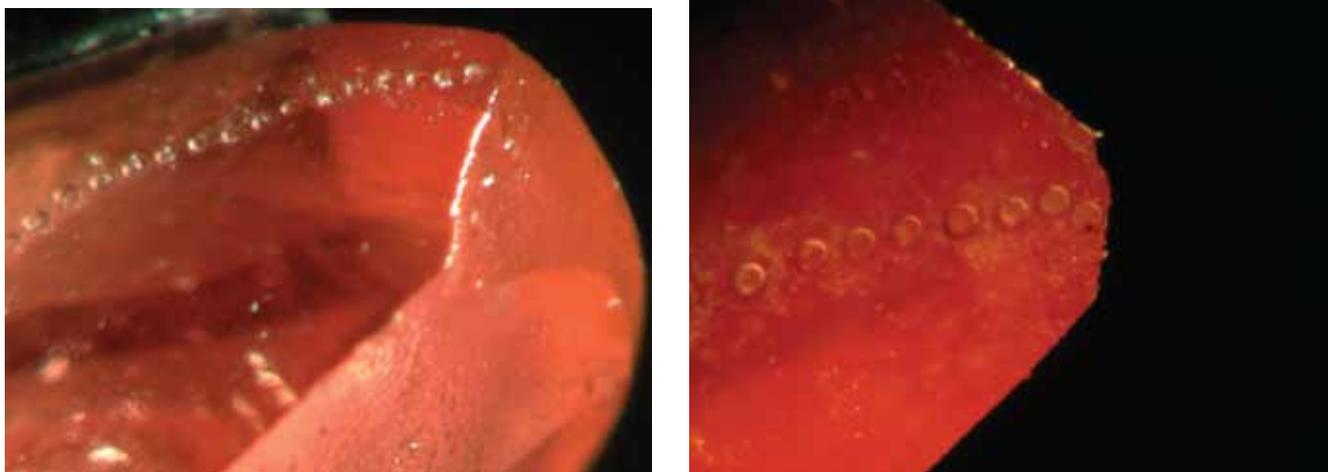
The color of the starting material of the orangy-pink sapphire (prior to heat-enhancement) was pink. The samples were each approx. 1 ct in size, and one sample was kept untreated. The samples were first checked by routine gemological testing, including recording of the absorption spectrum, and subsequently 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. 43 and Fig. 48). Two of the samples were later sliced into a 3mm thick plate and checked with Cathodoluminescence, as shown on page 29. Pink sapphires and unheated samples were measured for comparison, with the number of measured points by LA-ICP-MS indicated in Table 6. Typical measured profiles are shown in Fig. 43, 47, 48 and 66. 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. 44, 45, 46, 49, 50 and also given in the Appendix page 45-46, Tab. 3a, 4 and 7b.

Concentrations of *Beryllium* (Be), Magnesium (Mg), Titanium (Ti), Vanadium (V), Chromium (Cr), Iron (Fe), and Gallium (Ga) are shown in ppm (comparison with ED-XRF needs conversion into oxide wt.-%) – Table 3b. 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. 30ppm) 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, and not confined to the levels of the *Beryllium* concentrations (Fig. 44, 45 and 49). Regarding the origin of color, unstable yellow color centers (Fig. 29) are found in the outer zones of the rim where *Beryllium* concentrations are located. 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 and therefore produced by the new heat-enhancement method. The chemical trends with pronounced depletion in the rim were confirmed in total of seven profiles (Tab. 6). 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. 53 and Appendix). For comparison purposes, further samples unenhanced by heat and pink sapphires were analyzed (Fig. 64 and Appendix). 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. 64). In conclusion, element trends in the treated gemstones are therefore produced by the new E(IM1)-treatment – *Beryllium* has been introduced from outside sources, as it is not present in the original material.

Natural White Sapphires E(IM1) Results LA-ICP-MS

The sapphires were subjected to the new heat treatment and did not change in color (very pale cream). The sample was cut in half after the heat treatment experiment and studied with LA-ICP MS (as shown in Fig. 40-42). Fe concentrations of maximal 700ppm and more than 100ppm Mg were achieved by the new treatment in the gemstones more central portions, along with relatively high Ti concentrations (Ti = 100-200ppm, see Fig. 41a) 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. 4 and Fig. 5). Only unstable color centers at the rims were detected, obviously related to areas of lowest Ti, Fe and Cr and highest Be-concentrations and Mg greater than Be (Mg/Be-ratio approx. 10).



Sample No.GRS 12599

Fig. 43 Faceted orangy-pink sapphire cut in half after E(IM1) enhancement. 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 (approx) could be obtained.

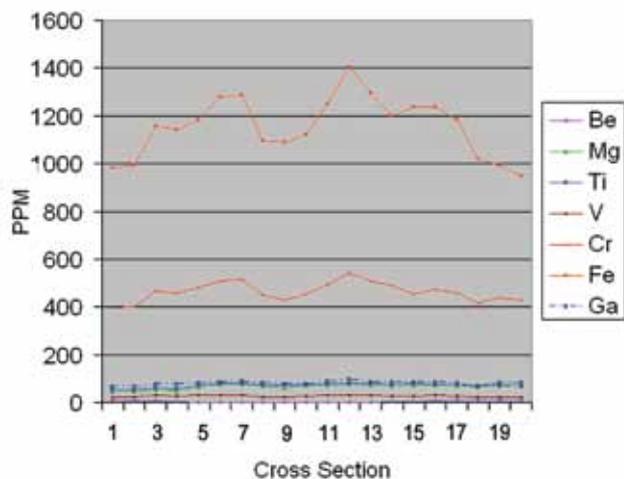


Fig. 44 Chemical variation in a profile through an orangy-pink sapphire enhanced with the new method. All the elements found are shown except Al (in ppm). Note: Dominant concentrations of Fe and Cr, and the symmetrical variation in composition (depletion of Fe, Cr, Ti, Mg in the outer zone (1-3 and 18-20) and enrichment in points 5-7 and 13-17.)

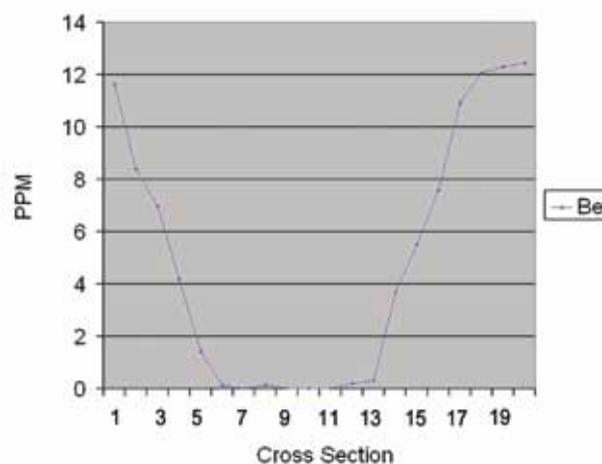


Fig. 45 Same profile as Fig. 44, but only the Beryllium concentrations are shown. Highest Be-concentrations (in ppm) are found in the rim (points 1-3 and 18-20). The Be-concentrations gradually decrease towards the center (penetration depth approx. 200-300 micrometer)

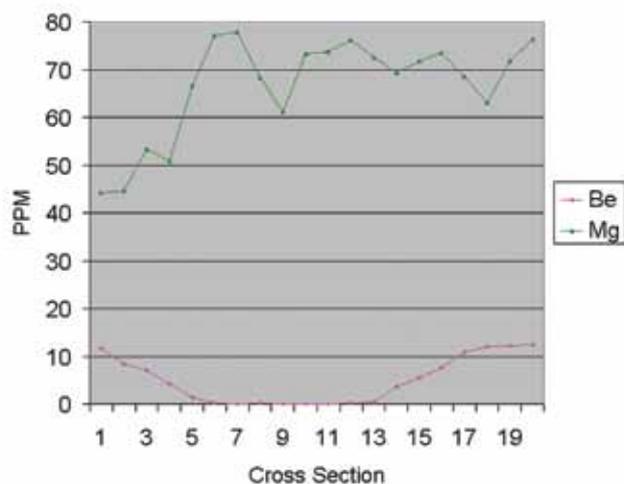


Fig. 46 LA-ICP-MS analysis in a profile across the sample. Comparison of Mg and Be-enriched zones in the enhanced sapphire. The Mg-concentrations (in ppm) are about 5-10 times higher than the Beryllium concentrations .

