Age Determination of Zircon Inclusions in Faceted Sapphires

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The age determination of zircon inclusions in faceted sapphires by LA-ICP-MS may provide a valuable tool to support geographical origin determination. In this initial study, U-Pb dating of a zircon inclusion in a pink sapphire from Madagascar yielded an age of 650 million years (Ma), suggesting a syngenetic origin (i.e. formed at the same time as the host sapphire) of the zircon. In a greenish blue sapphire from Madagascar, an included zircon yielded a U-Pb age of 1,750 Ma, pre-dating the host sapphire, and therefore indicating the zircon is an inherited inclusion (i.e. it originated from rocks that existed before the host sapphire crystallized). These results are supported by indications provided from conventional methods of geographical origin determination. This article also discusses the potential influence on U-Pb age dating of post-formation metamorphic events, laboratory heat treatment and the possibility of complex zoning in the zircon inclusions.

The Journal of Gemmology, 34(8), 2015, pp. 692–700, http://dx.doi.org/10.15506/JoG.2015.34.8.692

Introduction

Laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) has become an established tool in the past decade for use by prominent well-equipped gemmological laboratories (Breeding et al., 2010). Standard routines have been developed to measure trace-element concentrations in various gem materials to detect treatments and/or determine a stone's geographical origin (e.g. Günther and Kane, 1999; Guillong and Günther, 2001; Abduriyim and Kitawaki, 2006). The geographical origin of high-end coloured stones is seen by the trade as a key value driver, and has developed into one of the main tasks for gem-testing laboratories. Initially LA-ICP-MS was mainly applied to research samples, but with increasing experience and confidence, as well as improved instrumentation, this technique is now routinely used for analysing client-submitted stones. The biggest challenge and the highest priority are to gain meaningful data without damaging or affecting the quality of the stone (i.e. to work quasi-non-destructively).

LA-ICP-MS is a well-established and frequently used method in the geosciences for measuring *in situ* uranium-lead (U-Pb) ages of zircon (e.g. Jackson et al., 2004). Microscopic crystals or grains of zircon can be dated regardless of their host matrix, provided that they reach the surface of the stone and thus can be sampled by the instrument's laser beam.

Zircon inclusions in rough gem-quality corundum have been investigated by numerous researchers using LA-ICP-MS (e.g. Coenraads

Figure 1: These Sri Lanka and Madagascar sapphires are typical candidates for hosting zircon inclusions that could be used for age determination to better characterize their origins. The stones range between 1.4 and 29.7 ct, and are unheated with the exception of the yellow sapphire on the left. Photo by K. Link.

et al., 1990; Sutherland et al., 2008; 2015), and recently the technique was used to perform U-Pb age dating of blue sapphires from Myanmar, Madagascar and Sri Lanka that were sawn and polished to expose zircon inclusions on their surface (Elmaleh et al., 2015). However, determining the age of zircon inclusions in high-quality faceted gemstones such as those commonly submitted to gem labs (e.g. Figure 1) has not been reported until now. Since July 2015, this procedure has been routinely applied to client stones at the Gübelin Gem Lab (GGL) when zircon inclusions are exposed on the surface and age data is particularly helpful for origin determination (e.g. for separating some blue sapphires from Myanmar and Madagascar). It can also provide indications of heat treatment.

Age data for zircon inclusions in sapphires can shed light on the genetic conditions under which the sapphire formed, as well as point to the original host rocks. The latter is particularly important for sedimentary deposits without any connection to their primary host rocks, such as the economically important Ilakaka mining region in south-western Madagascar (Rakotondrazafy et al., 2008).

