GemTOF: A Pioneering Technique in Gemology

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Introduction

In the last few decades, gemstone testing has evolved from a rather basic characterization of physical properties (e.g. density, refraction indices, dispersion, absorption and fluorescence) into advanced material science, using sophisticated scientific techniques for detailed chemical and structural analyses. The newest addition to these scientific instruments is GemTOF – installed recently at the Swiss Gemological Institute SSEF – which is a next-generation elemental analytical technique – Laser Ablation Inductively Coupled Plasma Time-Of-Flight Mass Spectrometry (LA-ICP-TOF-MS).

Unlike the LA-ICP-Quadrupole-MS (LA-ICP-Q-MS) technique already established in the gemological field, GemTOF is able to record nearly all elements in the periodic table simultaneously and at ultra-high speeds and low limits of detection. This breakthrough technique therefore offers new research opportunities in origin determination, age dating, analysis of inclusions and chemical zoning in colored gemstones, diamonds and pearls.

The main development in advanced gemological instruments in the past decades was driven by challenging issues hitting the gem trade over these years rather than by fundamental research. In particular, the undisclosed appearance of Beryllium-diffusion treated sapphires, HPHT-treated diamonds and beadless cultured pearl products (such as 'Keshi' cultured pearls) at the turn of the new millennium has had a major impact on the evolution of analytical methods in gemology.

Over all these years, the chemical analysis of gemstones has been very important not only for material identification, such as identifying the garnet species within the garnet group, but also for the authentication of gemstones, such as separating them from their synthetic counterparts, or treatment detection, like the Ti-diffusion treatment of corundum.

The main driving force for detailed trace element analysis of gemstones, however, is the demand from the trade for laboratories to deliver a scientifically based opinion about the geographic origin of gemstones (Figures 1 and 4). This demand is essentially caused by the monetary impact, such as an origin 'label', for example Colombian emeralds or Kashmir sapphires, but also because there is a growing need for traceability of gems due to political (trade bans) or ethical (fair trade) reasons.

Figure 1: The chemical composition of these Colombian emeralds reflects the geological and geochemical conditions of growth in their host rock. GemTOF's ability to analyze their isotopic composition at high-speed offers insights into their geological history and is valuable for origin determination. (Photo: Laurent Cartier, SSEF)

Semi-quantitative to quantitative chemical analysis of trace elements in gemstones is traditionally performed using characteristic X-ray fluorescence (XRF). For about the last 15 years, LA-ICP-MS has proven to be a sensitive and versatile method for trace element analysis of gemstones (Guillong et al, 2001), despite requiring minute amounts of sampled material from the gemstone. This technique is used routinely by a number of international gemological laboratories in the form of LA-ICP-Quadrupole-MS (Abduriyim and Kitawaki, 2006; Nyfeler, 2016).

LA-ICP-MS allows access to a distinctly wider range of elements than traditional XRF methods, but also to a much better detection limit (especially for light elements such as Lithium, Beryllium, Boron and Sodium), and to different isotopes of the same element. During the past few years, a number of studies have been published, many of them focusing on the chemical characterization of gemstones from different origins (Giuliani et al., 2000; Rankin et al., 2003; Sutherland et al., 2008; Halicki, 2013; Schwarz, 2015).

Recently, a novel elemental analytical system, LA-ICP-Time-Of-Flight Mass Spectrometer, has been introduced into the market. In late 2015, SSEF initiated an evaluation project with three leading companies worldwide (TOFWERK AG, Switzerland; Thermo Fisher Scientific, Switzerland; Electro Scientific Industries Europe Ltd, UK) focusing on implementing such a system at the SSEF laboratory in Basel, Switzerland. The final system was installed in July 2016 at SSEF (Figure 2) and has been in operation for a while (Figure 3).