*LA-ICP-MS Analysis of Natural Orangy-pink Sapphires ("Padparadscha")
Enhanced with the New E(IM1)-Method*



Sample No. GRS 12598

Fig. 47 Heart-shaped pink sapphires were subjected to the new E(IM1)-enhancement. 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 enhancement process.

Fig. 48 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.

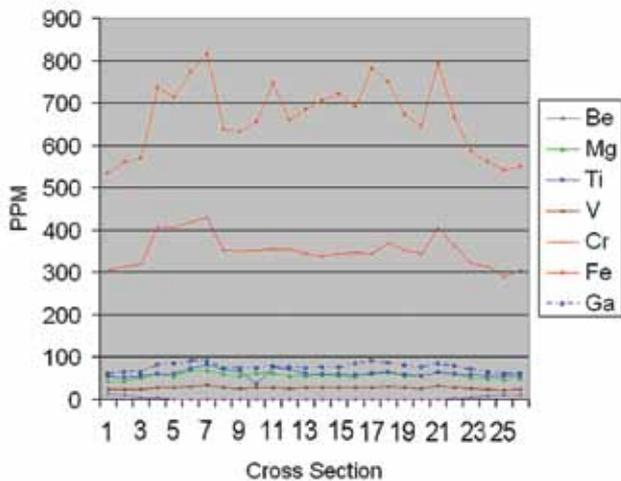


Fig. 49a The chemical variations in a profile across the faceted and E(IM1)-color-enhanced orangy-pink sapphire is shown (in ppm). Note depletion of trace elements in the rim (including Ti) of the faceted gemstone and enrichment in an inner rim (No. 5-8 and 19-22), including Cr, Fe and Mg.

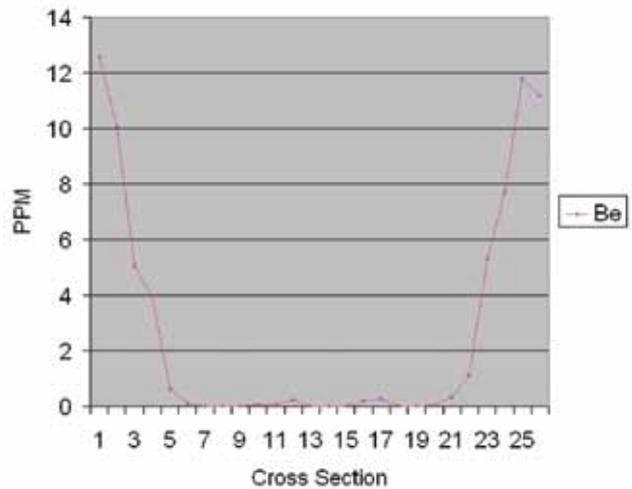


Fig. 49b The distribution of Beryllium in a profile through a faceted orangy-pink sapphire. Note: Be concentrations are found in the outer rim only (max. 14ppm).

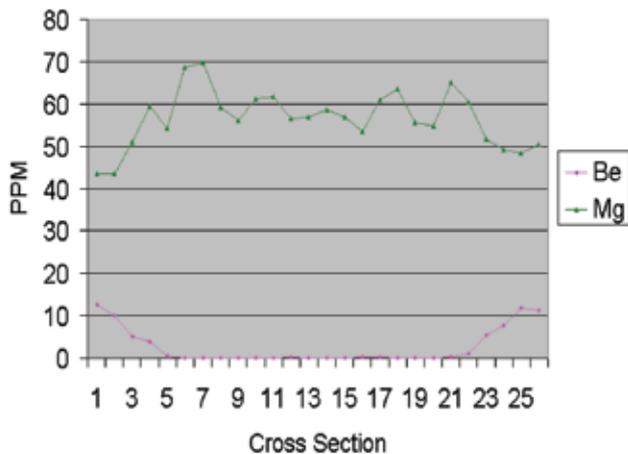


Fig. 50 LA-ICP-MS analysis in a profile across the sample (in ppm). Mg and Be-enriched concentrations in the enhanced sapphire is shown. The Mg-concentrations are depleted at the outer rim and the Be-concentrations are enriched

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 26).

Visual and spectroscopic cathodoluminescence investigations were carried out to characterize the natural orangy-pink sapphires enhanced with the new E(IM1)-method.

Methods

Natural orangy-pink sapphires enhanced with the new E(IM1) method 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.

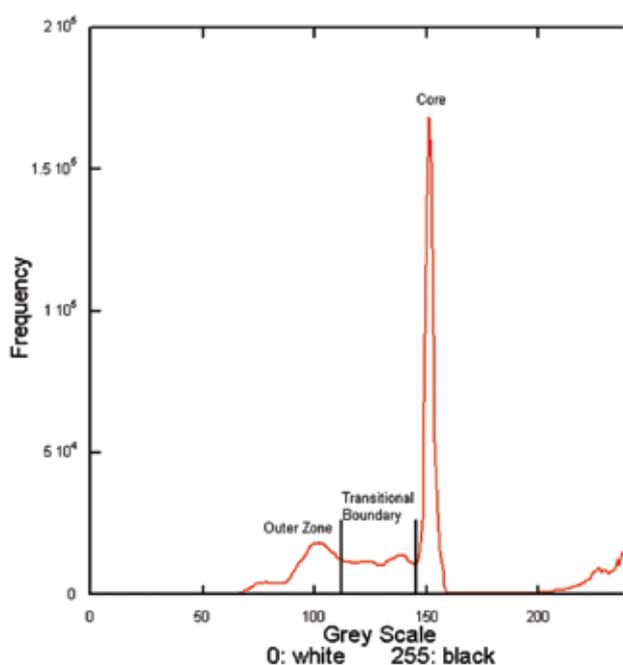


Fig. 51 Luminescence Intensity distribution of Figure 53.

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. 53). Between the core and the outer zone, a transitional boundary exists with a lower luminescence intensity than the outer zone (Fig. 51 and Fig. 53). The red CL from both areas contains identical peaks, with peak positions indicative for Cr³⁺-induced luminescence (Fig. 52). LA-ICP-MS data confirms the presence of Cr but also Mg, Fe, Ti, Be and Ga are present (Fig. 53). 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.

Further investigations on the interpretation of the CL data are in preparation (Ramseyer, Peretti and Mullis, in prep.).

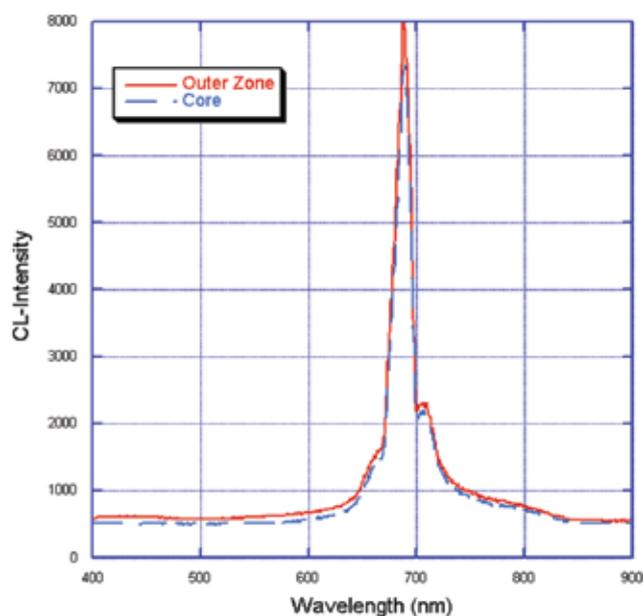


Fig. 52 Representative CL-spectra from the core (blue) and the outer transitional zone (red) of sample Fig. 53.

Correlation of LA-ICP-MS and Cathodoluminescence Analysis Natural Orangy-pink Sapphires (“Padparadscha”) Enhanced with the New E(IM1)-Method

Fig. 53 Cathodoluminescence (CL) microphotographs and projected chemical analysis (in ppm) as determined by LA-ICP-MS analysis (a-e) in an orangy-pink sapphire heat-treated with the new E(IM1)-method. Visual Color Zoning is concentrated in the transitional zone.

