Blue Diffusion-treated Natural & Synthetic Sapphires recently available in the Market
近日市場上的藍色擴散處理天然和合成藍寶石


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自2015年起在泰國尖竹汶市面出現了大量藍色擴散處理的合成藍寶石，此外2012年市面上亦出現了一種經藍色擴散處理的天然藍寶石。作者們利用常規實驗室設備及先進的檢測儀器，對該兩種藍寶石進行研究，比對各樣結果和發現。

Abstract

Since 2015 a large quantity of a new blue diffused synthetic sapphire has appeared in the Chanthaburi market. It is interesting to compare its gemmological properties with those of a blue diffused natural sapphire that came onto the market in 2012. In immersion both types of blue diffused sapphires showed the "spiders' web effect" – a cut-related colouration pattern – and rather high titanium content on the surface of the samples, both effects being diagnostic evidence of Ti-diffusion treatment. The synthetic test stone, however, also displayed strong chalky blue fluorescence to SWUV radiation (also in the DiamondView™), the presence of curved bands, of minute particles or gas bubbles under a microscope, very low Ga contents and no Fe^{3+}-related absorption peaks on the UV-Vis spectra. In contrast, the natural one showed the occurrence of tension discs, altered solid inclusions and altered fingerprints, often with colour concentration along healed fractures, cavities seen under the microscope, significant Ga content and some Fe^{3+}-related absorption peaks on the UV-Vis spectra.

The thickness of the blue colour rim of the diffused natural stone was apparently much thicker than that of the diffused synthetic one. The reason is that it is the penetration depth of titanium that controls the colour rim thickness of the natural stone, while it is the penetration depth of iron that controls that of the synthetic one. Because of the difference of the colour rim thickness and the re-polishing process, the "spiders' web effect" in the natural stone is less pronounced while that in the synthetic one is more obvious. The formation of the blue colour rim and multi-element diffusion found in both synthetic and natural sapphires are also discussed here.

Introduction

Treatment inducing the surface colouration of natural sapphire has been common since the late 1970s (Crowningshield, 1979; Hänni, 1982; Kammerling et al., 1990; Kane et al., 1990). This technique involves adding colouring chemicals during heat treatment which produces a thin layer of colour on the surface of colourless or light-coloured natural sapphire. The process involves the diffusion of colour-causing transition element(s), such as Ti and possibly Fe, into the stone surface at very high temperatures (1600-1700°C), to produce a blue colour rim (~0.1 up to ~0.5 mm thick; Kane et al., 1990; Hughes et al, 2017), and, less commonly, Cr to create a red colour rim (Carr and Nisevich, 1975; Crowningshield, 1979b; McClure, 1993). In 2012, a new blue diffused natural sapphire appeared in the market. A preliminary study of this sapphire revealed a deeper blue colour rim and the multi-element diffusion of titanium, beryllium and lithium from an external source into the stone (Pisutha-Arnond et al., 2012).

There are several methods of producing synthetic corundum. The Verneuil process, also called flame fusion, was developed as early as 1902 while Czochralski (though the basic process was originally developed in 1918) and the flux-grown process only developed in the 1960s (Webster, 1994; Thomas, 2008). However, only material produced by the flame-fusion technique is commonly used in the gem industry due to its lower manufacturing costs.

Why do synthetic Verneuil sapphires need diffusion treatment? Is it worth the additional cost? The reasonable answer must be *yes*, because the blue colouration in Verneuil grown blue sapphires is usually restricted to the rim of the boules. This is due to their prolonged exposure to high temperatures during formation, causing the colour-causing trace elements to migrate (diffuse internally) to the surface of the boules (Katia Djevahirdjian, 2019; pers. comm. via Prof. H. Hänni; see also Eigenmann et al., 1972).

There were early reports of flame-fusion synthetic sapphires that had been treated by the diffusion process (Fryer et al., 1982; Kammerling and Koivula, 1995; Choudhary and Golecha, 2006; Golecha, 2006). Then, when from 2015 on, a large quantity of a new blue diffused synthetic sapphire entered the Chanthaburi gem market, some of these stones were submitted to GIT-Gem Testing Laboratory (GTL) for testing. Even though some characteristics of the blue diffused synthetic sapphire had been reported earlier (McClure, 2012, 2013; Sun et al., 2017), the significance of these features had not yet been emphasised. There are in fact obvious differences from those found in the blue diffused, natural sapphire. We, therefore, considered it interesting to compare the gemmological characteristics and key identifying features of blue diffused sapphires treated from natural and synthetic starting materials, and this is the subject of this article.

Samples and Methods

A total of 10 new blue diffusion-treated synthetic sapphire samples (Fig. 1) and 58 recently created blue diffused natural sapphire samples (Fig. 2) collected from the gem market were used in this study.

Fig. 1 10 diffused synthetic sapphires weighing from 1.69 to 10.46 cts. were used in this study. *Photo by P. Ounorn*
本研究所採用的10顆經擴散處理的合成藍寶石，重量從1.69到10.46克拉。

Basic gemmological instruments were used for the measurement of the stone's properties. Internal features were observed with both standard gem microscope and immersion scope in methylene iodide solution. In addition, fluorescence images were taken using a DiamondView™. Their internal and external features were examined by gem microscope with Canon EOS 7D camera attached and recorded.