Gemstone Origin and Authenticity Determination

LA-ICP-MS can measure unique chemical fingerprints consisting of major, minor, trace and even ultra-trace elemental compositions in gemstones. These chemical fingerprints are linked to the specific formation conditions and geochemical

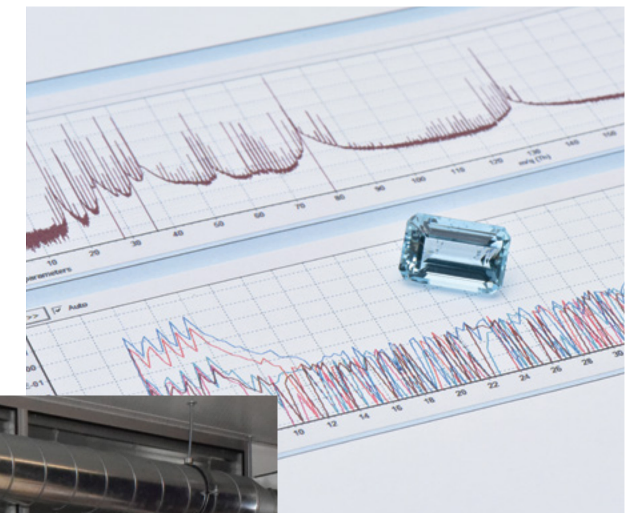

Figure 3 (Top): GemTOF full mass spectrum and laser ablation transient signal, shown here for an aquamarine as an example, offers detailed quantitative information of major to trace and even ultra-trace elemental concentrations in gemstones. (Photo: Laurent Cartier, SSEF)

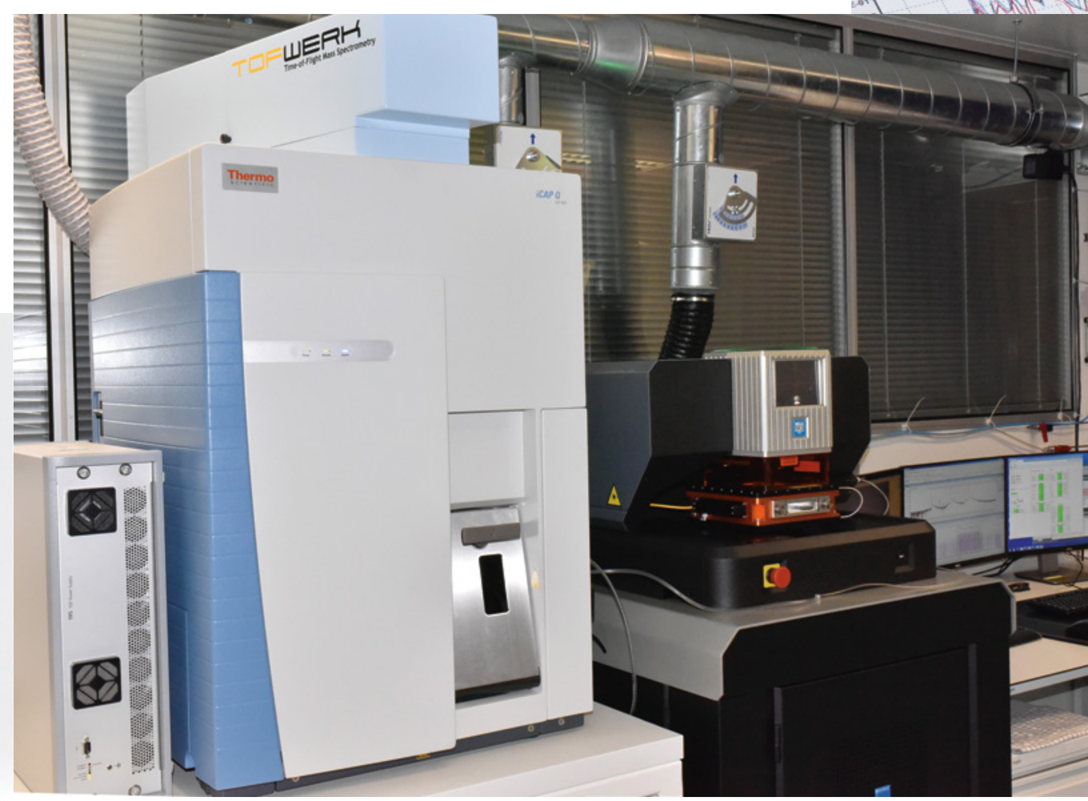

Figure 2 (Left): GemTOF setup at SSEF consists of two units, the ICP Time-Of-Flight Mass Spectrometer on the left and the Laser Ablation system (193nm wavelength) on the right. (Photo: Laurent Cartier, SSEF)

environment in which the gemstone has formed. Although it requires a minute ablation volume at the surface (normally on the girdle) of a gem, LA-ICP-MS provides valuable chemical data in addition to traditional gemological analyses. This opens up important opportunities for origin determination of gemstones such as emerald, ruby, sapphire, spinel, alexandrite, garnets and other colored gems. The acquired chemical information can be displayed in different types of plots in order to categorize gemstones in groups – often gemstone origins – (see Figure 4).

