10 Years of Laser Ablation - ICPMS Applied in Gem Labs
激光燒蝕 - 電感耦合等離子體質譜儀 (LA-ICPMS) 在寶石鑑定所的十年應用回顧

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本文描述了激光燒蝕—電感耦合等離子體質譜儀(LA-ICPMS)在近十年的寶石學應用。LA-ICPMS是高度精密分析成分和含量的儀器，早期應用集中在檢測微量和痕量元素，例如：帕帕拉恰藍寶石的鈹擴散處理，以至判斷多種寶石來源產地等。及後引用地質學上常用的鋯石U-Pb同位素測年，以此開拓LA-ICPMS寶石學應用的新一頁。

Laser Ablation - Inductively Coupled Plasma - Mass Spectrometry (LA-ICPMS) is a highly sophisticated analytical method of obtaining quantitative measurements of the concentrations of trace- and ultratrace-elements in solid materials. In 2006, the Gübelin Gem Lab was the first gem testing laboratory to acquire its own LA-ICPMS system (Fig. 1). This investment triggered a cascade of developments and initiated a push in technology which has eventually been followed by other gem labs. The insights gained by the use of this method have significantly improved our capabilities of both determining the origins of gemstones, and detecting certain treatments and synthetics. This article looks back at the developments over the last 10 years.

The need to invest in LA-ICPMS was triggered by a new treatment introduced in the early 2000s, where large numbers of pink sapphires were subjected to beryllium diffusion treatment. This treatment turned pink sapphires into more valuable orangey-pink sapphires, presented to the public as padparadscha sapphires. The ability to detect the beryllium in these sapphires was a challenge for gem labs, because the ED-XRF devices, which were the state-of-the-art analytical instruments used to detect trace elements at that time, were not able to recognize light elements such as beryllium. Laser Induced Breakdown Spectroscopy (LIBS) was presented as a cheaper alternative to LA-ICPMS in the quest to detect beryllium. However, the LIBS technology was never widely adopted because it was not sufficiently sensitive to detect the sometimes low concentrations of beryllium (occasionally as low as 2 parts per million, ppm) in diffusion treated sapphires. Eventually the discovery of significant beryllium contents (10 ppm and above) in natural, untreated sapphires from Madagascar and Sri Lanka sidelined LIBS as a suitable form of technology to detect beryllium-treated sapphires.

Fig. 1 The LA-ICPMS system operated at the Gübelin Gem Lab in Switzerland. It shows the 193nm gas laser in the centre, and the ICPMS in the background on the left.

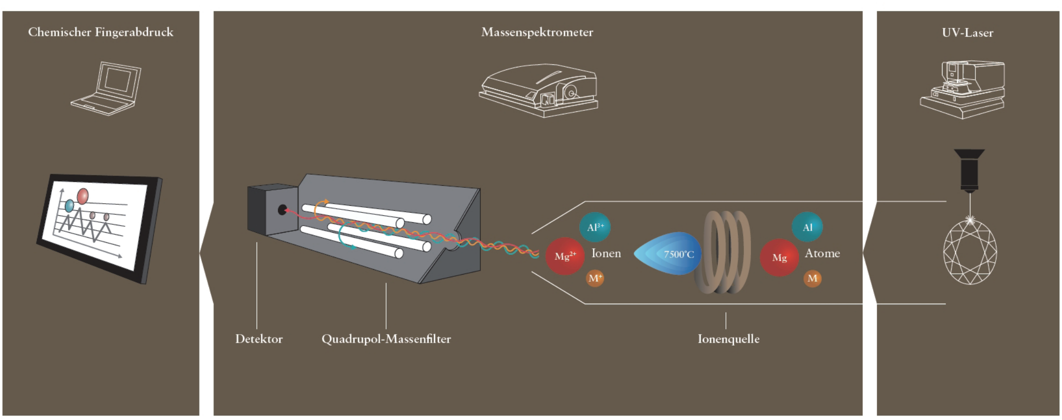
With LA-ICPMS it is possible to produce highly accurate measurements of almost all chemical elements of the periodic table in very low concentrations, down to the parts per billion level (Fig. 2). The laser is directed onto the girdle of the gemstone and ablates tiny amounts of sample material. The ablated particles disintegrate and are ionised in a plasma, and the isotopes are separated by their masses and charges so that they can be measured with high accuracy. The laser creates a small pit on the girdle of the gemstone, with a diameter and depth of 0.030 to 0.070 millimeters. This is less than half of the diameter of a human hair, invisible to the naked eye, and hardly detectable by loupe. The pit has no effect on the weight, appearance or value of the gemstone whatsoever. The method is hence referred to as quasi-nondestructive.

Aside from the detection of beryllium treatment, this method has also proved useful for the detection of other diffusion treatments such as titanium, lithium and cobalt as well as the detection of a series of trace elements that indicate a possible synthetic origin, such as platinum, nickel, rhodium, molybdenum, or iridium.

The most important and substantial advantage of LA-ICPMS in gem labs today is, however, the wealth of chemical data boosting the quality of the origin determination method. Since the 1990s, the main coloured stone gem labs have all experienced limits to their ability to determine the origin of gemstones, especially in the case of blue sapphires. The similarities of the geology in which these gems grow leads to overlapping microscopic and spectroscopic properties. These overlaps have limited the ability of labs to determine, absolutely, the origin of all gemstones, leading to the somewhat unpopular "no-origin" reports. LA-ICPMS, though, has helped with this, giving labs a significant number of additional discriminating factors that have potentially helped to separate the different origins. It has allowed gem labs to make their basis of the origin determination methodology much more robust. Obviously, a key prerequisite is a complete reference collection of gemstones from all commercially relevant mines worldwide in order to establish the database required for the comparison.