Materials and Methods

The samples comprised two faceted fancy-colour sapphires (pink and greenish blue; see Figure 2), each weighing ~12 ct, that were submitted to the Gübelin Gem Lab in Lucerne by professional gem traders. Both samples contained zircon inclusions that reached the surface at the girdles, and routine origin determination procedures performed in our laboratory clearly indicated that both stones were from metamorphic-type deposits in Madagascar. The pink sapphire had clusters of small, colourless, rounded anhedral zircon that each measured a maximum 60 μm long and 30 μm wide (Figure 3a). Although heat treatment at relatively low temperatures could not be excluded, the stone clearly had not been exposed to high-temperature heating. The greenish blue sapphire, which was found to be untreated, contained randomly scattered zircon inclusions with subhedral elongated shapes (e.g. Figure 3b,c). The investigated zircon crystal in the greenish blue sapphire was ~90 μm long and 35 μm wide.

To avoid leaving eye-visible traces from LA-ICP-MS analysis, client stones are typically sampled

Figure 2: These pink and greenish blue sapphires (each ~12 ct) were submitted to the Gübelin Gem Lab in 2015. Both sapphires had surface-reaching zircon inclusions on their girdles, so age determination could be conducted. Photos by Janine Meyer, GGL.

Figure 3: (a) In this cluster of zircon inclusions within the pink sapphire, the surface-reaching zircons that were analysed for age determination are circled. (b) Internal features in the greenish blue sapphire consist of isolated zircon crystals (top-centre and top-right), among other inclusions. (c) This zircon inclusion in the greenish blue sapphire was used for in situ *age determination; the circle marks the position and size of the applied laser pit. Photomicrographs (a) and (c) by Klaus Schollenbruch, GGL; (b) is courtesy of Bulgari, image width ~2 mm.*

with the laser only on their girdle (with some exceptions). The pit diameter must not exceed 50–70 µm, and the depth of the pit usually does not exceed its diameter. The resulting pits are not eye visible and have no significant effect on the weight of the stone.

For the U-Pb age dating of zircon inclusions in sapphires, to avoid sampling the corundum host, the LA-ICP-MS signal is carefully controlled for any sudden change in indicative elements such as Si or Zr. Although corundum usually does not contain significant U or Pb, and slightly ablating the host sapphire therefore should not disturb the results, we are sure to avoid any such possible contamination. For both samples described here, the spot diameter of the laser was limited to 30 µm by the size of the outcropping zircon inclusions (Figure 3), and this limited the depth of the pits to ~30 µm as well. The weight loss of the samples after analysis was calculated to be only approximately 0.000004 ct.

The analytical conditions used for this study are listed in Table I. The LA-ICP-MS system at the Gübelin Gem Lab consists of an ESI NWR193^{UC} ArF excimer-based UV laser ablation system with a large-format sample chamber and a flexible cup that collects the ablated material, which is coupled with a PerkinElmer ELAN DRC-e quadrupole ICP mass spectrometer (Figure 4). The laser has a wavelength of 193 nm, which allows precise ablation at the micrometre scale without cracking or splintering the sample. The ablated

Table I: LA-ICP-MS analytical parameters.

Laser	**NWR193^{UC} from ESI**
System	193 nm ArF excimer laser
Sample cell	High-performance two-volume chamber system
Sample carrier gas	1,000 ml/min He
Laser pulse rate	14 Hz
Laser energy	6.3 J/cm^2
ICP-MS	**PerkinElmer ELAN DRC-e quadrupole ICP-MS**
Auxiliary gas	0.66 l/min Ar
Nebulizer gas	0.675 l/min Ar
Plasma gas	16.5 l/min Ar
RF power	1,350 W

Figure 4: The instrumentation at the Gübelin Gem Lab used for this study consists of an ICP-MS (left side) and a laser ablation unit (right side). Photo by K. Link.