To illustrate the use of LA-ICP-TOF-MS, full mass spectra of four sapphires of documented provenance were recorded. The quantitative results of trace elements Magnesium (Mg), Iron (Fe) and Gallium (Ga) are plotted in a three-dimensional scatter plot (Figure 4) together with data from a previous study (Halicki, 2013) using LA-ICP-Q-MS on sapphires documented from Kashmir, Sri Lanka and Myanmar of SSEF reference collection with various color saturation.

The scatter plot reveals that these reference sapphires from three origins (circles in Figure 4) plot in noticeably separated areas. The four sapphires analyzed by TOF-MS (triangles in Figure 3) fit well into the expected plotting areas for the Kashmir, Sri Lanka and Myanmar origins.

In addition to multi-element information, isotopic analysis of one chemical element (isotopes differ in their masses but are naturally present in constant ratios of abundance in gemstones) could provide further insights in origin determination or separate synthetic from natural gemstones. The specific growth conditions of gemstones and pearls may lead to slight differences in isotopic ratios, e.g. carbon source for diamonds (Pay et al., 2014). In contrast to conventional Quadrupole-MS, GemTOF intrinsically provides isotopic ratio information in a higher degree of precision due to its simultaneous acquisition. Further research is required with regards to isotopic analysis and origin determination of gemstones such as ruby (Figure 5).

Detection of Undisclosed Diffusion Treatments or Coatings

GemTOF collects almost all elemental information in the periodic table routinely. When performing a measurement, any unexpected signal intensity is readily spotted in real-time already during the analysis on the computer monitors of the system (Figure 6), which is perfectly adapted to detect new and undisclosed chemical treatments such as chemical diffusion or coatings.