Sample No.GRS 12910.1

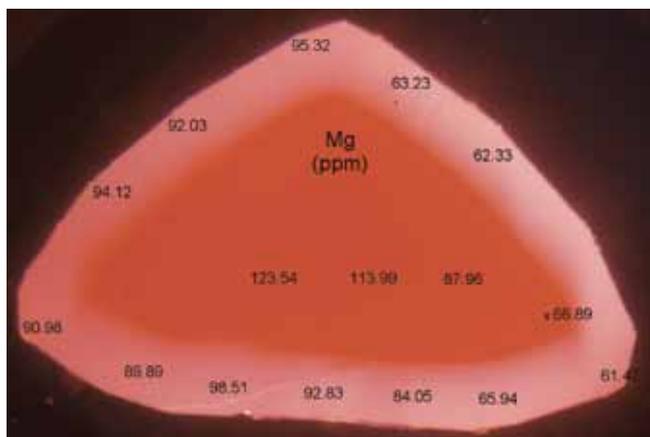


Fig. 53a Magnesium (Mg) – concentrations (in ppm) depleted in the outer zone,

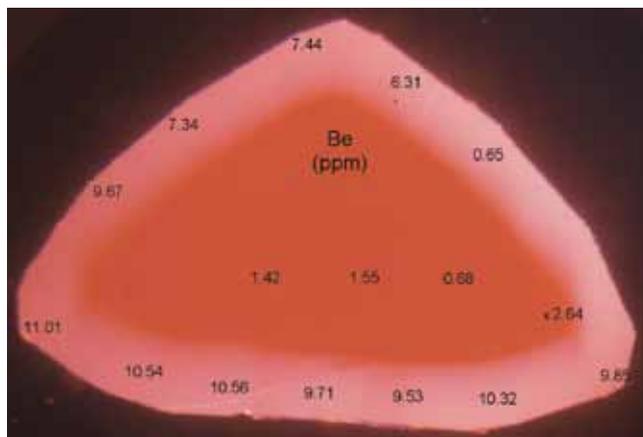


Fig. 53b.) Beryllium (Be) – concentrations (in ppm) enriched in the outer zone.

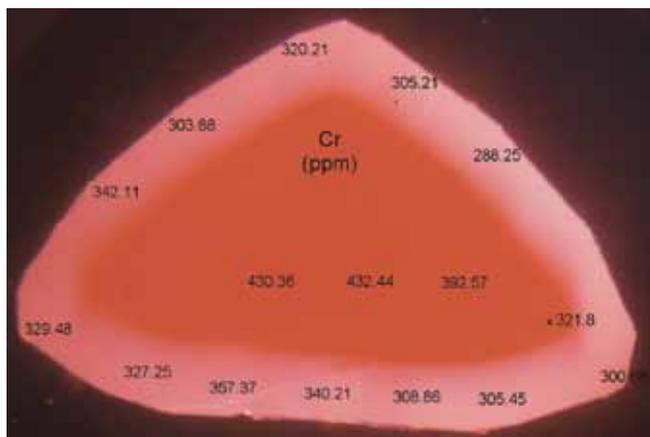


Fig. 53c Chromium (Cr) – concentrations (in ppm) depleted in the outer zone.

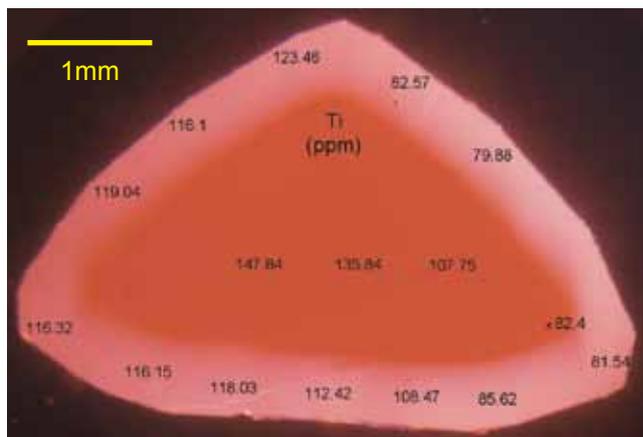


Fig. 53c Titanium (Ti) – concentrations (in ppm) depleted in the outer zone.

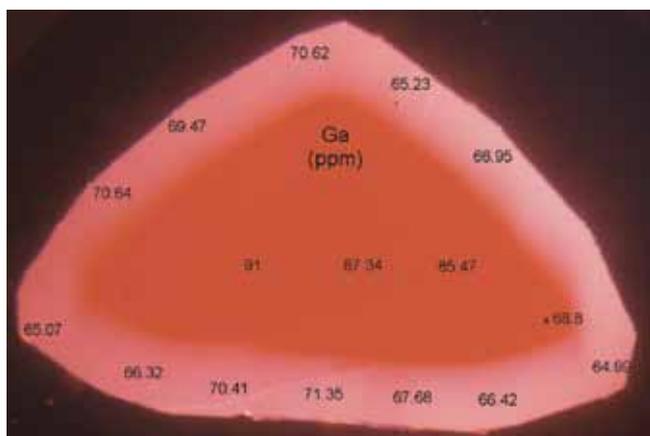


Fig. 53d Gallium (Ga) - concentrations (in ppm) depleted in the rim.

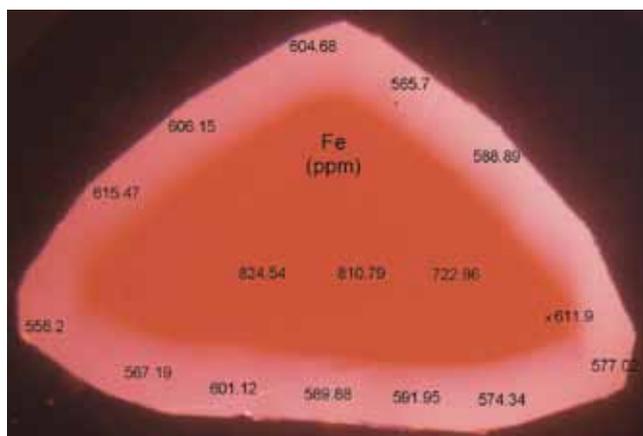
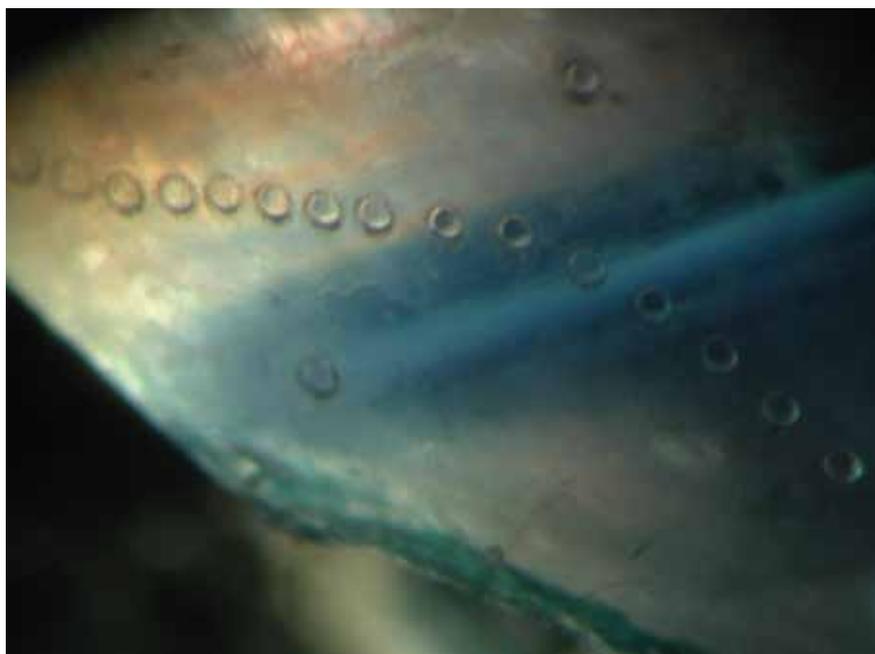
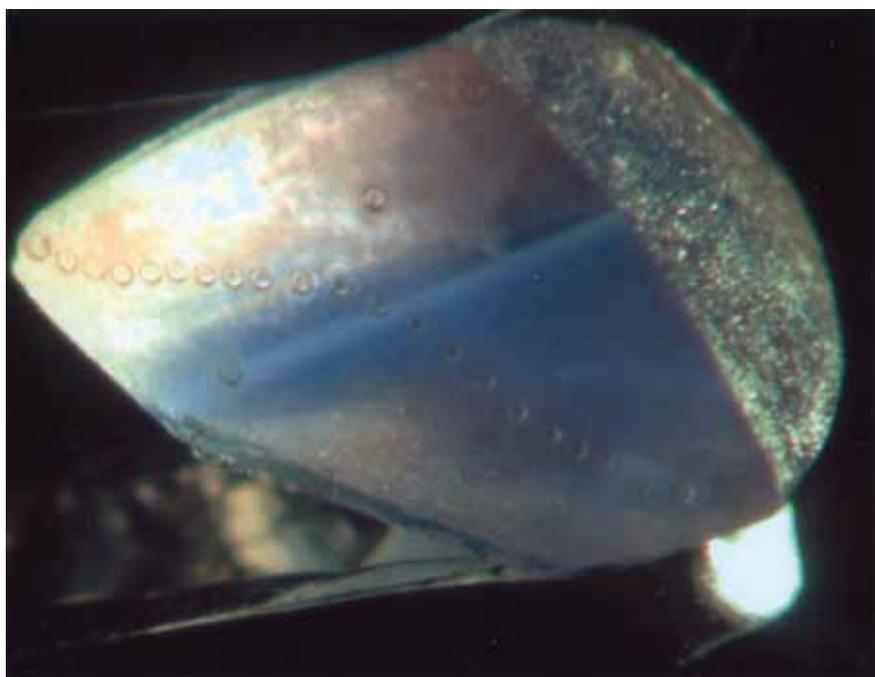


