Figure 1: This 9.1 ct sapphire from the Ambatondrazaka area of Madagascar shows vivid pink colouration (far left). After exposure to a long-wave UV lamp for a few minutes, the stone changed to a vivid pinkish orange typical of that shown by padparadscha sapphires (centre). With fade testing, the colour shifted back to the chromium-related pink colour (below). Composite photo by Vito Lanzafame, SSEF.

Unstable Colouration of Padparadscha-like Sapphires

Michael S. Krzemnicki, Alexander Klumb and Judith Braun

ABSTRACT: After the October 2016 discovery of a new gem deposit at Bemainty near Ambatondrazaka, Madagascar, a number of sapphires with padparadscha-like colour entered the trade. However, most of these stones were found to have unstable colour, which changes from pinkish orange to more-or-less pure pink after a few weeks in daylight. In this study, the authors investigate the colour stability of padparadscha-type sapphires of metamorphic origin—mainly those originating from Madagascar (Ambatondrazaka and Ilakaka) and Sri Lanka. The 48 samples could be separated into three groups after colour-stability testing: sapphires that did not show a noticeably different appearance (case A); sapphires with a slight-to-moderate colour difference within the padparadscha range (case B); and fancy-colour sapphires showing a distinct change in appearance that fell outside of the padparadscha range (case C). The last situation was especially common for the stones from Ambatondrazaka, thus revealing that careful colour-stability testing is mandatory for proper gemmological identification of any sapphire showing a yellow to orange colour component.

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In late 2016, a 9.1 ct stone was submitted to the Swiss Gemmological Institute SSEF by a client as a padparadscha sapphire, a sought-after variety of corundum showing pinkish orange to orangey pink colour (cf. Crowningshield, 1983). After the routine analytical work was completed, it became evident that the stone was vivid pink instead of showing a padparadscha appearance. This colour difference led us to perform further research on the causes and stability of padparadscha colouration.

Our examination revealed that the colour of the stone changed considerably to a vivid pinkish orange by simply exposing it to a long-wave UV lamp for a few minutes (Figure 1). The orange colour component, however, was not stable and slowly faded in the course of several days to weeks (or hours with colour-stability testing), as was later confirmed by the client who had submitted the stone as a padparadscha sapphire.

Having encountered a number of similar cases in the past few months (Krzemnicki, 2018), this article presents our findings on padparadscha-like sapphires with unstable colour, with special emphasis on such stones from a recently discovered deposit at Bemainty, near Ambatondrazaka, Madagascar.

PADPARADSCHA: DEFINITION, COLOUR CAUSES AND STABILITY

Padparadscha sapphires are generally described as exhibiting a pinkish orange to orangey pink colour of moderate to low saturation (Crowningshield, 1983; Notari, 1996; LMHC, 2018). Originally known from alluvial deposits in Sri Lanka, today this attractive variety of corundum is also mined in Tanzania (e.g. Tunduru; Johnson and Koivula, 1997) and Madagascar (e.g. Ilakaka; Milisenda et al., 2001), with additional production coming from a recently discovered deposit near Ambatondrazaka, which is also a source of exceptional blue sapphires of large sizes (Perkins and Pardieu, 2016; Krzemnicki, 2017; Pardieu et al., 2017).

From a gemmological viewpoint, padparadscha colour can be described as a subtle and variable mixture of pink and orange, commonly resulting from the absorption of visible light by Cr^{3+} (main bands at 410 and 560 nm, responsible for the pink component) and one or more yellow to orange colour centres (Schmetzer et al., 1983, Nassau and Valente, 1987; Schmetzer and Schwarz, 2005; Hughes et al., 2017 and references therein) that are partly superposed by absorptions from Fe^{3+} at 385, 390 and 450 nm. As such, padparadscha sapphires can show variable absorption spectra. In terms of colour stability, it can further be assumed that the pink colour is stable, as it is only related to the concentration of Cr^{3+}. However, the stability of the yellow-to-orange colour component is more complex. It has been known for many years that yellow to orangey yellow hues induced by colour centres (formed naturally or by artificial irradiation) in corundum are not always stable (i.e. type 2 of Nassau and Valente, 1987), thus resulting in a yellow colour that fades slowly upon exposure to daylight (Schiffmann, 1981; Nassau and Valente, 1987; Hughes et al., 2017). Additional cases of colour centres that are unstable in daylight are not uncommon in mineralogy, as seen, for example, in some amethyst (Hatipoğlu et al., 2011), and also quite dramatically in Maxixe-type beryl (Nassau et al., 1976) and in hackmanite—a rare sulphur-bearing variety of sodalite that becomes stunningly purple after brief exposure to UV radiation before fading (rather quickly) to greyish white in daylight (Medved, 1954; Kondo and Beaton, 2009).