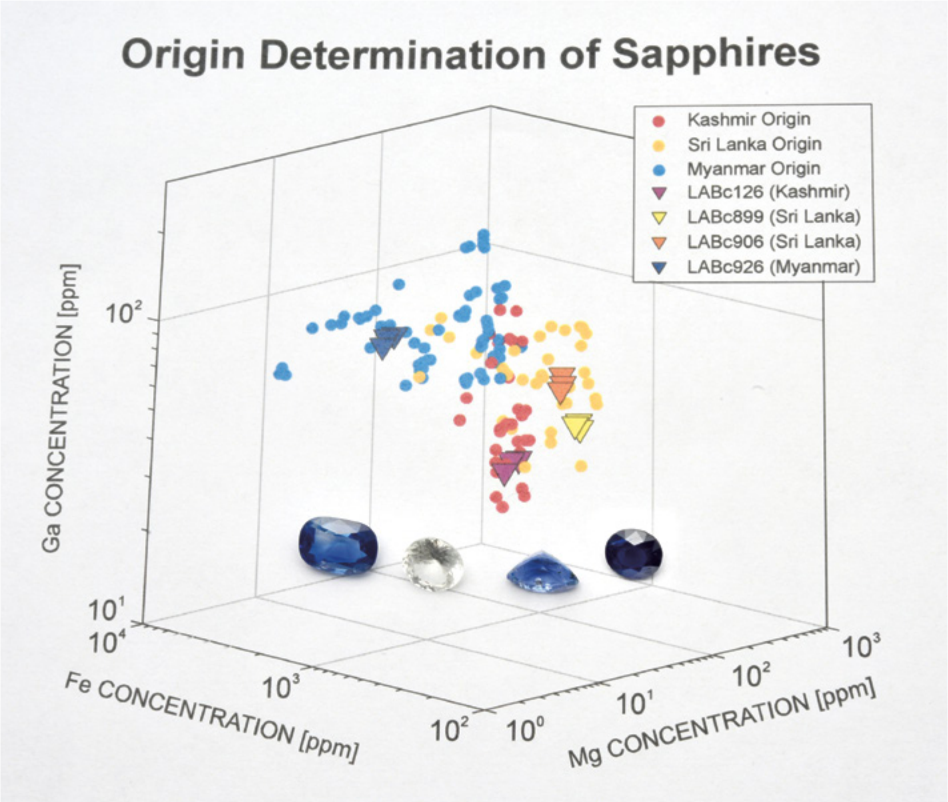

Figure 4: Three dimensional plot of quantitative results of sapphires from the SSEF (H.A. Hänni) collection using LA-ICP-TOF-MS, together with reference sapphires from Kashmir, Sri Lanka and Myanmar. Trace elements concentration of Mg, Fe and Ga are displayed in logarithmic scales.

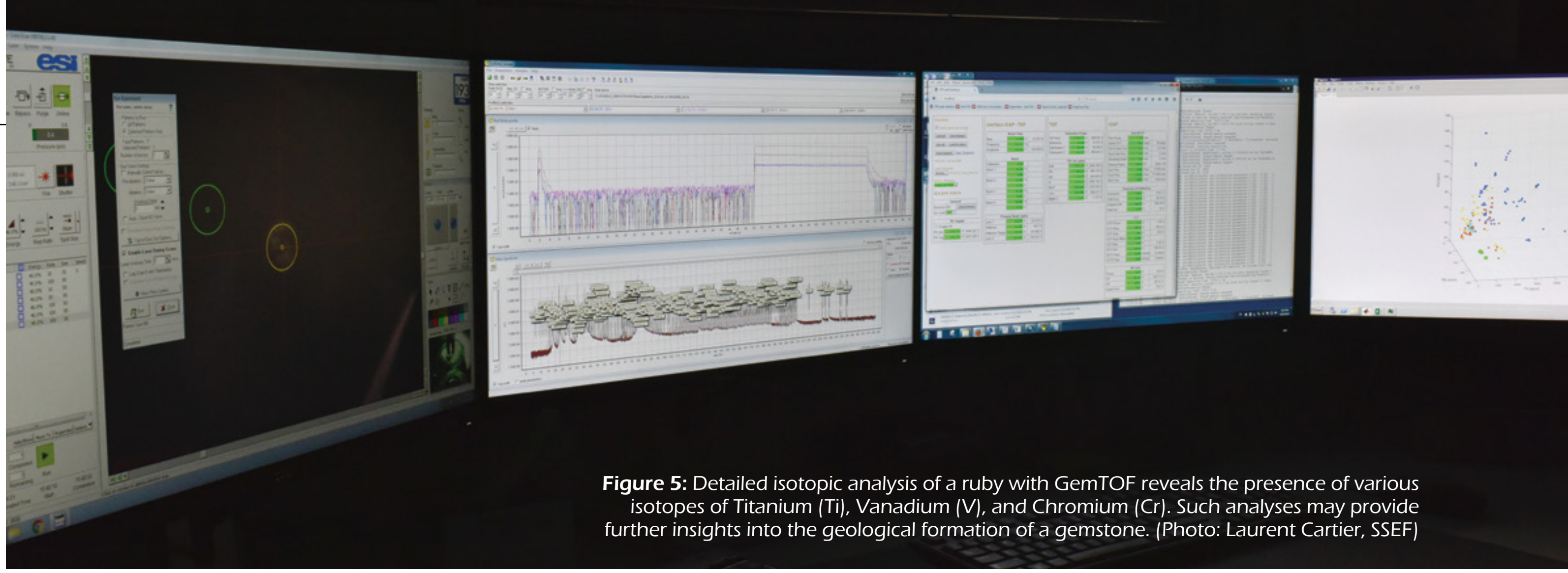

Figure 5: Detailed isotopic analysis of a ruby with GemTOF reveals the presence of various isotopes of Titanium (Ti), Vanadium (V), and Chromium (Cr). Such analyses may provide further insights into the geological formation of a gemstone. (Photo: Laurent Cartier, SSEF)