For the advanced tests, polarised UV-Vis-NIR absorption spectra of the samples were collected € ⊥ C (o-ray) and € // C (e-ray) by using a PerkinElmer Lambda 950 spectrophotometer in the range 300-850 nm with a sampling interval of 3.0 nm and scan speed of 441 nm per minute. The chemical analysis was carried out using an EDAX Eagle III for Energy-dispersive X-ray Fluorescence (EDXRF) spectroscopy EDAX Eagle III. A laser ablation-inductively coupled plasma-mass spectroscopy (LA-ICP-MS), Agilent 7500cs

Fig. 2 Altogether 58 blue diffused natural sapphires (33 faceted stones weighing from 0.91 to 2.06 cts. and 25 cabochons weighing from 0.24 to 2.90 cts.) *Photo by N. Narudeesombat*
合共採用了58顆經藍色擴散處理的天然藍寶石（33顆經切瓣的，重量從0.91到2.06克拉，25顆弧面形，重量從0.24到2.90克拉）。

equipped with New Wave Research UP213 laser ablation system, was also used for the analysis of sensitive and versatile trace-elements. All LA-ICP-MS analyses were done with a pulse rate of 5 Hz and a beam energy of approximately 0.5 mJ per pulse, producing a spatial resolution of 30-50 µm in diameter on the samples. Quantitative results of isotopes for ten trace elements (Li7, Be9, B11, Mg24, Ti47, V51, Cr53, Mn55, Fe56 and Ga71) were obtained through calibration of relative element sensitivities using the NIST-610 multi-element glass standard and pure Al_2O_3 as internal standards. The BCR2G basaltic glass standard was also used as an external standard. The contents are reported as µg/g or ppm by weight. The detection limits vary from analysis to analysis and are typically less than 1 ppm for Li, Be, V and Ga; less than 4 ppm for B, Mg, Mn and Ti; less than 6 ppm for Cr; less than 25 ppm for Fe. In addition, laser-induced breakdown spectroscopy (LIBS) was used to detect any trace beryllium on the surface of the stones.

Results

General Gemmological Properties

Blue diffused synthetic sapphire: The refractive indices (~1.760-1.770), birefringence (~0.008-0.010) and S.G. values (~3.96-3.98) of the blue diffused synthetic sapphire samples fell within the normal properties of corundum. All the samples were mainly inert to LWUV radiation and fluoresced unevenly, strong chalky blue to SWUV, which may indicate their synthetic origin. When tested with a dichroscope, the samples showed slightly to moderately greenish blue to purplish blue pleochroism. The stones, when immersed in methylene iodide solution, clearly showed strong evidence of diffusion treatment; notably varying blue colour concentrations on different facets along facet junctions and girdles due to re-polishing after treatment (Kane et al., 1990), the so-called "spiders' web effect" (Matlins and Bonanno, 2008) — a cut-related colouration pattern (Fig. 3 left).

Blue diffused natural sapphire: The diffused natural sapphires tested were pale, medium, and dark blue. The basic gemmological testing gave RI ~ 1.762-1.771, Birefringence ~0.009 and S.G. values ~3.91-4.07. The stones were inert to strong orange-red under LWUV, inert to weak chalky green-blue under SWUV, and showed greenish blue to purplish blue pleochroism. In immersion, the "spiders' web effect" appeared less obvious, but the colour concentration could clearly be seen along the rims, surface-reaching fractures and cavities (Fig. 3 right) where such fractures and cavities are normally absent in the diffused synthetic stones (Fig. 3 left).

Thickness of the Diffused Blue Surface Layer

Diffused sapphires are normally treated from colourless to pale-coloured starting stones. To calculate and compare the thickness of the colour rim of these blue diffused corundum, some samples were slab-cut and polished into thin slices (~0.4-0.5 mm thick). Two blue diffused synthetic sapphire slices showed thin blue colour rims (~0.15-0.2 mm, Fig. 4a&b), whereas the induced blue surface layers of the two blue diffused natural sapphire *slices* were much thicker (~0.5-1.1 mm, Fig. 4c&d).