Fig. 53e Iron (Fe) - concentrations (in ppm) depleted in the rim.

Natural Blue Sapphires E(IM1) Results LA-ICP-MS

The study of the blue sapphires enhanced with the new method 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 migration of titanium, seen as a blue halo around the white band, occurred. The migration 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. 57). The chemical



Sample No. GRS 12925.1

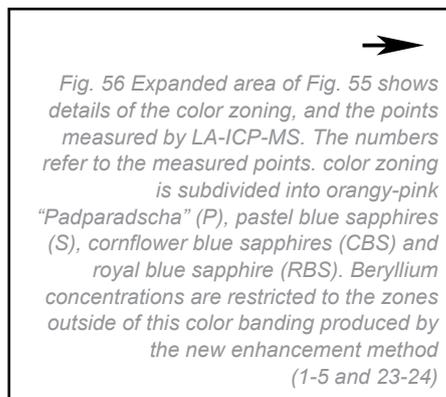


Fig. 56 Expanded area of Fig. 55 shows details of the color zoning, and the points measured by LA-ICP-MS. The numbers refer to the measured points. color zoning is subdivided into orangy-pink "Padparadscha" (P), pastel blue sapphires (S), cornflower blue sapphires (CBS) and royal blue sapphire (RBS). Beryllium concentrations are restricted to the zones outside of this color banding produced by the new enhancement method (1-5 and 23-24)

Fig. 54 Microphotograph of a princess cut sapphire enhanced by the new method (second half of the piece shown in Fig. 58). 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. 55 Extended part of Fig. 54 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 migration zone on each side

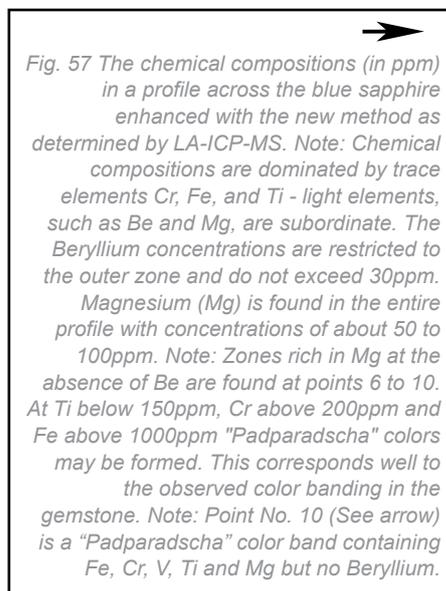
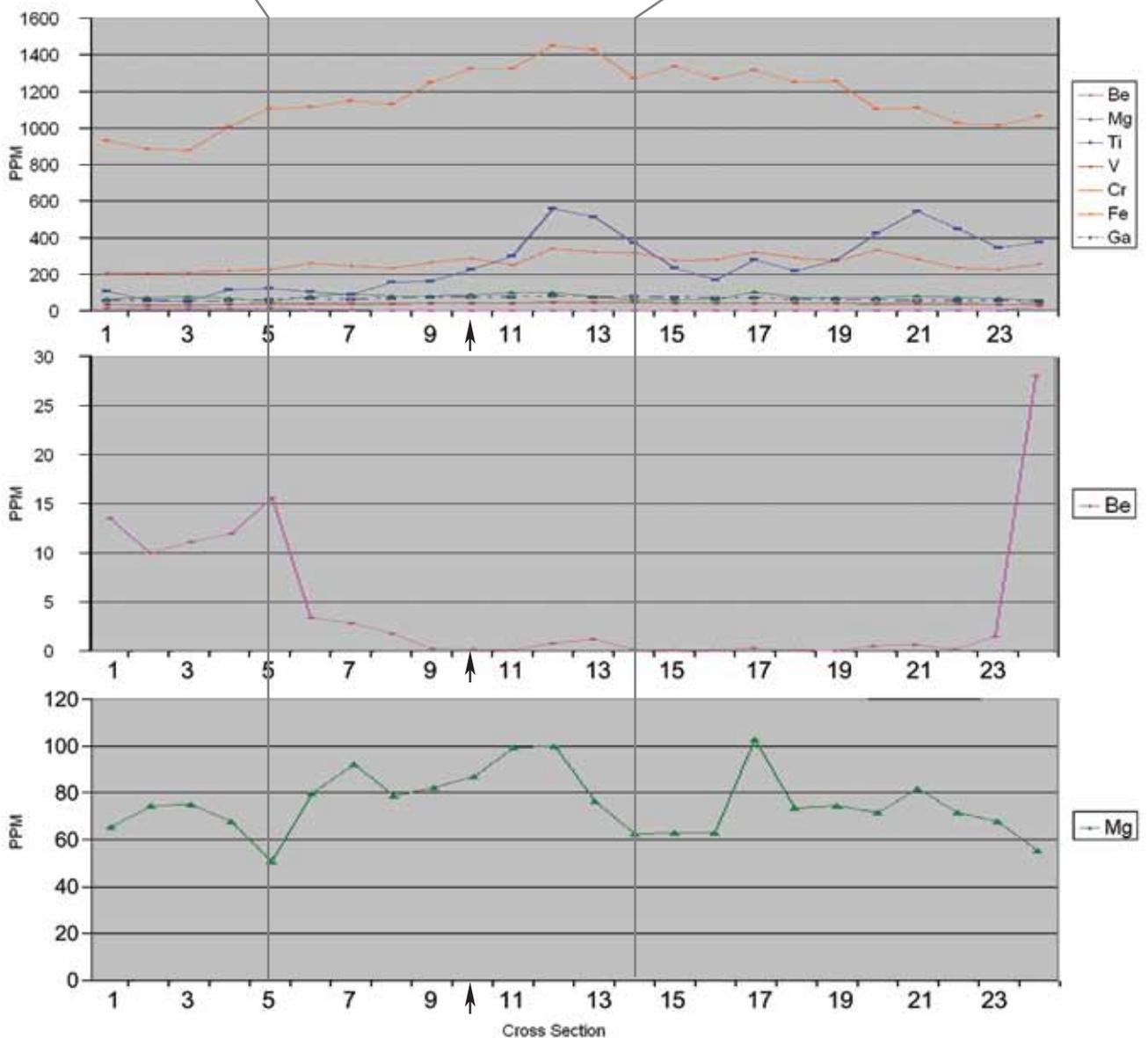
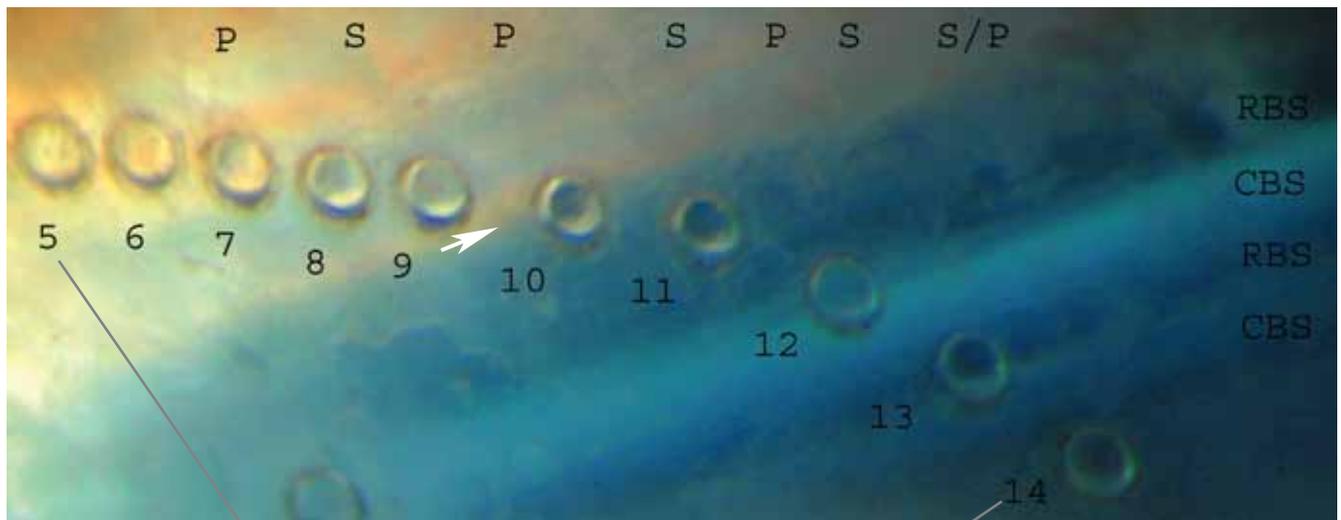