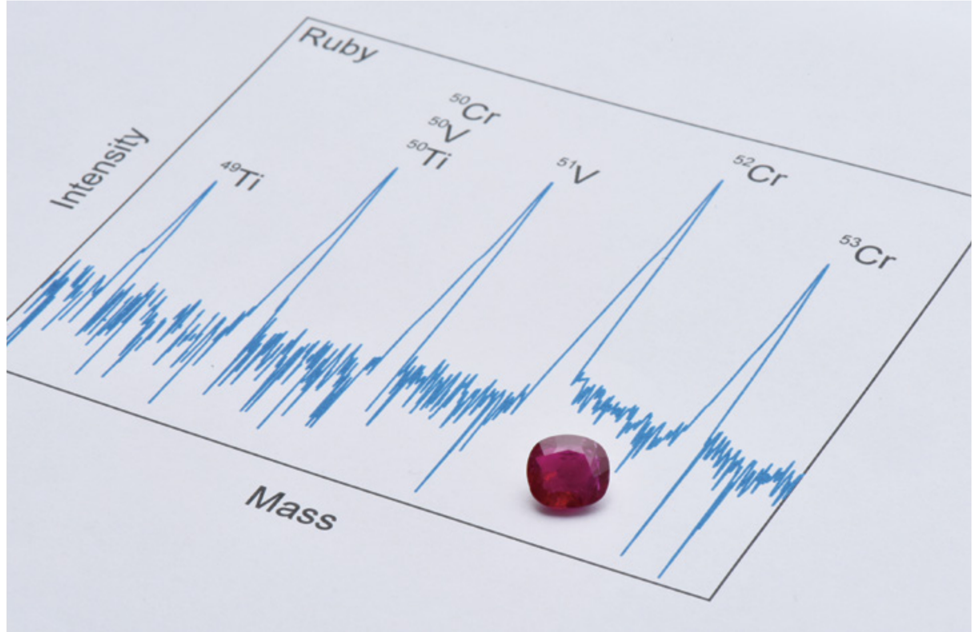

Figure 6: Real-time monitoring of the presence of elements in a gemstone by GemTOF. By doing so, any chemical irregularity which might be due to an undisclosed treatment can be detected immediately. (Photo: Laurent Cartier, SSEF)

This is very much in contrast to more conventional LA-ICP-Quadrupole-Mass Spectrometry which analyses only a predefined list of elements/isotopes, but is missing any information about elements not included in this predefined list. We thus believe that GemTOF is an analytical breakthrough in gemology and will help to avoid a situation such as when beryllium diffusion treated corundum hit the market (and gemological laboratories) unprepared and first unnoticed.

Age Dating and Inclusion Analysis of Gemstones

Gemstones from different origins are likely to have formed at different geological periods. Therefore, age information can be helpful when origin determination of a gemstone is required. Direct age dating of gemstones, such as sapphires, can be difficult. Fortunately, small inclusions such as zircon (often found in sapphire, see Figure 7) can provide useful data. Zircon is one of the most popular minerals for age dating, as it provides a Uranium (U) - Lead (Pb) dating system ('geological clock').

In order to precisely measure the U-Pb dating system, multiple isotopes from U and Pb have to be acquired within this small amount of sample (inclusion). The smaller the inclusion the shorter the transient signal. LA-ICP-TOF-MS that measures all isotopes simultaneously is able to acquire fast enough chemical information even in minute zircon inclusions for a reliable age dating. Recently, age dating of zircon inclusions analyzed by LA-ICP-Quadrupole-Mass Spectrometer focused on faceted sapphires from origins relevant to the gem trade (Coenraads et al., 1990; Link, 2015).

These studies have proposed that age dating can be used as a valuable tool for origin determination in gemological testing, reflecting different formation times for these sapphires from different geological contexts. Other inclusions may provide additional key information about the formation and chemical environment conditions of a gemstone.