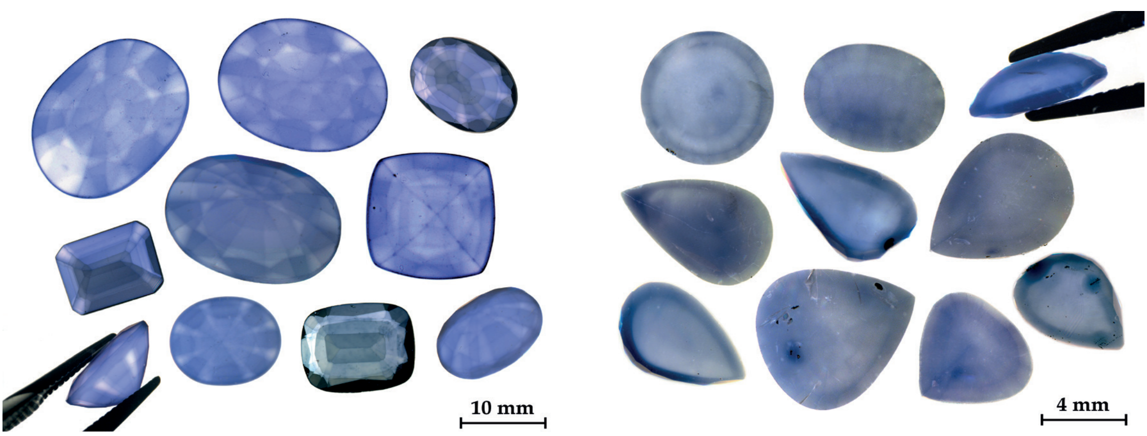


Fig. 3 When viewing the stones in methylene iodide solution with diffused-transmitted white light, blue diffused synthetic stones clearly display a "spiders' web effect" (left). Blue diffused natural sapphires show only vague "spiders' web effect", but strong colour concentration along the rims, fractures and cavities (right). *Photos by P. Ounorn & S. Promwongnan*
當在二碘甲烷溶液中利用漫透射白光觀察兩種樣本時，藍色擴散處理的合成藍寶石清楚地顯示出"蜘蛛網"效應（左）。藍色擴散處理的天然藍寶石只顯示出模糊的"蜘蛛網"效應，但沿著邊緣，裂縫和空洞（右）的顏色濃度卻很高。

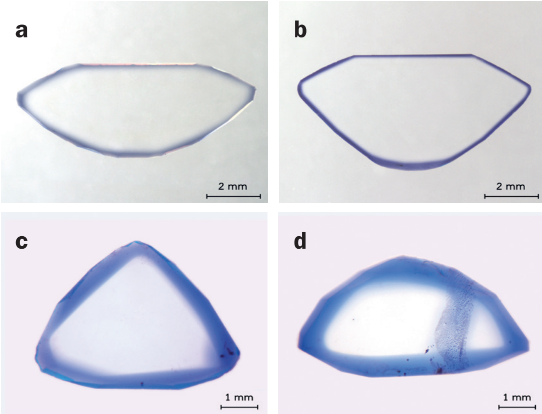


Fig. 4 (a&b) slices of two blue diffused synthetic sapphire samples show thin colour rims (~0.15-0.2 mm) and the colourless inner areas; **(c&d)** slices of two blue-diffused natural sapphire samples show thicker colour rims (~0.5-1.1 mm) and colourless cores with blue colour concentration along an open fracture in (d). Immersion in methylene iodide solution. *Photos by S. Promwongnan and T. Sripoonjan*
在二碘甲烷溶液中觀察：**(a&b)** 兩顆藍色擴散處理合成藍寶石樣品的切片顯示薄的帶色邊緣（約0.15-0.2毫米）和無色的內部區域；**(c&d)** 兩顆藍色擴散處理天然藍寶石樣品的切片顯示較厚的顏色邊緣（~0.5-1.1mm）和無色色芯，在（d）中沿著開放的裂縫中藍色濃度高。

Luminescence

Under the high-intensity ultra-short-wave UV (<225 nm) luminescence imaging system of a DiamondView™, all samples displayed varying degrees of chalky blue fluorescence. When comparing the samples viewed in immersion in methylene iodide solution and ultra-shortwave UV radiation, the diffused synthetic sapphire clearly showed that the white or paler blue-coloured facets seen in immersion fluoresced strong chalky blue, while the deeper blue coloured facets, facet junctions and girdle fluoresced less (see Fig. 5a&b). This evidence confirms that the synthetic colourless starting stones fluoresce strong chalky blue. The weaker fluorescent area of the deeper blue coloured surface is probably caused by the presence of diffused iron that can suppress the fluorescence (see Fe profiles in Figs. 8&9 below, and also Hughes and Emmett, 2005; Choudhary and Golecha, 2006; Sun et al., 2017). On the other hand, the diffused natural sapphire fluoresced slightly along ill-defined facet junctions, girdle, and cavities in contrast to the non-fluorescent area of the whole stone (see Fig. 5c&d).

Microscopic Features

Blue diffused synthetic sapphire: Some samples showed small induced fingerprints that suggest the stones had undergone high-temperature heating. Curved bands of minute particles were also observed (Fig. 6a). On careful examination at higher magnification with fibre optic light illumination, the stones revealed unusual clouds of straight and curved lines of tiny gas bubbles (Fig. 6b). This evidence indicates the melt-growth (flame-fusion and/or crystal pulling) synthetic origin of the starting stones (Webster, 1994). However, when all the samples were viewed in the direction of the optic axis in immersion between crossed