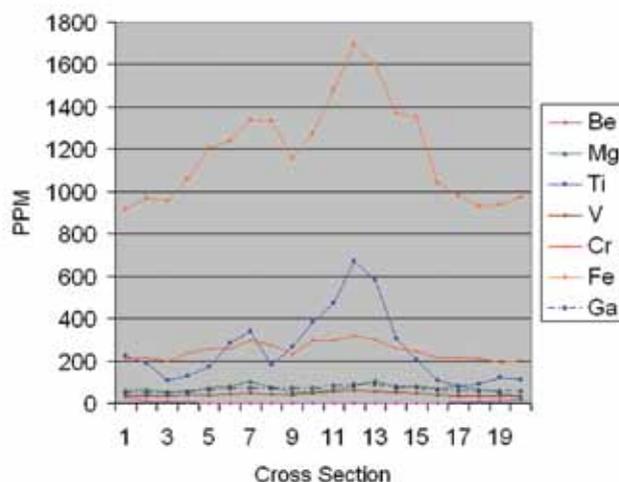
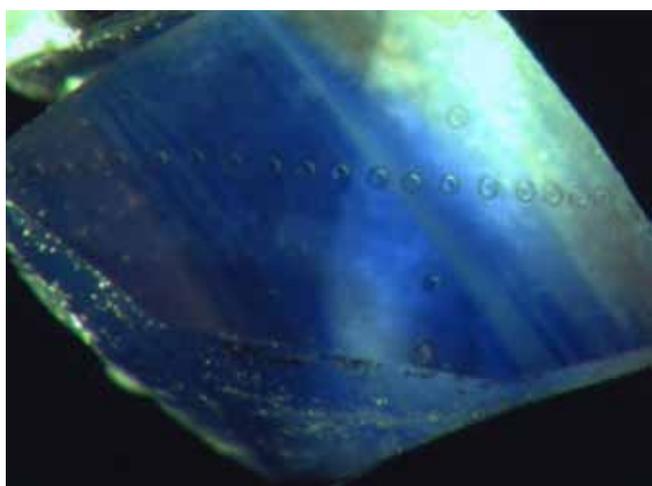
Fig. 57 The chemical compositions (in ppm) in a profile across the blue sapphire enhanced with the new method as determined by LA-ICP-MS. Note: Chemical compositions are dominated by trace elements Cr, Fe, and Ti - light elements, such as Be and Mg, are subordinate. The Beryllium concentrations are restricted to the outer zone and do not exceed 30ppm. Magnesium (Mg) is found in the entire profile with concentrations of about 50 to 100ppm. Note: Zones rich in Mg at the absence of Be are found at points 6 to 10. At Ti below 150ppm, Cr above 200ppm and Fe above 1000ppm "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.

LA-ICP-MS Analysis of Natural Blue Sapphires Enhanced with the New E(IM1)-Method with Details of Trace Element Concentrations



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 800ppm, Cr greater than 200-300 ppm, Ti lower than 200ppm, and Mg greater than 80ppm, while blue colors were produced at Fe greater than 800ppm and Ti greater than 200ppm. This is in strong agreement

with the results from the study of the orangy-pink sapphires (See Fig. 49 and 53). All the trace elements found in these samples which are responsible for the color can be found in the natural unheated colored sapphires (Fig. 23, 64 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. 4).



Sample No.GRS 12925.2

Fig. 58a,b The chemical compositions (in ppm) in a profile across the blue sapphire enhanced with the new method 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 ppm) are restricted to the outer zone and do not exceed 30ppm. 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 106ppm). At high Ti concentrations (Ti>Mg) no "Padparadscha" colors are formed.

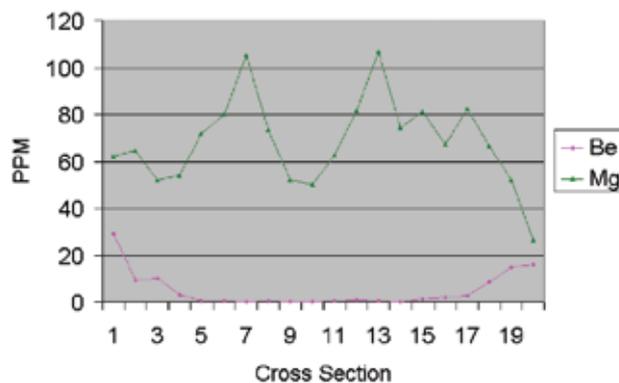
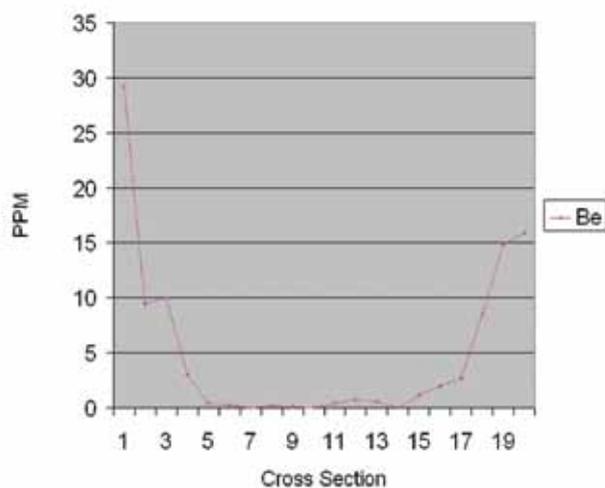


Fig. 59 (a,b) LA-ICP-MS analysis in a profile across the sample. It is shown that the Beryllium concentrations (in ppm) are restricted to the outer rim outside the observed color zonings. The maximum concentrations are below 30ppm. In Fig. 59b (on right), it is evident that Beryllium (Be)-enrichments occurred outside the enrichment of Mg.