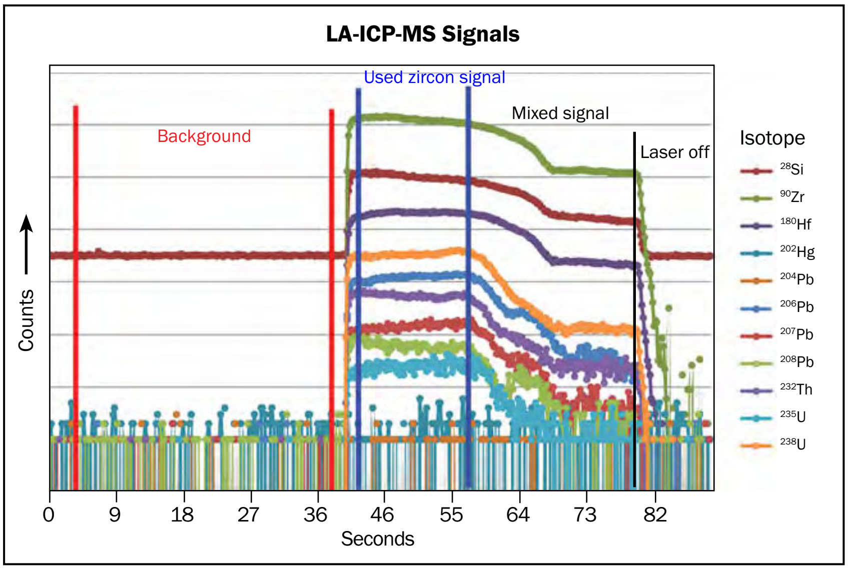


Figure 5: This diagram shows the raw signals for various isotopes obtained during the ablation of the zircon inclusion in the greenish blue sapphire. The portions used for data reduction are marked in red and blue.

material is transported in a flow of He carrier gas to the Ar plasma of the mass spectrometer. Within the plasma, the 60–150 nm-sized particles are disintegrated at ~7,000°C into ions that are selectively detected by the mass spectrometer.

The optimal laser conditions were found by monitoring the U-Pb ratios and searching for the minimum deviation to reduce the errors in age calculations. The dwell times for individual mass scans were 10 milliseconds for all measured isotopes (^{28}Si, ^{90}Zr, ^{180}Hf, ^{202}Hg, ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{232}Th, ^{235}U and ^{238}U). The background was analysed for 40 seconds, and the ablation signal from the zircon was measured until it became unstable after around 15 seconds (Figure 5). Only the area of the signal showing a flat plateau was used for integration. A Plesovice zircon (Sláma et al., 2008) was used for standardization; a GJ zircon (Jackson et al., 2004) and an in-house reference zircon were used for quality control.

For age determination (see Box A and Table II), ^{207}Pb/^{235}U ratios were calculated from the measured ^{206}Pb/^{238}U and ^{207}Pb/^{206}Pb ratios using a constant value for present-day ^{235}U/^{238}U. The ICP-MS was optimized on a daily basis for a maximum sensitivity to heavy elements with minimum (<0.5%) oxide generation (monitored using Th/ThO). Data reduction and the time-dependent laser- and mass spectrometer-induced inter-element mass fractionation (Pb/U) corrections were applied using in-house Microsoft Excel worksheets. Ages, errors (2σ) and concordia diagrams were produced using Isoplot3 macros for Excel (Ludwig, 2003).

Common lead was monitored via non-radiogenic ^{204}Pb, and ^{202}Hg was checked to estimate the interference of ^{204}Hg on ^{204}Pb. For both samples, ^{204}Pb was below the detection limit, so we assumed that no common lead was present.

Results and Discussion

The results of U-Pb age dating of the zircon inclusions are presented in Table II and shown in Figure 6.

Pink Sapphire

The analysed zircon from the inclusion clusters in the pink sapphire yielded a concordant U-Pb age of 652 ± 41 Ma (Figure 6a). From the appearance of the zircon inclusions, they are interpreted as syngenetic with the host sapphire, and are considered to be in equilibrium with the corundum. Thus, the age we obtained should correspond to the formational age of this sapphire. The crystallization ages of the sapphires from Madagascar are not yet well known, but published work (e.g. Rakotondrazafy et al., 2008, and references therein) indicates ages around 560 Ma. Associated granulite- and amphibolite-facies rocks and linked felsic intrusives cluster between 560 and 650 Ma (Kröner et al., 1999). The basement rocks of Madagascar were affected by the Pan-African tectono-metamorphic event (730–550 Ma; Black and Liegeois, 1993), which extended across a broad region that included other sapphire-bearing areas such as East Africa