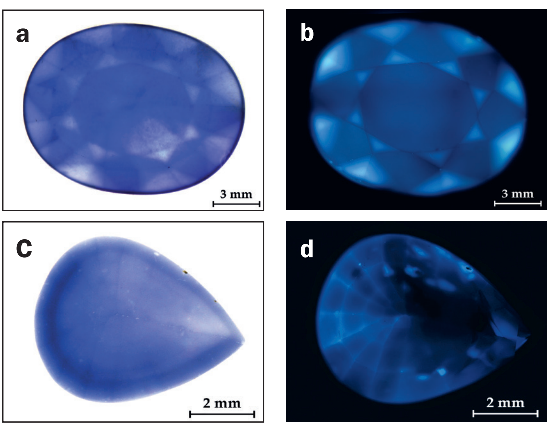


Fig. 5 (a&b) An image of a blue diffused synthetic stone viewed at the same position in methylene iodide solution (a) and ultra-shortwave UV radiation in DiamondView (b). **(c&d)** An image of a blue diffused natural sapphire viewed at the same position in immersion (c) and ultra-shortwave UV radiation in DiamondView (d). *Photos by S. Promwongnan*
(a和b) 藍色擴散處理合成藍寶石的圖像在浸入二碘甲烷溶液(a) DiamondView下和(b)短波紫外線射的相同位置觀察的。**(c&d)** 在DiamondView下(d)和(c)短波紫外射線的相同位置觀察的藍色擴散處理天然藍寶石。

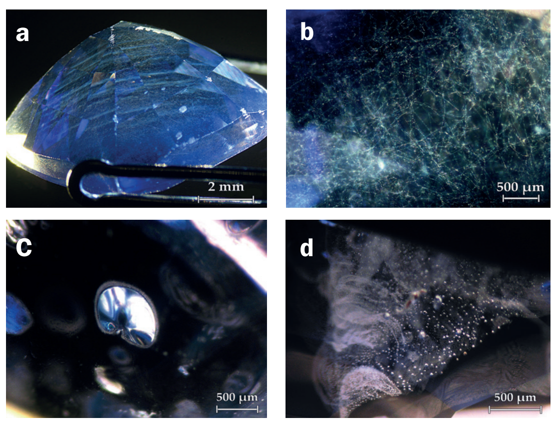


Fig. 6 (a) curved bands of minute particles and **(b)** the unusual clouds of straight and curved lines of tiny gas bubbles in blue diffused synthetic sapphire samples; **(c)** tension disc and **(d)** altered fingerprints in blue diffused natural sapphire samples. Dark field and/or fibre optic illuminator. *Photomicrographs by P. Ounorn, S. Promwongnan & N. Narudeesombat*
暗域照明器：**(a)**具微小顆粒的彎曲帶和**(b)**藍色擴散處理合成藍寶石樣品中具微小氣泡的直線和曲線的異常雲狀物；**(c)**張力盤和**(d)**藍色擴散處理天然藍寶石樣品中變異的指紋狀物。

polarisers, no Plato lines were observed. Nonetheless, such features in colourless flame-fusion synthetic sapphire could disappear after heat treatment (Kammerling and Koivula, 1995; Elen and Fritsch, 1999).

Blue diffused natural sapphire: Because the starter stones were pale to colourless natural sapphires that had previously been unsuccessfully treated by normal heating, it was not surprising that the internal features of blue-diffused natural sapphire displayed tension discs (Fig. 6c), altered solid inclusions and altered fingerprints (Fig. 6d), all commonly observed features of repeatedly high-temperature-heated stones.

Advanced Testing

UV-Vis-NIR Spectra

Blue diffused synthetic sapphire: The polarised UV-Vis-NIR absorption spectra of the blue diffused synthetic sapphires (Fig. 7 left) clearly displayed broad absorption bands that peaked at around 570 nm (o-ray) and 730 nm (e-ray), responsible for their blue colouration as the result of Fe^{2+}/Ti^{4+} inter-valence charge transfer (IVCT) mechanism (Lehmann and Harder, 1970; Krebs and Maisch, 1971; Nassau, 1994; Häger, 2001). No Fe^{3+} related-absorption peaks appeared in the spectra of synthetic stones.

Blue diffused natural sapphire: The polarised UV-Vis-NIR spectra of the blue diffused natural sapphires (Fig. 7 right) similarly displayed broad Fe^{2+}/Ti^{4+} IVCT absorption bands at around 570 nm (o-ray) and 730 nm (e-ray), responsible for their blue colouration with additional Fe^{3+} related-absorption peaks at 377, 387, and 450 nm commonly observed in low iron metamorphic sapphire origin.

Chemical Analyses

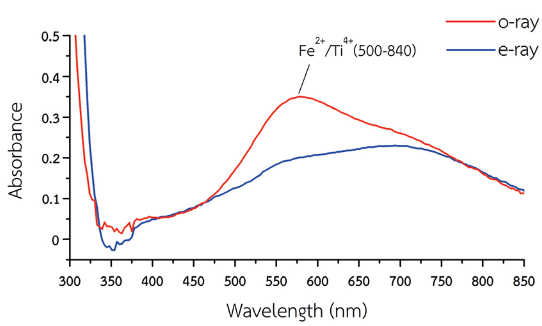
EDXRF Result

Blue diffused synthetic sapphire: The semi-quantitative EDXRF analyses on the table facets of 10 diffused synthetic sapphire samples gave high contents of titanium (0.19-0.29 wt.% with the average of 0.22 wt.% TiO_2), moderate contents of iron (0.07-0.20 wt.% with the average of 0.09 wt.% Fe_2O_3) and very low contents of gallium (<0.01 wt.% Ga_2O_3). Such high Ti contents but low Ga contents found on the surface of these stones (e.g., as compared to the EDXRF analyses of our 24 Sri Lankan blue sapphire reference samples: TiO_2 ~0.01-0.11 and av.~0.05 wt.%; Fe_2O_3 ~0.05-0.18 and av.~0.10 wt.%; Ga_2O_3 ~0.01-0.06 and av.~0.03 wt.%) confirmed that they are indeed Ti-diffusion-treated from synthetic starting materials (Hänni, 1982; Hänni and Stern, 1982; Stern and Hänni, 1982).