The sheer volume of data generated by testing several tens of thousands of reference samples with LA-ICPMS calls for a completely new approach to handle and evaluate that data. Sophisticated algorithms digest the data that has been collected and establish individual patterns of the gemmological properties of each stone, resulting in much more reliable and reproducible interpretations and conclusions. Thanks to computer-supported evaluations, inconsistencies caused by humans can be reduced significantly. Nowadays, on Gübelin Gem Lab reports, more and more results are based fully or partially on some kind of computerized interpretation algorithms.

INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICPMS)



Abgleich mit Referenzsteinsammlung Messen minimaler Spurenelementkonzentrationen Probenahme im µ-Bereich

Fig. 2 This is a schematic representation of the LA-ICPMS, with the laser on the right. In the middle section, it shows how the ablated particles are disintegrated and ionised, and how they enter the mass spectrometer, in which they are separated by mass and charge, and counted by a detector. The raw counts are mathematically transformed into concentrations.

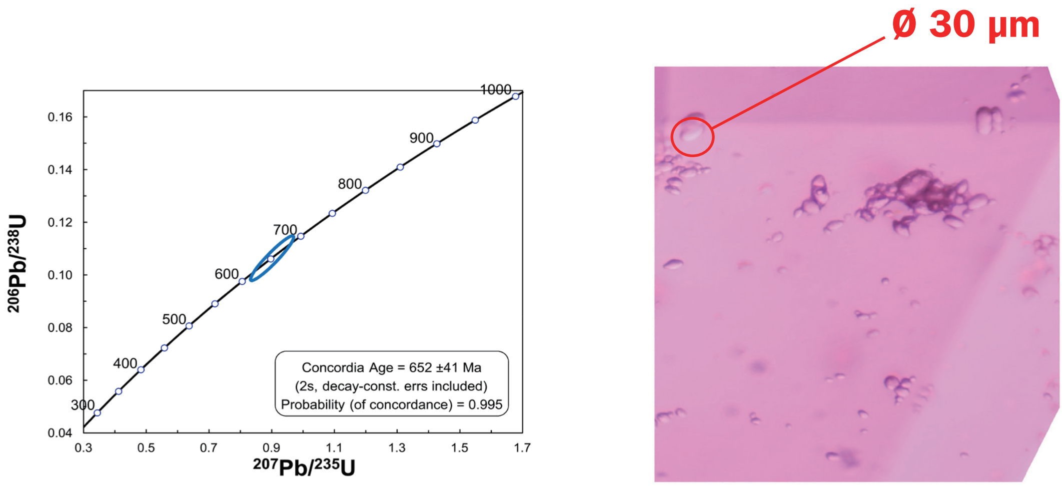


Fig. 3 On the right, tiny crystal inclusions of zircon are shown in the 13ct pink sapphire. The circled crystal on top is analysed, yielding concentrations of uranium and lead indicating an age of formation of the zircon crystal of 652 million years plus/minus 41 million years. This age of formation supports the expected Pan-African age of the pink sapphire.

In 2009, after having analysed several thousands of stones to establish a solid database, Gübelin Gem Lab started to use LA-ICPMS to test some stones belonging to clients, namely Paraiba tourmalines. Emeralds and alexandrites followed in 2010 and red to pink spinels in 2011. Some of the best qualities of gemstones often lack any meaningful microscopic inclusions, so the chemical fingerprint is often the only way to determine their origin. This applies especially to Paraiba tourmalines, alexandrites and spinels. In 2013, the Gübelin Gem Lab started to use LA-ICPMS to test marble-type rubies and, in the year following it did the same with blue sapphires from metamorphic deposits. In the same year, we changed from the 213 nm solid state laser to a more powerful 193 nm gas laser. This investment allowed the improved positioning of the laser spot, a further reduction of the pit size, and an even better detection limit.

In the late summer of 2015, another substantial milestone was achieved: for the first time ever, the age of formation could be determined directly on a faceted, high-value gemstone. By measuring uranium and lead isotopes in zircon inclusions in sapphires from Madagascar (Fig. 3), the radiogenic age of the gemstone was determined to be around 650 million years, consistent with the age published for these rocks in the scientific literature. The ability to determine the absolute age of formation of a gem gives strong support to the argument that it is possible to distinguish different geologic events and environments.

For example, the gemstones formed during the Pan-African orogenesis (comprising rubies and sapphires from all East African countries including Madagascar and Sri Lanka) can clearly be separated from those formed during the Alpine-Himalayan orogenesis (including Kashmir and Burma). The Pan-African event occurred between 450 and 650 million years ago, while the Alpine-Himalayan event took place only some 15 to 40 million years ago. LA-ICPMS can tap new sources of information from a gemstone, obtaining new insights from each gemstone that would have been inaccessible beforehand.

This complex chemical pattern together with the precise age is unique for every single gemstone, comparable to the DNA in living organisms. It allows new and astonishing background information and stories to be communicated to the final customer, highlighting the uniqueness and individuality of coloured gemstones.

At the Gübelin Gem Lab we are convinced that the push enabled by the technological progress of LA-ICPMS has opened a new era of how labs, the trade and the end consumer will look at coloured gemstones. It offers us new insights into a gem and its formation, comparable to those that the insight pioneers like Dr Eduard Gübelin gained when they started to study microscopic inclusions in gemstones more than 80 years ago.

Reference

Link, Klemens; 2015. Age determination of zircon inclusions in faceted sapphires; The Journal of Gemmology, 34(8)