Box A: Zircon Geochronology

Zircon ($ZrSiO_4$) is a mineral of great benefit for geochronologists. It occurs in nearly all rock types and is very resistant to physical abrasion as well as thermal alteration. In addition, zircon has no or only limited susceptibility to chemical diffusion with its environment under most conditions in the earth's crust. The zirconium cations (Zr^{4+}) in the crystal lattice have an ionic radius that is only about 15% less than uranium ions (U^{4+}), so uranium is somewhat compatible in zircon and can be incorporated up to a few hundred parts per million. Lead cations (Pb^{2+}) are around 50% larger, so that they are far too big for zircon's crystal structure and therefore highly incompatible. Any Pb that may have been incorporated during zircon formation is ideally below the detection limit of LA-ICP-MS.

Starting at the time the zircon is formed, U isotopes undergo radioactive decay to form Pb daughter isotopes ($^{235}U \rightarrow ^{207}Pb$ and $^{238}U \rightarrow ^{206}Pb$) according to their decay constants. Measuring the radiogenic Pb allows one to precisely calculate the formation age of the zircon. The two measurable radioactive U isotopes provide two independent radioactive systems ('clocks'). This gives valuable information for determining the plausibility of the calculated ages. If both systems yield the same ages within their errors, the age can be considered as robust or concordant (i.e. it can be assumed that the isotopic system was not disturbed by any chemical or physical process after zircon formation). A good way to visualize and validate U-Pb ages is with a *concordia* diagram, as introduced by Wetherill (1956; see Figure 6 in the text of this article). The concordia diagram plots the isotopic ratios of the two radioactive systems $^{206}Pb/^{238}U$ versus $^{207}Pb/^{235}U$. All possible concordant ages plot along a concordia curve in the centre of the plot. Samples with older ages (higher radiogenic lead and lower radioactive uranium, leading to higher Pb/U ratios) plot further to the top and right on the curve, and younger samples plot toward the bottom left. The different decay constants for the two radioactive systems cause the curved shape. The age including the errors (typically 2σ) is presented as an ellipse in the diagram. The ratios and the sizes of the individual errors define the form, size and orientation of the ellipse. Disturbances of the isotopic system in the zircon corresponding to episodic or continuous Pb diffusion out of the system will cause a sample to plot on a straight *discordia* line. Such values plot below the concordia curve, between the original formational age of the zircon and a younger age-disturbing event.

Using the ratio in the decay constants between ^{238}U and ^{235}U, and assuming that a zircon did not incorporate any common lead during its formation, it is possible to combine the two isotopic U-Pb systems by simply taking the ratio of the two daughter isotopes $^{207}Pb/^{206}Pb$, as this ratio is only a function of time. The Pb-Pb ages can be quite useful since they do not depend on measuring the ratios of two different elements (U and Pb). Besides requiring fewer fractionation corrections, this method allows one to validate the concordance of U-Pb ages and to obtain ages even for disturbed systems, as such processes would affect only the element ratios (U/Pb) and not the isotopic ratios (Pb/Pb). The Pb-Pb ages are particularly important for very old time scales. For extra assurance, Pb-Pb ages are commonly considered minimum ages.

and Sri Lanka, and led to the formation of the so-called Mozambique Belt. More research is needed on Madagascar and other Pan-African-related sapphire age populations before using them as hard criteria for origin determination.

Greenish Blue Sapphire

The zircon analysed in the greenish blue sapphire gave a concordant age of 1,742 ± 70 Ma (Figure 6b). The individual ages given in Table II for the various isotopic pairs ($^{207}Pb/^{235}U$, $^{206}Pb/^{238}U$

Table II: Geochronological results for zircon inclusions in the two sapphires.