Blue diffused natural sapphire: The semi-quantitative EDXRF analyses on the table facets of 33 diffused natural sapphire samples gave rather high titanium contents (0.05-0.21 wt.% with an average of 0.11 wt.% TiO_2), moderate iron contents (0.05-0.41 wt.% with an average of 0.15 wt.% Fe_2O_3) and significant gallium contents (0.01-0.02 wt.% with an average of 0.015 wt.% Ga_2O_3). Again, such high Ti contents and significant Ga contents found on the surface of these stones indicate that they are Ti-diffusion-treated from natural starting materials (Hänni, 1982; Hänni and Stern, 1982; Stern and Hänni, 1982).

LA-ICP-MS Result

Blue diffused synthetic sapphire: Edge-to-edge-transverse analyses by LA-ICP-MS technique were carried out on the surface of the thin slice



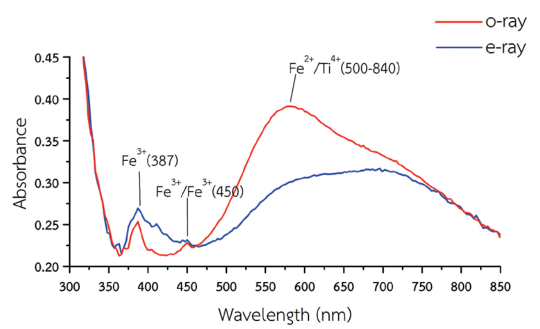


Fig. 7 (Left): UV-Vis-NIR absorption spectra of a blue diffused synthetic sapphire show typical absorption bands due to Fe^{2+}/Ti^{4+} IVCT without Fe^{3+} related-absorption peaks. **(Right):** UV-Vis-NIR absorption spectra of a blue diffused natural sapphire show typical absorption bands due to Fe^{2+}/Ti^{4+} IVCT and some Fe^{3+} related absorption peaks.
(左)：藍色擴散處理合成藍寶石的UV-Vis-NIR吸收光譜顯示由Fe^{2+}/Ti^{4+} IVCT引致的典型吸收帶，卻沒有Fe^{3+}相關的吸收峰。
(右)：藍色擴散處理天然藍寶石的UV-Vis-NIR吸收光譜顯示出由Fe^{2+}/Ti^{4+} IVCT和一些Fe^{3+}相關吸收峰引起的典型吸收帶。

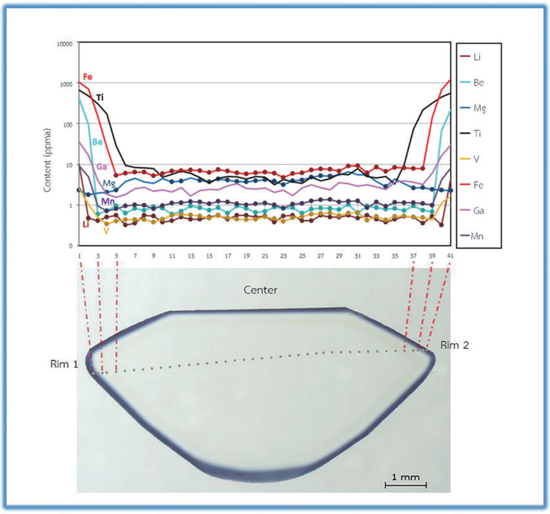


Fig. 8 Edge-to-edge-41-spots-traverse analysis by LA-ICP-MS on the thin slice of a blue diffused synthetic sapphire sample (bottom) and trace element variation profile (top) show higher contents of Fe, Ti, Be, Ga, Mn, Li and V near both rims and mostly levelling off below detection limits (bdl) in the colourless inner area (solid dots mark where the values of bdl are used for plotting). Ti apparently diffused into the stone more deeply (spots 1-5 and 37-41) than most of other elements including Fe, in particular. Moreover, the penetration depth of Fe is approximately equal to the thickness of the blue colour rim. *Photo & graph by S. Promwongnan*

LA-ICP-MS在藍色擴散處理合成藍寶石樣品（底部）和微量元素變化曲線（頂部）的薄片上進行邊到邊 41 - 橫向分析，顯示出更高的Fe、Ti、Ga、Mn、Li和V含量在兩個邊緣附近的，並且在無色內部區域中大為減低至低於檢測極限（bdl）（實心點標記bdl的值用於繪圖）。 Ti顯然比大多數其他元素（尤其是Fe）更深地擴散到寶石中（1-5和37-41）。此外，Fe的穿透深度大致與藍色邊緣的厚度相約。