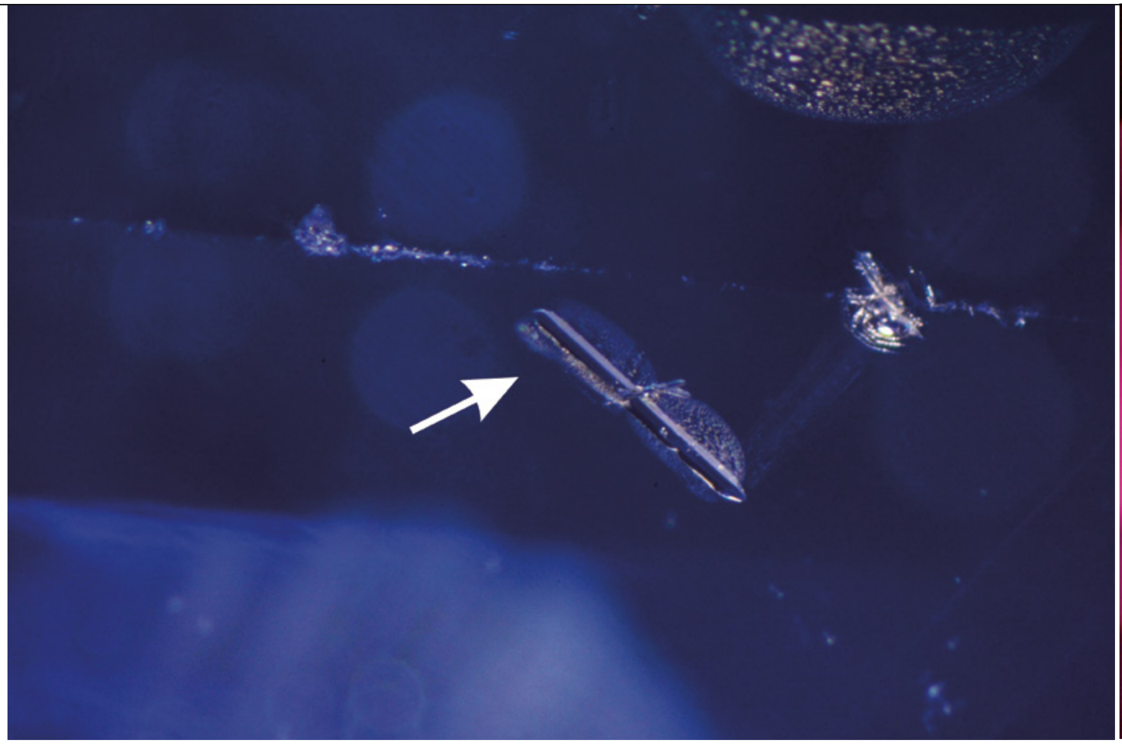

Figure 7: A long-prismatic zircon inclusion (white arrow) close to the surface of a Kashmir sapphire. The zircon is key for age dating of gemstones. (Photo: Michael Krzemnicki, SSEF)