Data	$^{207}Pb/^{235}U$	± 1σ	$^{206}Pb/^{238}U$	± 1σ	$^{207}Pb/^{206}Pb$	± 1σ	roh[a]
Pink sapphire	0.9003	0.045	0.1064	0.0056	0.0617	0.0019	0.94
Greenish blue sapphire	4.5779	0.212	0.3144	0.0202	0.1074	0.0051	0.72
Age (Ma)	$^{207}Pb/^{235}U$	± 2σ	$^{206}Pb/^{238}U$	± 2σ	$^{207}Pb/^{206}Pb$	± 2σ	prob[a]
Pink sapphire	651	32	651	34	663	20	0.99
Greenish blue sapphire	1745	80	1762	112	1755	86	0.82

[a] Abbreviations: roh = error correlation between $^{207}Pb/^{235}U$ and $^{206}Pb/^{238}U$ ratios; prob = probability of concordance (taken from Isoplot).

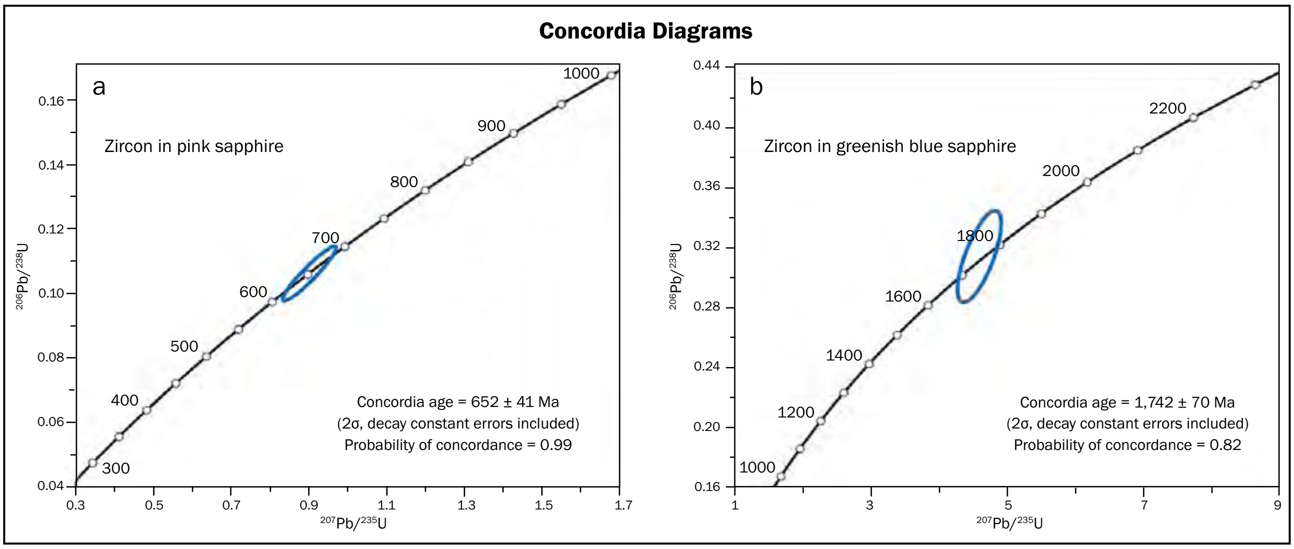
and $^{207}Pb/^{206}Pb$) show a slightly greater variance than those from the pink sapphire, but within their errors they provide good matches with the integrated concordia age, and correspond to an 82% probability of concordance. The reasons for the slightly varying individual ages may be related to post-formation diffusion processes, elemental zoning (see below), or slight differences in the accuracy or precision of measuring the various isotopes.

The ~1,740 Ma age does not coincide with the assumed Pan-African-associated formation of this Madagascar sapphire. Hence, this subhedral zircon is more complicated to interpret (see below).