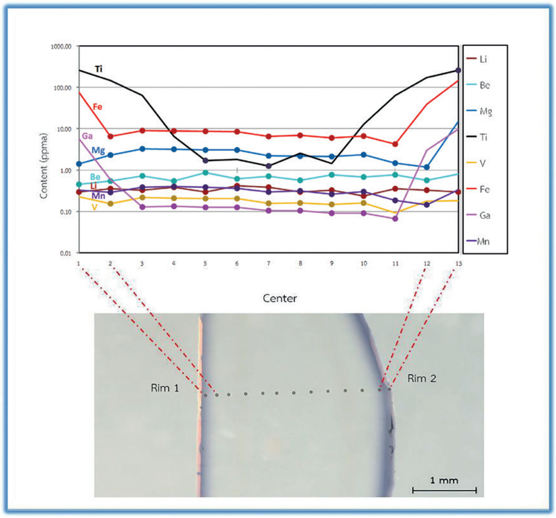


Fig. 9 Edge-to-edge-13-spots-traverse analysis by LA-ICP-MS on the thin slice of a blue diffused synthetic sapphire (bottom) and trace element variation profile (top) show higher contents of Ti, Fe, Ga near both rims and mostly levelling off bdl in the colourless inner area (solid dots mark where the values of bdl are used for plotting). Other trace elements, namely, Be, Mg, Mn, Li and V are mostly bdl. Ti apparently diffused into the stone more deeply (spots 1-4 and 10-13) than Fe and Ga did. Again, the penetration depth of Fe roughly matches the thickness of the blue colour rim. *Photo & graph by S. Promwongnan*

通過LA-ICP-MS在藍色擴散處理合成藍寶石（底部）和微量元素變化曲線（頂部）的薄片上進行邊對邊13 - 橫向分析，顯示兩者附近的Ti、Fe、Ga含量比在無色內部區域中的邊緣和低至檢測極限(bdl) 為高（實心點標記bdl的值用於繪圖）。其他微量元素，即Be、Mg、Mn、Li和V主要是在bdl。 Ti顯然比Fe和Ga更深地擴散到樣品中（1-4和10-13）。同樣，Fe的穿透深度大致與藍色邊緣的厚度相約。

of two blue diffused synthetic sapphire samples (Figs. 8&9). The trace element profiles of both slices similarly reveal very high Ti and Fe contents at both rims and their contents level off in the colourless inner areas. Not only Ti and Fe but also Be, Ga, Mn, Li and V were found to have infiltrated into the surface of the colourless synthetic sapphire hosts. In contrast, the colourless inner areas contain insignificant amounts of all trace elements (mostly below detection limits), which are a good confirmation of its synthetic origin. As also seen from both profiles, Ti can penetrate the stones much more deeply than most other trace elements, surprisingly including Fe and even Be (which is very small in atomic size). It is noteworthy that the thicknesses of the blue colour rims match reasonably well with the penetration depths of Fe (rather than Ti) on the rims of both these two stones. Beryllium was also detected on the surfaces of nearly all the diffused synthetic samples by LIBS.

Blue diffused natural sapphire: Edge-to-edge transverse analyses by LA-ICP-MS across the surface of the thin slice of two blue-diffused natural sapphire samples (Figs. 10&11) clearly show significantly high contents of Ti, Be and Li on the rims and at the healed fracture but low in the colourless core areas. In contrast, the contents of Fe, B, Mg, Cr, V and Ga are constant across the traverse profiles. Furthermore, the high contents of Fe, Mg and Ga throughout the section profiles are a good confirmation of the stone's natural origin. The profile also reveals that both Ti, Be and Li infiltrated the stone's surfaces in which Ti, surprisingly, penetrated more deeply than Be & Li. Moreover, the penetration depths of Ti (rather than Fe as in the case of the synthetics) correspond quite well with the thicknesses of the blue colour rims on both sides of the stones.

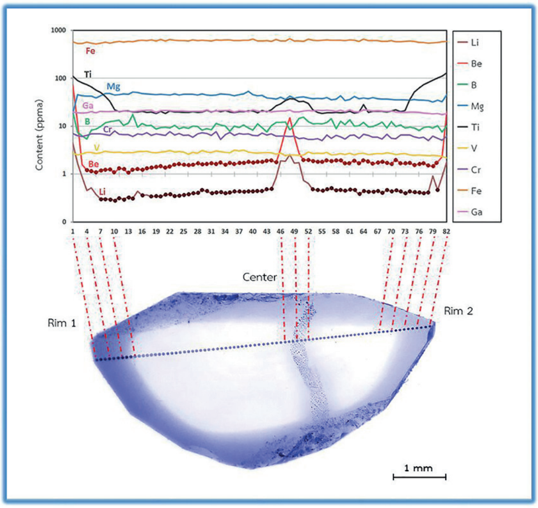


Fig. 10 Edge-to-edge-82-spots-traverse analysis by LA-ICP-MS on the thin slice of a blue diffused natural sapphire (bottom) and trace element variation profile (top) show high contents of Ti, Be and Li near both rims and at the healed fissure (blue in the middle right of the slice at spots 46-52) and level off in the colourless core area (solid dots mark where the values of bdl are used for plotting). Ti apparently diffused into the stone more deeply (spots 1- 9 and 74-82) than Be and Li did (spots 1-2 and 81-82). Moreover, the penetration depth of Ti is approximately equal to the thickness of the blue colour rim. Other trace elements such as Fe, Mg, V, Cr, B and Ga are relatively constant throughout the profile. *Photo by T. Sripoonjan & graph by S. Promwongnan.*