Table 6: Sampling and Probing Strategy for LA-ICP-MS Analysis
(Part A and Part B)

Sample	ct	color	material	treatment	preparation	source	origin	LA-ICP exper.
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	recut 0.35	orangy-pink	Natural pastel Padparadscha	E(I M1)	1. treated new method 2. faceted 3. recut by GRS	Chantaburi market	Madagascar	girdle analysis 5 spot analysis
12910 Peretti1	center slice 0.21	pinkish-orange	Natural pastel Padparadscha	E(I M1)	1. faceted 2. treated new method 3. cut thick section	GRS supply to Chantaburi Factory Jan-02	Madagascar	scattered 2 dim. 32 spot analysis
12911 Peretti2	center slice 0.22	pinkish-orange	Natural pastel Padparadscha	E(I M1)	same as above		Madagascar	scattered 2 dim. 26 spot analysis
12599	0.26* 0.24*	pinkish-orange	Natural pastel "Padparadscha"	E(I M1)	1. Faceted 2.treated new method 3. Cut half for profile	GRS supply to Chantaburi Factory Dec-01	Madagascar	1 profile 20 spot points
12598	0.28* 0.29*	pinkish-orange	Natural pastel "Padparadscha"	E(I M1)	same as above	(for samples below)	Madagascar	4 profiles 66 spot points
12540	0.09* 0.16*	vivid yellow	Natural Yellow Sapphire	E(I M1)	same as above		Madagascar	1 Profile 3 control points 20 spot points
12925	2 pieces	blue	Natural Sapphire	E(I M1)	same as above		Madagascar	4 profiles 50 spot points
12922	0.13* 0.084*	colorless to light cream	Natural white Sapphire	E(I M1)	same as above		Madagascar	4 profiles 46 spot points
12922		vivid orange	Natural Orange Sapphire	E(I M1)	1. Faceted 2. treated new method (surface analysis)		Madagascar	surface analysis 4 spot analysis
782	0.33* 0.39*	vivid orangy-red	Fancy Sapphire "Intense Padparadscha"	E(I M1)	1.heated 2. faceted 3. cut half	Chantaburi market Jan-02	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-02	natural white sapphire origin not known	2-dimensional mapping 16 spot analysis
12571	0.08*	purplish-pink	Natural pink sapphire	E	cut half piece (keep for reference before treatment)	GRS supply to Bangkok Factory Feb-02	Madagascar	1 Profile 14 spot analysis
12571	0.07*	pinkish-orange	Natural pastel "Padparadscha"	E(I M2)	heat treated (not repolished)		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"	E(I M2)	1. faceted 2. cut half 3. heated new method 4. cut half for profile	GRS supply to Bangkok Factory Feb-02	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"	E(I M2)	1. cut half 2. treatment of half piece	GRS supply to Bangkok Factory Feb-02		Surface profile depth profile 42 spot analysis
12702	0.22*	pinkish-orange	Natural pastel "Padparadscha"	E(I M2)	1. cut half piece 2. treatment 3. cut half after treating			core/rim 3 analysis
12737	half-piece *	"pinkish-orange slightly brown"	Natural pastel "Padparadscha"	N	keep half piece for ref untreated	GRS supply to Bangkok Factory Feb-02	Madagascar	17 spot analysis 34 spot analysis
12737	0.22*	orange-pink	Natural "pastel" Padparadscha	E(I M2)	1. cut half 2. treatment of half piece		Madagascar	surface profile depth profile
1999	0.26*	purplish-pink	Natural Purplish-pink	E	keep half piece for ref untreated	GRS's collection	Madagascar	profile 14 spot analysis
1999	0.32*	orange-pink	Natural "pastel" Padparadscha	E(I M2)	1. cut half 2. treatment of half	GRS supply to Bangkok Factory Feb-02	Madagascar	surface profile depth profile 31 spot analysis
12570		orange-pink	Natural "pastel" Padparadscha	E(I M2)	1. faceted 2. treated 3. cut half piece	GRS supply to Bangkok Factory Feb-02		1 Profile 16 spot analysis surface analysis 4 spot analysis
Inclusion 121001	0.69*	vivid orangy-red	Fancy Sapphire "Intense Padparadscha"	E(I M1)	1.heated 2. faceted 3. recut to expose inclusion with halo	Chantaburi market Jan-02	Songea (Tanzania)	profile over inclusion 8 spot analysis
12636	0.45*	vivid yellow	Natural Yellow sapphire	E at elevated pressures (oxidizing conditions)	1. Heated 2. Recut	Rogers (Bangkok)	Sri Lanka	2 Profiles 40 spot analysis

PART A

PART B



Sample No.GRS 12540

Fig. 60 Microphotograph of a princess cut yellow sapphire enhanced by the new method. The sample was cut in half after treatment and probed by LA-ICP-MS in a profile across the sample (See craters).

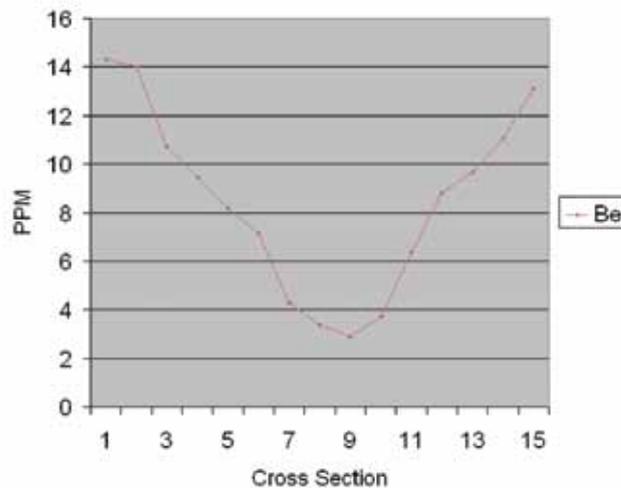
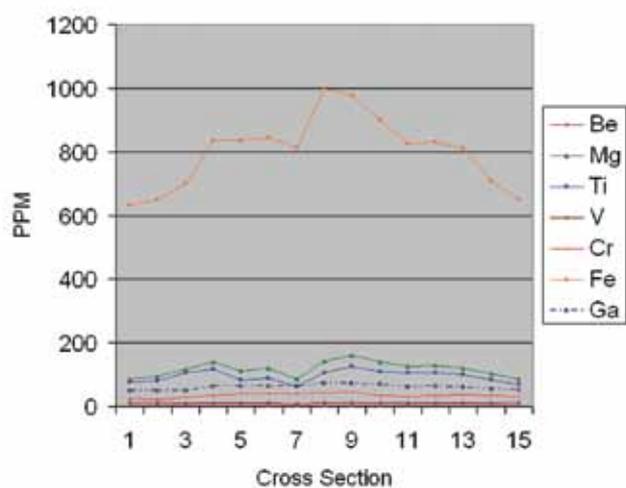


Fig. 61a,b Chemical compositions (in ppm) in a profile across the yellow sapphire enhanced with the new method as determined by LA-ICP-MS. Note: Chemical compositions are dominated by trace element Fe and Mg compositions, while light elements, such as Beryllium are subordinate (in ppm). The Beryllium concentrations are restricted to the outer zone and do not exceed 15ppm. Decrease of Fe and Mg concentrations towards the rim, and the increase towards the center of the faceted gemstone. Mg/Ti-ratio is greater than one.

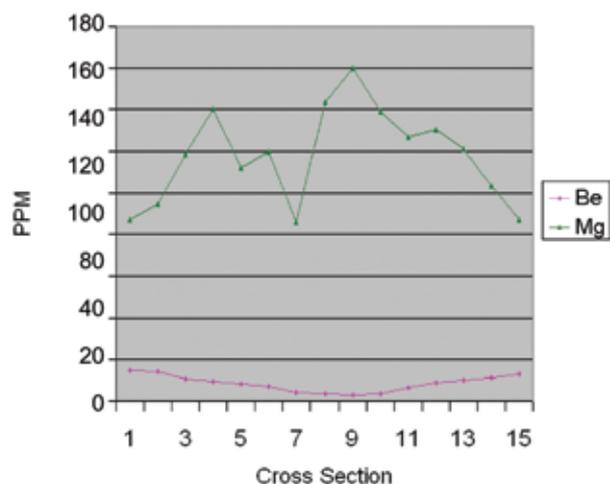


Fig. 62 LA-ICP-MS analysis in a profile across the sample. It is shown that the Beryllium concentrations (in ppm) are restricted to the outer rim. Mg is enriched in an inner rim. The maximum Beryllium concentrations are below 15ppm.