Influence of Post-Formation Metamorphism on Zircon

Once a zircon has crystallized, very high pressure-temperature conditions are required to destroy it (Watson, 1996). The closure temperature of zircon, which is above 900°C at most geologically relevant time scales (Cherniak and Watson, 2003), marks the condition at which diffusion becomes sufficient to exchange U and/or Pb, and therefore disturb the U-Pb system and thus the age determination. In most cases, temperatures during metamorphism are less than 1,000°C (i.e. combined with high pressures, as with upper granulite facies conditions). Since the Pb content of zircon is preserved through all but the most extreme conditions of metamorphism, its original formation age is usually not disturbed by such events (Watson, 1996). However, depending on the duration of a high-temperature metamorphic event, there may be a severe impact on the zircon (Blackburn et al., 2011). Uranium is rather compatible in the zircon structure, whereas Pb is not (Cherniak and Watson, 2003). Increasing temperatures drive recrystallization processes as well as diffusion rates (Nasdala et al., 2001). This leads to enhanced Pb diffusion toward the outer rim or completely out of the zircon. The loss of

Figure 6: Concordia plots made with Isoplot software (Ludwig, 2003) are shown for the zircon inclusions in the pink sapphire (a) and the greenish blue sapphire (b).



(radiogenic) Pb changes the U/Pb ratio and resets the 'radiogenic clock'. This may be visualized in a concordia diagram (described in Box A), in which the so-called concordia line in the centre of the plot shows the U-Pb ratios for undisturbed, 'closed' systems where all the Pb originates from U decay. Disturbed U-Pb ratios result in combined ratios lying below the concordia on a line called the discordia which leads toward younger ages. In an ideal case, the discordia points to the age of the event that 'opened' the U-Pb system (Dickin, 2005). If the measured U-Pb data plot nicely on the concordia, it can be assumed that the U/Pb ratios were undisturbed by later events such as metamorphism.

Rocks affected by the Pan-African event were tectonically overprinted under amphibolite- to granulite-facies pressure/temperature conditions. Nevertheless, old inherited zircons that preserve the age of the rocks before the intense deformation are well known in the literature (e.g. Kröner et al., 1999). The 1,742 Ma age we obtained for the zircon inclusion in the greenish blue sapphire coincides with the age of zircons possibly derived from granulites found, for example, in southern Madagascar (Kröner et al., 1999). These granulites are interpreted to have formed at 1,740 Ma and to have been later tectonically overprinted during the Pan-African event. The somewhat rounded, resorbed-appearing morphology of the zircon inclusions in this sapphire supports an inherited (protogenetic) origin for these crystals (cf. Corfu et al., 2003). If this is correct, then these zircon inclusions must have been derived from the host rock and trapped in the corundum during its crystallization. Although proving such a scenario is beyond the scope of this article, it does fit well with the Madagascar origin of this sapphire. This is further supported by zircon inclusions in sapphires from Madagascar that have been previously described as ranging around 1,500 Ma (Elmaleh et al., 2015). In addition, the author is not aware of a similar published age for the other potential areas of origin such as Sri Lanka and East Africa.

Potential Effect of Heat Treatment

It is well known that sapphires are commonly heat treated to enhance their appearance. What is the effect of heat treatment on the calculated U-Pb age of their zircon inclusions?

Previous experiments indicate that sapphire heat treatment has an effect on the crystallinity of zircon inclusions — depending on temperature and time — although the extent of this effect is a matter for debate (Nasdala et al., 2001; Wang et al., 2006). Furthermore, it is not clear if or to what extent Pb loss in a diffusive process is measurable for these heated stones. Zircon heating experiments have been done to investigate the amount of Pb loss due to diffusion. Cherniak and Watson (2003) claimed that below 1,200°C, the time to reach 1% Pb loss in an effective 10 μm zone exceeds one year. More relevant is the temperature range between 1,200°C and 1,450°C. At these temperatures, measurable Pb loss can be assumed for heating periods of less than one day (Cherniak and Watson, 2003). Also, the diffusion rate may increase due to strong radiation damage in metamict zircon. Above 1,400°C, zircon ($ZrSiO_4$) becomes unstable and partially melts to form baddeleyite (ZrO_2) and silicate-rich phases (Wang et al., 2006; Váczi et al., 2009). More experiments in the range of 1,200–1,400°C are required to better quantify the diffusive effect on Pb in zircon.