The effect of fading in daylight and reactivation by UV radiation is known in the scientific literature as *reversible photochromism* or *tenebrescence* (Medved, 1954; Kirk, 1955). Interestingly, this effect has been reported previously for synthetic corundum (Hughes et al., 2017) and for a light blue heat-treated sapphire (Gaievskyi et al., 2014), and has also been observed in SSEF's in-house colour-stability studies on a small number of unheated yellow sapphires from Sri Lanka (cf. Hughes, 1997). In all of these cases, the stones consistently gained slight brownish yellow to marked yellow hues after UV exposure, which under normal lighting conditions faded out over a period of several days (or hours with fade testing; see below for parameters). So far, none of the tenebrescent unheated yellow sapphires we have seen changed completely to colourless after fade testing, but instead they showed a noticeable reduction in their yellow colour saturation, which suggests they were coloured by a combination of stable (in terms of exposure to daylight) and unstable yellow colour centres.

MATERIALS AND METHODS

Over a period of several months, the authors analysed 48 sapphires of metamorphic origin that showed padparadscha-like colour (see Table I). All of them were unheated except for one sample from Ambatondrazaka. Apart from microscopic observation and routine gemmological testing—as well as chemical analysis, Fourier-transform infrared (FTIR) spectroscopy and Raman spectroscopy—all studied samples were investigated using SSEF's standardised colour-stability testing protocol. Their

Table I: Sapphires of padparadscha-like colour investigated for this study.

Origin*	No. samples	Weight range (ct)	No. samples with a distinct change of colour
Sri Lanka	12	1.14–20.2	1 (8.3%)
Madagascar (Ilakaka)	17	0.88–3.07	3 (17.6%)
Madagascar (Ambaton-drazaka)	11	4.18–30.4	9 (81.8%)
Unknown origin	8	1.17–12.4	1 (12.5%)

* The indicated origin is based on a combination of analytical data and microscopic observation.

colour was observed in three stages: initially just after submission to the laboratory (stage 1), after fade testing (stage 2) and finally after exposure to a long-wave UV lamp (stage 3). When a pink stone was submitted, stages 2 and 3 were swapped, thus performing the long-wave UV exposure and then (if it changed to a padparadscha-like colour) subsequently pursuing the fade testing.

For fade testing, we followed a protocol used at SSEF for many years to examine the colour stability of gems (K. Schmetzer, pers. comm., 2009), mostly for yellow sapphires. The stone is placed in a reflecting bowl made of aluminium foil and exposed for three hours to a daylight-equivalent light source (100 W halogen Fiberoptic Heim LQ 1100). (During this process, the stone is slightly heated by the light exposure, but never above approximately 70°C.) For UV activation testing, the stone is placed in a black box for 10 minutes directly on the glass plate of a long-wave UV lamp (6 W Vilber Lourmat VL-6.LC).

After each stage, visual colour grading was performed by at least two gemmologists using the padparadscha sapphire chart developed by Notari (1996) and Munsell colour charts under daylight-equivalent illumination. The stones were also photo-documented in a white light box (cube of approximately 1 m^2 with a colour temperature of 5,500 K) using a Nikon F7 camera under standardised settings and lighting conditions. In addition, polarised absorption spectra in the 300–800 nm range were collected (ordinary ray) after each stage using either a Cary 500 ultraviolet-visible–near infrared (UV-Vis-NIR) spectrophotometer or SSEF's portable UV-Vis spectrometer manufactured by SattGems SA, a subsidiary of SSEF.

RESULTS AND DISCUSSION

Properties of the Ambatondrazaka Samples

Interestingly, most of the sapphires with unstable padparadscha-like colour originated from the Ambatondrazaka area of Madagascar (see below). Based on our observations, these sapphires commonly contain very few inclusions, and they are often characterised by distinct purple colour zoning (Figure 2). Also typical are fine 'milky' lamellae with a spacing of approximately 100 μm (Figure 3). Similar zoning features have been seen occasionally in blue sapphires from this deposit (e.g. Krzemnicki, 2017). In addition, we observed small zones of dispersed (presumably exsolved) particles (Figure 4) resembling those seen in yellow and padparadscha sapphires from Sri Lanka (cf. Hughes et al., 2017, p. 603). These particle zones were, however, less pronounced and less common than in stones from Sri Lanka.

A few of the studied samples from Ambatondrazaka contained very tiny inclusions of slightly rounded prismatic shape that were identified by Raman spectroscopy as zircon. They showed broad Raman peaks resulting

Figure 2: This exceptional 30 ct fancy-colour sapphire from Ambatondrazaka displays a distinct purplish colour zone, and therefore would not be termed 'padparadscha'. Composite photo by Luc Phan, SSEF.