通過LA-ICP-MS在藍色擴散處理天然藍寶石（底部）和微量元素變化曲線（頂部）的薄片上進行邊對邊 - 82 - 橫向分析顯示高含量的Ti、Be和Li在兩個邊緣和癒合的裂縫（在46-52處切片的中間右側為藍色）及在無色核心區域中處於低水平（圖中實心點標記的bdl值）。Ti顯然比Be和Li更深入地擴散到樣本中央（1-9和74-82）（1-2和81-82）。而且Ti的穿透深度約等於藍色邊緣的厚度。其他微量元素如Fe、Mg、V、Cr、B和Ga在整個檢測中相對恆定。

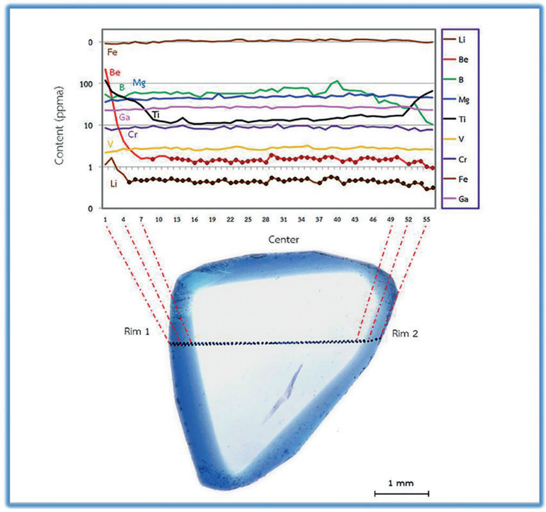


Fig. 11 Edge-to-edge-55-spots-traverse analysis by LA-ICP-MS on the thin slice of a blue diffused natural sapphire (bottom) and trace element variation profile (top) show high contents of Ti near both rims and Be and Li near left rim, and level off in the colourless core area (solid dots mark where the values of bdl are used for plotting). Ti apparently diffused into the stone more deeply (spots 1-8 and 52-55) than Be and Li did (spots 1-4). Again, the penetration depth of Ti roughly matches the thickness of the blue colour rim. Other trace elements such as Fe, Mg, V, Cr, B and Ga are relatively constant throughout the profile. *Photo by T. Sripoonjan & graph by S. Promwongnan.*

通過LA-ICP-MS在藍色擴散處理天然藍寶石（底部）和微量元素變化曲線（頂部）的薄片上進行邊到邊55 - 橫向分析，顯示在兩個邊緣含高量Ti，而左邊緣附近含高量的Be和Li，而在無色核心區域則處於低水平（圖中實心點標記的bdl值）。 Ti顯然比Be和Li更深入地擴散到樣本中央（1-8和52-55）（1-4）。同樣，Ti的穿透深度大致與藍色邊緣的厚度相約。其他微量元素如Fe、Mg、V、Cr、B和Ga在整個檢測中相對恆定。

Table 1 Summary of the properties of diffusion-treated synthetic and natural blue sapphires
擴散處理的合成和天然藍色藍寶石的性質

Properties	Diffusion-Treated Synthetic Blue Sapphires	Diffusion-Treated Natural Blue Sapphires
RI, SG	Normal (~1.760-1.770, 3.96-3.98)	Normal (~1.762-1.771, 3.91-4.07)
Pleochroism	Greenish blue to purplish blue	Ditto
Fluorescence	**SWUV:** strongly uneven chalky blue **LWUV:** inert	**SWUV:** inert, slightly chalky blue along facet junctions **LWUV:** inert to strongly orange-red
"Spiders' web effect"	Clearly visible, Stones mostly without fracture and cavity	Vague, Also blue colour concentration along fractures and cavities
Inclusions	Curved bands of minute particles or gas bubbles	Tension discs, altered solid inclusions and altered fingerprints
Plato lines	Yes or No	No
Colour Rim Thickness	Relatively Thin (~0.15-0.20 mm)	Relatively Thick (~0.5-1.1 mm)
UV-Vis-NIR	No Fe^{3+}-related absorption peaks	Some Fe^{3+}-related absorption peaks
EDXRF	Very Low Ga (<0.01 wt.% Ga_2O_3) High Ti (0.19-0.29 wt.% TiO_2) Moderate Fe (0.07-0.20 wt.% Fe_2O_3)	Significant Ga (0.01-0.02 wt.% Ga_2O_3) High Ti (0.05-0.21 wt.% TiO_2) Moderate Fe (0.05-0.41 wt.% Fe_2O_3)
LA-ICP-MS	Diffusion of Ti, Fe, Be, Ga, Mn and V. The penetration depth of Fe is equal to and controls the thickness of the blue colour rim	Diffusion of Ti, Be and Li, The penetration depth of Ti coincides with and controls the thickness of the blue colour rim