Therefore, sapphire heat treatment may to some extent lead to Pb loss from zircon inclusions. As this does not consider the lifetime of the various U-Pb decay systems, the decay loss must result in an effect similar to natural Pb loss from high-temperature metamorphism. Thus the U-Pb ages of zircon inclusions in heated sapphires would be expected to plot beneath the concordia curve and follow linear trends towards younger ages. Conversely, this implies that concordant-plotting zircons most probably were not exposed to high-temperature heat treatment. U-Pb data that plot discordantly could be the result of exposure to either intense laboratory heat treatment or natural high-temperature metamorphism. Even apparently concordant-plotting zircons may to a minor extent be affected by Pb loss (their error ellipses plot on the concordia line, but the true ages within the ellipses can be slightly discordant). In such cases, the calculated ages represent minimum ages.

With a calculated probability of concordance of 99% (Table II), the zircon in the pink sapphire clearly yielded a concordant age. The age obtained from the zircon in the greenish blue sapphire was 82% concordant, so despite the high level of confidence there is some possibility of slight discordance. As heat treatment of that sapphire could be excluded, this may be due to tectono-metamorphic events that the zircon was exposed to after its formation and before being trapped in the sapphire.

Highly Zoned Zircons

A potential complication for age dating could be caused by complexly zoned zircons, in which the varying zones represent different times of formation. If the zones with different ages are smaller than the spatial resolution of the laser spot, then mixed ages would result. In the concordia diagram, such results may plot similarly to zircons that have experienced Pb loss. In some cases, different growth zones might be indicated by sudden trace-element concentration changes in the mass spectrum during ablation. If available, cathodoluminescence (CL) imaging is the most powerful tool to identify these zones. The minimum spot size of the LA-ICP-MS instrument (and ion probes such as SIMS or SHRIMP) is around 10–15 μm in diameter, depending on the amount of U and Pb in the zircons, thus dictating the minimum homogeneous zone in a zircon that is required for a 'good' age determination. The zircon inclusions analysed for this article showed no evidence of multiphase mineral formation (i.e. there were no sudden variations in trace-element composition during the analyses).

Conclusions

LA-ICP-MS is effective for determining the age of zircon inclusions, even in valuable faceted stones, without damaging the host sapphire. The limiting conditions are the technical capabilities of the analytical devices on one hand and the characteristics of the zircon inclusions on the other (i.e. the sapphire must contain surface-reaching zircons, preferably on the girdle, that are large enough to analyse and lack fine-scale chemical zoning). The dating methods are applicable to any gemmological laboratory operating a LA-ICP-MS. Age data for zircon inclusions in sapphires provides useful information for origin determination, and can in some cases indicate the crystallization age of the host sapphire. Zircon ages that far exceed the inferred age of the surrounding sapphire can also provide valuable information. Depending on the error ranges, it may be more dependable to consider the data as minimum ages rather than the exact time of formation. This especially applies to those stones where heat treatment cannot be excluded. Although a discordant U-Pb age may be the consequence of a high-temperature (i.e. >1,200°C) heat treatment that was applied for a relatively long period, such discordance might also indicate that a high-grade metamorphic overprint caused loss of Pb and possibly U, or even point to a mixed age from sampling a complexly zoned zircon inclusion.

Although the routine age determination of zircon inclusions in sapphire is not yet frequently accomplished in gemmological laboratories, it is expected that this procedure will become more common in the future as LA-ICP-MS instrumentation becomes more available and better constraints are obtained on the ages of sapphires and their host rocks. It may even become an additional service requested by clients in addition to origin determination.

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Acknowledgements

The author thanks the three anonymous reviewers for their helpful and constructive suggestions and the Gübelin Gem Lab team for its support whenever help was needed. Figure 3b was kindly supplied by Bulgari (Rome, Italy).