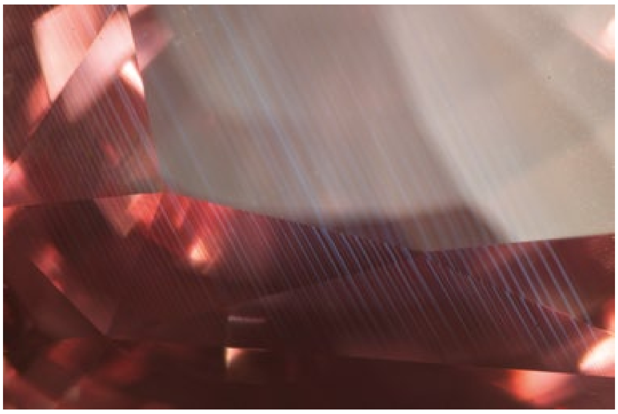

Figure 3: Fine 'milky' lamellae are seen in this fancy-colour sapphire from Ambatondrazaka. Photomicrograph by M. S. Krzemnicki; magnified 30×.

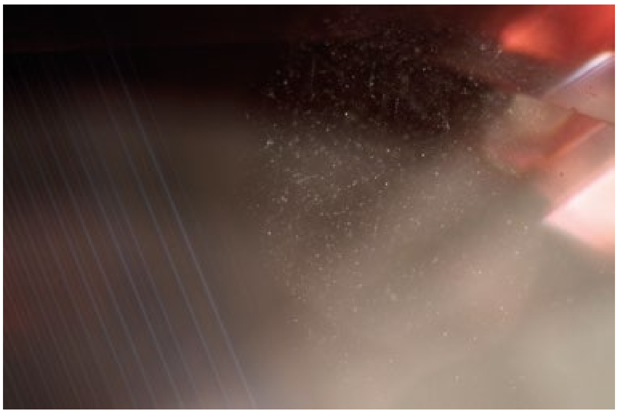

Figure 4: A group of tiny particles are present in a fancy-colour sapphire from Ambatondrazaka. See also the 'milky' lamellar zoning on the left side of the image. Photomicrograph by M. S. Krzemnicki; magnified 50×.

from metamictisation (Figure 5), a feature also characteristic for Kashmir-like blue sapphires from the same deposit (Krzemnicki, 2017).

Colour-Stability Testing

The samples could be separated into three groups after fade testing: sapphires with no notable difference in appearance (case A); sapphires that showed a slight-to-moderate shift of colour within the padparadscha colour range (case B); and fancy-colour sapphires with unstable colour that distinctly changed from padparadscha-like pinkish orange to pink (case C). These groups mostly apply to unheated sapphires of padparadscha-like colours, although they may also be encountered in some heated stones of similar colours. Interestingly, most of the 'case C' stones were found to originate from the Bemainty deposit near Ambatondrazaka in Madagascar, while fewer of this type were noted from the more 'classic' sources of Ilakaka and Sri Lanka.

Case A. Colour-Stable Samples: Nine of the 48 study samples showed no noticeable change in appearance after fade testing (four from Sri Lanka, two from Ilakaka and three of unknown origin). Their colour ranged from 'classic' padparadscha (see Figure 6, inset photos) to orangey pink (including vivid orangey to reddish pink