**Natural Yellow Sapphires E(IM1)
Results LA-ICP-MS**

The yellow sapphire was produced from a near colorless sapphire by the new treatment, cut in half, and then the chemical compositions were measured in a profile across the sample (See Table 6). Chemical zoning was found in the gemstone confined to the faceted surface of the sample as shown in Fig. 61 and 62. This zoning was therefore produced by the new E(IM) treatment.

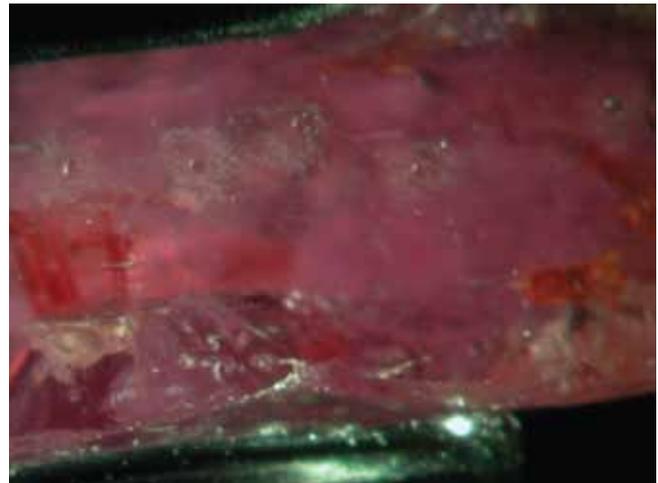
The dominant trace element in this gemstone is Fe, while all other elements found in the gemstone are below 200ppm. *Beryllium* concentrations are restricted to the gemstone's outer zone (15 ppm maximum), the rim of the gemstone shows a depletion in Fe, and Fe and Mg is enriched towards the center. A large portion of the gemstone reaches levels higher than approx. 800ppm of Fe-, and Mg concentrations are always greater than Ti-concentrations. This seems to be the ideal combination for coloring the sample yellow by the new treatment (such as Mg²⁺-Trapped Hole Color Centers) (Lit. 4).

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 1). These faded after mild exposure to heat.

**Natural Unheated Purple Sapphires
Results LA-ICP-MS**

This sample is representative for those that can be successfully heat treated with the new method (See Table 6) and Fig. 23 (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 Fancy Sapphires not enhanced by heat. Of particular interest is the ratio of Mg/Ti which in this sample is almost equal to 1.

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



Sample No. GRS 1498

Fig. 63 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 the new method.

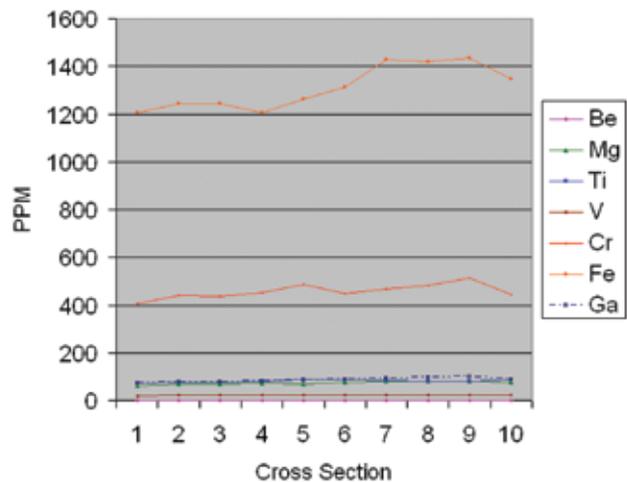


Fig. 64 Profile across the sample of Fig. 63 shows the chemical variations (in ppm) in the gemstone due to its natural composition. No depletion and no symmetric chemical zonings were present, particularly regarding the lighter elements Mg and Ti. Note: Similar chemical compositions (dominantly Fe, Cr, 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 (Details see Appendix page 46 and 47).

Comparison of E(IM)-enhanced Sapphires with Surface Diffusion-Treated Sapphires (T)

Diffusion-treated and fancy sapphires enhanced by the new treatment (pastel colors and vivid colors) can be easily distinguished by both gemological properties (Lit. 16 and Internet Lit. 04) and chemical composition as discussed below. For comparison purposes, we use a blue surface diffusion-treated sapphire. The randomly selected diffusion-treated sample (Fig. 65 and Table 7a) 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 $\text{Fe}^{2+}\text{-Ti}^{4+}$ pairs (For further discussions See Table 7a-7c).

Final Conclusion

Over the course of the new E(IM) heating technique 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. 42, 45, 49b, 57, 62 and Table 7c).

2.) Unstable color centers are formed in the zones containing *Beryllium*. They are interpreted as crystal defects (Fig. 4, 5 and 29) not corresponding to fading color centers caused by irradiation (Lit. 19).

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. 53)).

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. 41, 44, 49a and 57. In the Songea (Tanzania) samples, the entire crystal is involved and the trace elements are enriched at the core (Table 7c).

5.) The color is formed at a particular mix of trace elements, including Fe^{3+} , Cr^{3+} , and with Mg^{2+} where crystal defects are present (Fig. 26, 27, 28, 29, 30). In

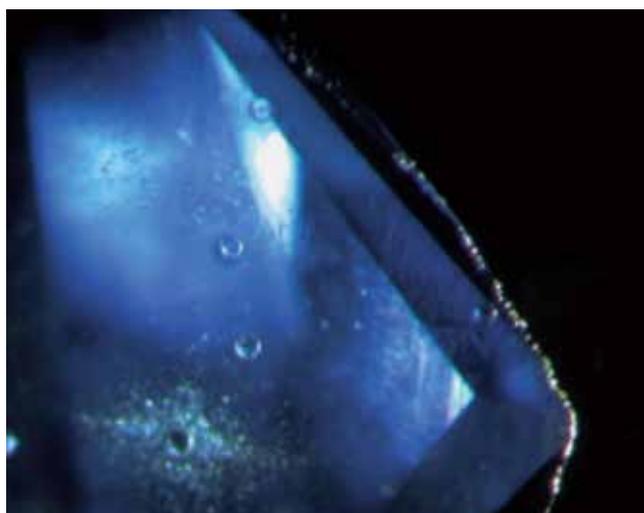


Fig. 65 Sample No.GRS T-Blue Surface Diffusion-treated Sapphire (T). Craters from scattered LA-ICP-MS Testing.

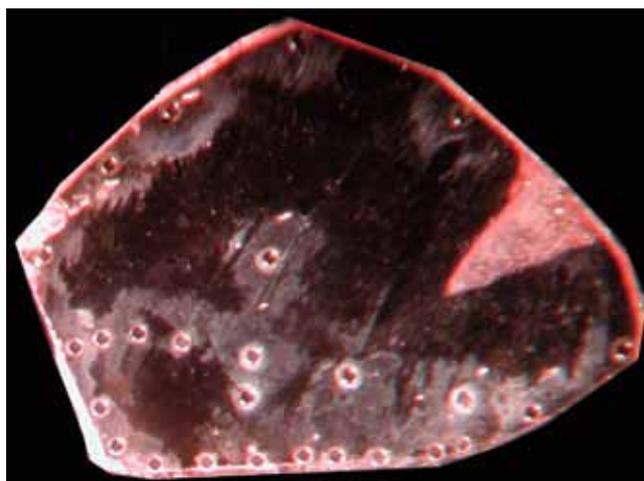


Fig. 66 Sample No.GRS 12910 Natural Orangy-Pink Sapphire enhanced by new E(IM)-method.Craters from LA-ICP-MS Testing (3 Profiles).