Discussions and Conclusions

Based on these findings (see the summary in Table 1), it can be concluded that the appearance of the "spiders' web effect" in immersion and rather high Ti contents on the sample surfaces still provide diagnostic evidence to confirm that all the test stones had been subjected to a surface Ti-diffusion treatment. However, to differentiate further as to whether each of those diffused stones has a synthetic or natural origin, additional evidence is necessary. The important characteristics that support the synthetic nature of a starting stone are; the chalky blue fluorescence to SWUV radiation (also in DiamondView™), the presence of curved bands of minute particles or gas bubbles under a microscope, very low Ga contents (by both EDXRF and LA-ICP-MS) and no Fe^{3+}-related absorption peaks on the UV-Vis spectra. However, the presence of minute particles alone (sometimes rather difficult to identify whether they are gas bubbles or pinpoint natural inclusions) and the lack of Plato lines could mistakenly suggest that the stones are of a natural origin. In contrast, the diagnostic features that indicate a natural starting stone are: the presence of tension discs, altered solid inclusions and altered fingerprints plus colour concentration along healed fractures seen under a microscope (synthetic stones usually lack fractures unlike natural ones), significant Ga contents (by both EDXRF and LA-ICP-MS techniques) and some Fe^{3+}-related absorption peaks on the UV-Vis spectra.

Even though both the synthetic and natural blue diffused sapphires show the "spiders' web effect" in immersion, the effect in the natural stone is much less pronounced than in the synthetic ones due to the difference of the thickness of the blue colour rim. In fact, the thickness of blue colour rim of the diffused natural stones (i.e., ~0.5-1.1 mm thick) appears to be much thicker than that of the diffused synthetic ones (i.e., ~0.15-0.2 mm). When re-polishing occurs after treatment from a thinner blue colour rim, the "spiders' web effect" of the synthetic stones becomes more visible.

Moreover, the difference of the thickness of the blue colour rim between the natural and synthetic stones can be explained by the fact that the penetration depth of Ti controls the colour rim thickness of the natural stones, whereas the infiltration depth of Fe controls that of the synthetic ones. For the diffused natural sapphire, the starting stones usually have sufficient Fe in the crystal lattice (see the Fe profiles in Figs. 10&11) to create a Fe^{2+}/Ti^{4+} IVCT mechanism causing blue colouration when enough Ti is introduced into the stones from an external source. As such, the infiltration depth of Ti determines the thickness of the blue colour rim in these natural stones. However, for the diffused synthetic sapphire, the starting colourless stones do not usually have enough of either Fe or Ti in the first place to create the Fe^{2+}/Ti^{4+} IVCT or the blue colouration. Hence, the synthetic starting stones required both Fe and Ti to be diffused into the stone's surface from external sources. As shown in the Fe and Ti profiles of the synthetic stones in Figs. 10 & 11, it appears, surprisingly, that the effective penetration depth of Ti into the stone's surface is much deeper than that of Fe. Thus, the penetration depth of Fe dictated the thickness of the blue colour rim in these synthetic stones.

It is noteworthy in the profiles in Figs. 8-11 that Ti diffused into both synthetic and natural stones much more deeply than most other trace elements, surprisingly, even Be, which is quite unusual. Let's consider the multi-element diffusion of the synthetic blue sapphires. Did the heat-treaters intentionally diffuse multi-trace elements into the synthetic stones [McClure (2013) also reported on the diffusion of Be, Ti, Fe, V, Ga; and Sun et al. (2017) on that of Be, Mg, Ti, Fe, Ga and the presence of Mo], believing that Be could help promote the diffusion of Ti and Fe into sapphire lattices and create a deeper blue colouration as well as Ga, Mn, V, Mg to make the stone's chemical composition similar to a natural stone? If so, we should observe a much deeper penetration depth of Be into the stones relative to Ti and other trace elements as it is small in size and can be diffused almost freely into the sapphire's lattice (see Emmett at et al., 2017). However, this is not really the case. Hence, one probable explanation for the diffusion of Be, Ga, Mn, Li, V, Mg, other than Ti and Fe, into the surface of the blue-diffused synthetic sapphires is that they could have been contaminants from a reused crucible and/or furnace during the high temperature treatment.

In the case of multi-element diffusion of natural blue sapphires, the presence of Be and Li, other than Ti, in the diffusion-treated stones [Dutoit (2009) also reported on the diffusion of Ti and Be] could have been remnants from the starting stones that had previously been un-successfully treated by the Be-diffusion process (pers. comm.). As such, Be and Li could have been diffused freely out of the stone instead of diffusing-in, which could explain such observed trace element profiles.

Furthermore, some questions related to the diffusion-treated synthetic blue sapphire may need to be answered. For instance: Why did the heat-treaters use synthetic colourless sapphires diffused to produce blue while there were plenty of lab-grown blue sapphires available in the market? Why not use synthetic blue sapphires for cutting in the first place? Because the Verneuil grown blue sapphire has blue colour only on the rim while the inner core is still colourless. Thus this makes it rather difficult to control the size and the homogeneity of colour of the cut stones. Whereas, by using a rather homogenous and cheap synthetic colourless starting material for diffusion treatment, the heat-treaters had better control over the colour, quality, consistency and yield of the products (pers. comm.). Moreover, this way, the treaters were also able to produce large stones due to the vast availability of synthetic colourless material as compared to that of natural starting stones.

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