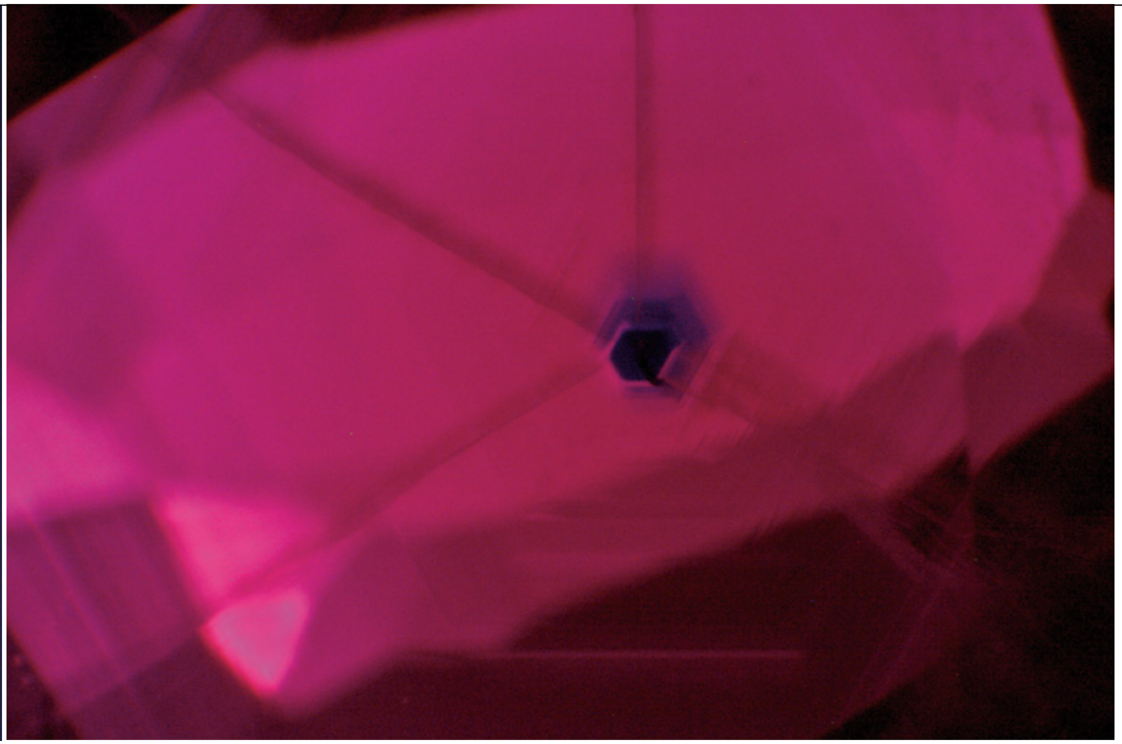

Figure 8: Characteristic (chemical) color zoning in ruby from Mong Hsu, Myanmar (Burma). (Photo: Michael Krzemnicki, SSEF)

Mapping Chemical Zoning for Gemstone Research

The formation of gemstones is a complex process both in terms of space and time. Chemical (and color) zoning is common (see Figure 8), caused by intrinsic factors such as oscillatory growth zoning, or extrinsic ones such as a change of rock chemistry due to fluid infiltration. A detailed mapping of elemental distribution may provide valuable information about formation kinetics which is not readily perceived based just on few single analysis spots. Preferably in high spatial resolution, the imaging of trace element distribution in a gemstone by GemTOF can thus be a powerful tool. A homogenized 10µm laser spot or even less is needed to provide quantitative element distribution images of high spatial resolution. By controlling the ablation process, it is possible to gain two-dimensional or even three-dimensional elemental distribution images by GemTOF.

Conclusion and Outlook

GemTOF is a new and highly sensitive instrument for chemical analysis of colored gemstones, diamonds and pearls. The main advantage is the simultaneous acquisition of full elemental mass spectrum with high mass resolving power and ultra-high acquisition speed. Therefore, it is not necessary to preselect isotopes of interest, which always requires assumptions about the trace element composition of samples and careful considerations of possible peak interferences before measurement.

As the full mass spectrum is recorded, Time-Of-Flight-Mass Spectrometer allows the adjustment of isotope selection even after ablation and analysis, in contrast to Quadrupole-MS, where a re-ablation (at a slightly different position) would be needed. Laser ablation pits from GemTOF are not visible to the naked eye, do not lead to a weight change in a gemstone, and the amount of ablation carried out on a (client) stone is minimized as much as possible.

With the GemTOF, the Swiss Gemological Institute is again introducing a new and pioneering method for advanced gemstone testing after introducing LIBS in 2004 and X-ray micro-tomography in 2010 into routine analytical procedures. GemTOF enables us to conduct high-quality elemental analyses, to produce multidimensional data, and to feed our database for statistical analyses.

The combination of improved sensitivities and low background noise guarantees a superior limit of detection for heavy elements in parts per billion and for light elements in parts per million. In addition to routine measurements, this new and sophisticated analytical method will complement other gemological testing methods used at SSEF. This will enhance trace element characterization of gemstones and pearls for origin determination, treatment detection and isotopic analysis, and open new research opportunities for age dating, inclusion studies or high spatial resolution chemical mapping of gems.

Finally, for a more detailed article on LA-ICP-Time-Of-Flight-MS use in gemology please see a featured article in the Journal of Gemology (Wang et al., 2016).♦

Acknowledgements

The authors would like to acknowledge Tofwerk AG (Thun, Switzerland), ESI (Huntingdon, UK) and ThermoFisher Scientific (Reinach/Basel, Switzerland) for general support. The Swiss Association of Gemstone Dealers (ASNP) is appreciated for their generous donation. Thanks to the entire SSEF team for their support for this project and fruitful discussions.

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