Fig. 67 Sample No.GRS 782 Natural Orange-red Sapphire from Songea (Tanzania) enhanced with the new E(IM)-method. Craters from scattered LA-ICP-MS Testing.

**Averaged LA-ICP-MS Data of Representative Natural Orangy-Pink Sapphires - E(IM1),
Surface Diffusion-Treated Blue Sapphires - (T)
and Natural Vivid Orange-Red Sapphires - E(IM)**

Table 7a

T - Example: Surface Diffusion-treated Sapphire.

Chemical composition (LA-ICP-MS in ppm) of a diffusion-treated sapphire (Fig. 65). 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 (Al fixed by normalisation to 526604ppm).

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 7b

**E(IM1) - Example: Natural Orangy-Pink Sapphire ("Padparadscha").
Origin: Madagascar**

Chemical compositions (LA-ICP-MS in ppm) of a Madagascar orangy-pink sapphire ("Padparadscha") (Fig. 66) enhanced with the new E(IM1) method 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	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

Table 7c

E(IM) - Example: Natural Orange-Red Sapphire of Songea (Tanzania)Origin.

Chemical composition (LA-ICP-MS in ppm) of orange-red sapphire from Songea (Tanzania) (Fig. 67) enhanced with the new E(IM) method. Note: Presence of Cr, Ti and Fe within the gemstone, along with Beryllium of approx 8ppm. 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).

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

this case study, *Beryllium* concentrations are ten times lower than the Mg-concentrations (Table 4) and thus their direct contribution to the color is questionable and needs further research (Compare also Lit. 15 and Internet Ref. 11). The yellow or orange color is formed at Mg/Ti greater than one, and at relatively lower Cr-concentrations (Fig. 41, 57, 61). The orange color is formed outside the zone containing *Beryllium* (See Fig. 57). The presence of Ti above 150ppm hampered the formation of these orange color centers (Fig. 57). The nature of these orange color centers are interpreted as Mg²⁺-trapped-hole type (See Lit. 04). Orangy-pink colors "Padparadscha" are formed in the presence of different color causes, such as Fe³⁺-pairs, Cr³⁺, Mg²⁺-trapped-hole color centers, and at Ti-concentrations below a critical level (Fig. 26, 27, 28, and 29).

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. 50, 57 and 62), this suggests Be replaces Mg positions in the corundum lattice. Profile studies show that the migration of Mg towards the core occurred (e.g. Fig. 50 and Fig. 62), however other elements - such as Ti - also migrate. Ti-migration is best seen when related to pre-existing whitish rutile dust bands (Fig. 57), or around Ti-oxide minerals (Fig. 68). A very distinct blue halo is formed (Fig. 68), interpreted as color from Fe²⁺-Ti⁴⁺ pairs (Ti from migration and Fe from the sapphire's composition) (Fig. 57).

7.) During the heating process, iron is oxidized (Fe²⁺ is transformed into Fe³⁺). At high concentrations of iron, this contributes further to the yellow color, particularly by Fe³⁺-pairs (Fig. 30). By this oxidation process the purple or brown color can be removed (Fig. 34).

The color in the enhanced sapphire 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. 41 and 57). 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 7b,c). The use of a high temperature is indicated by the surface melting of the sapphires (Fig. 14 and 15).

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).

The migration of cations towards the center of the gemstones may be related to Be-diffusion in the heating runs (Fig. 8, See Internet Ref. 11).

Identification Test

The identification of this material can be based on gemological tests, including the use of a microscope (Internet Ref 01, 03, 04 and Fig. 68), particularly in differentiating against diffusion-treated gemstones. Use of special methods - including the detection of *Beryllium* - are extremely difficult and costly. It uses SIMS (Internet Ref. 07), or LA-ICP-MS (this work). These instruments are commonly unavailable for routine testing. In addition to the Internet published test, the additional UV-Experiment can be of help (Table 1, Fig. 4 and Fig. 6). This test cannot be used to differentiate against irradiated gemstones or unheated gemstones, but can help to differentiate against other heated gemstones (group E).

Consequences for New Product Disclosure

The enhancement process producing these colors by internal migration seems to be related to diffused elements from outside sources (Internet Ref. 05, 09, 11, Lit. 18).

We agree with GIA's On-line publication on the Internet when they state that the results of their investigation strongly suggests that *Beryllium* is not the direct cause of the surface-related orange color layers and that it is possible that the diffusion of *Beryllium* and perhaps other elements into the stone may be creating a reaction with the inherent chemistry in the corundum that gives rise to the yellow to orange coloration (Internet Ref. 11).

Diffusion of light elements (e.g. hydrogen, deuterium etc.) into gemstones in course of the heat enhancement process is not a new aspect (Lit. 05). As long as the elements involved in the treatment are not directly causing the color, these type of treatments were traditionally considered gemstone enhancements (E) and were not classified as "diffusion treated" (T). The new enhancement must not be classified as surface diffusion-treated (See Internet Ref. 03) - the term 'treated' (Internet No. 08) or 'bulk diffusion' (Internet Ref. 12) may be more appropriate. The word 'diffusion' is commonly understood in the trade as coloring by introducing trace elements (Fe, Cr or Ti) from outside into the gemstone's surface (Lit. 16), and thus it is suggested not to disclose the new treatment with a phrase including the word 'diffusion' (See example Internet Ref. 12 or Internet Ref. 03).

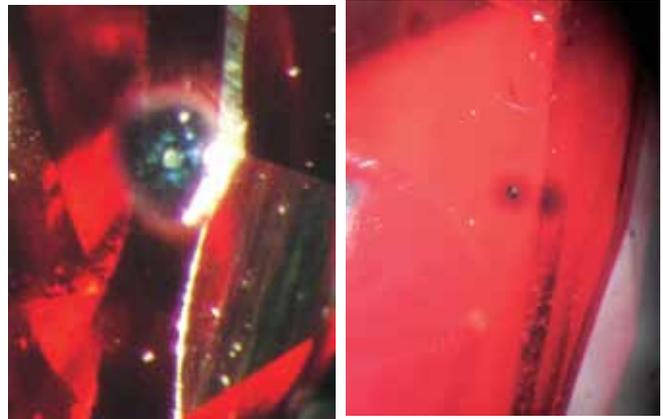
To recognize these facts the disclosure of the gemstones in the enhanced category can be proposed as following:

Enhanced (E) by heat and diffusion inducing color zoning by internal (I) migration (M) of trace elements and defects, and formation of color centers

Or in short: E(IM)*

Box Disclosure and Abbreviations	
T	Surface Diffusion Treatment
E(IM)	Enhanced by Inducing Internal Migration and Formation of Color Centers
E	Enhanced by Traditional Heat Treatment
N	Unheated, Natural Color

Fig. 68. Solid inclusions in a natural orange-red sapphire from Songea (Tanzania) enhanced with the new E(IM)-method with inclusions showing a blue halo. Note: The blue halos around the inclusions (See Fig. 13) are absent in samples unenhanced by heat. The formation of blue halos is induced by Ti migration



* E(IM) is a registered Trademark of GRS Gemresearch Swisslab AG, Lucerne, Switzerland.

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Trace element concentrations (in ppm) of a Natural White Sapphire enhanced with the new E(IM1)-Method 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

Trace element concentrations (in ppm) of a Natural Yellow Sapphire enhanced with the new E(IM1)-Method 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
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	10.7	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

Trace element concentrations (in ppm) of a Natural Blue Sapphire enhanced with the new E(IM1)-Method 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
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
19	14.83	51	121	33.6	193	936	55.0
20	15.91	26	111	34.2	204	971	55.6

Trace element concentrations (in ppm) of a Natural Blue Sapphire enhanced with the new E(IM1)-Method 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

Trace element concentrations (in ppm) of a Natural Orangy-pink Sapphire "Padparadscha" enhanced with the new E(IM1)-Method. 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	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

Trace element concentrations (in ppm) of a Natural Orangy-pink Sapphire "Padparadscha" enhanced with the new E(IM1)-Method. 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	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

Trace element concentrations (in ppm) of a Natural Orangy-pink Sapphire "Padparadscha" enhanced with the new E(IM1)-Method. 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

Trace element concentrations (in 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

Trace element concentrations (in 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	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

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