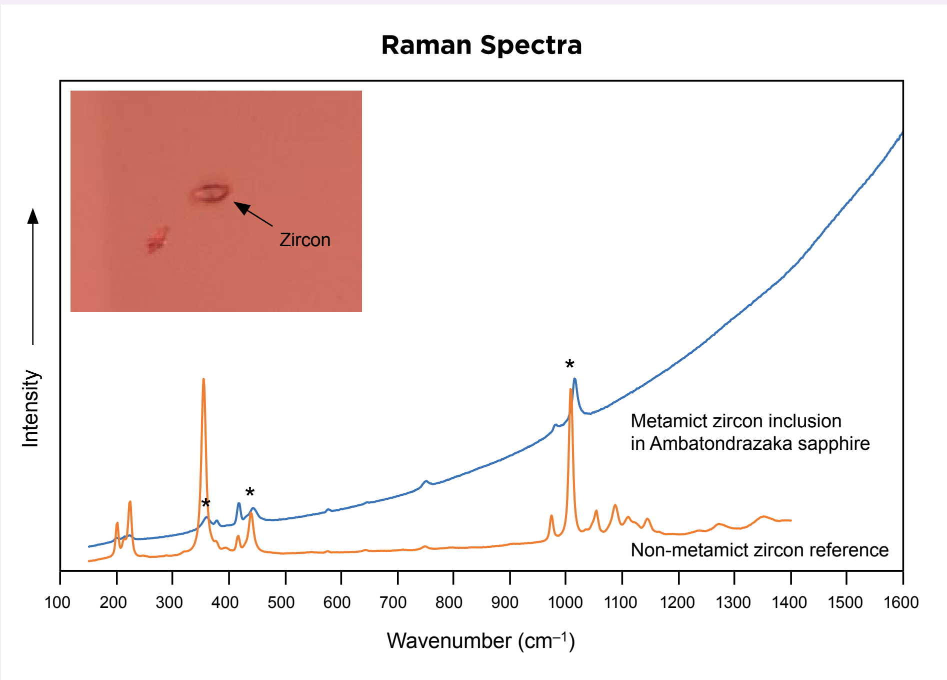

Figure 5: The Raman spectrum of a zircon inclusion in a padparadscha-like sapphire from Ambatondrazaka reveals its metamict nature, compared to a reference spectrum of a non-metamict zircon inclusion (together with some additional tiny Raman peaks). Asterisks mark the main Raman peaks of zircon shown by the inclusion. Inset photomicrograph by M. S. Krzemnicki; magnified 50×.

that was strongly zoned, and thus out of the padparadscha colour range as defined by SSEF and LMHC; e.g. Figure 7). Case A stones also showed only very minor differences in their absorption spectra before and after fade testing (again, see Figures 6 and 7). Their spectra revealed a general and more-or-less steady increase in absorption towards the ultraviolet region due to stable yellow colour centres, overprinted by broad Cr^{3+} bands and more-or-less prominent Fe^{3+} absorption peaks.

Case B. Samples with Somewhat Unstable Colour: A slight to moderate shift of colour was shown by 25 of the studied samples after fade testing (and/or long-wave UV exposure). Their shift in appearance mostly affected the intensity of the orange hue (Figure 8), but not enough to disqualify them from the padparadscha colour range (Notari, 1996; LMHC, 2018). Sapphires of this group mostly originated from Sri Lanka (seven samples) and Ilakaka (12 samples); six were of unknown origin.

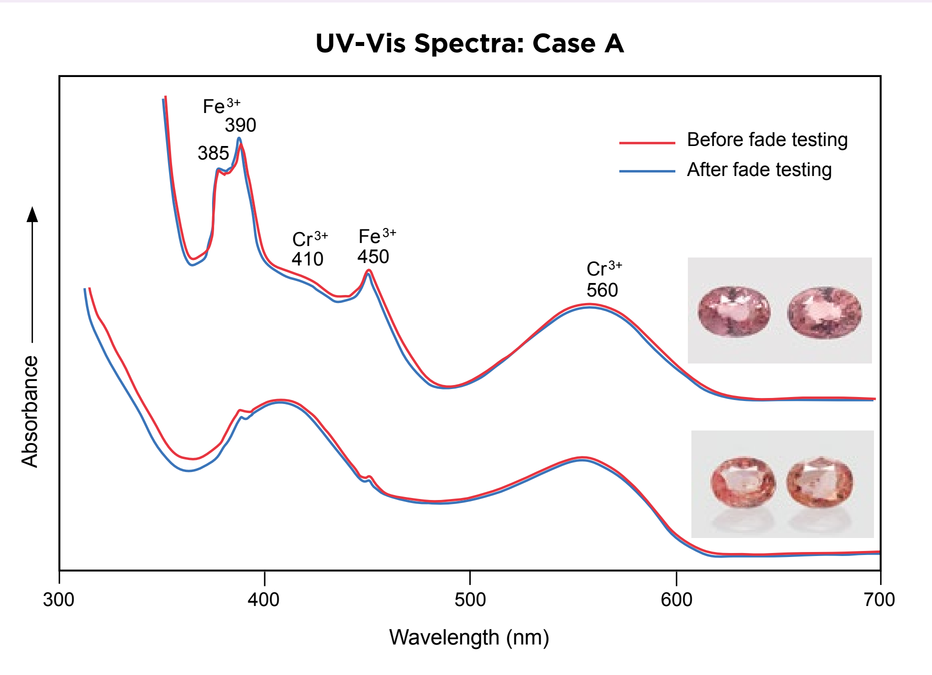

Figure 6: UV-Vis absorption spectra (ordinary ray) are shown for two padparadscha sapphires that do not display any noticeable difference in colour before and after fade testing (case A). The stones differ mainly in the intensity of their Fe^{3+}-related absorptions. The sapphires weigh 5.42 ct (top) and 5.05 ct (bottom), and the images show the stones before (left) and after (right) fade testing. Inset photos by M. S. Krzemnicki.

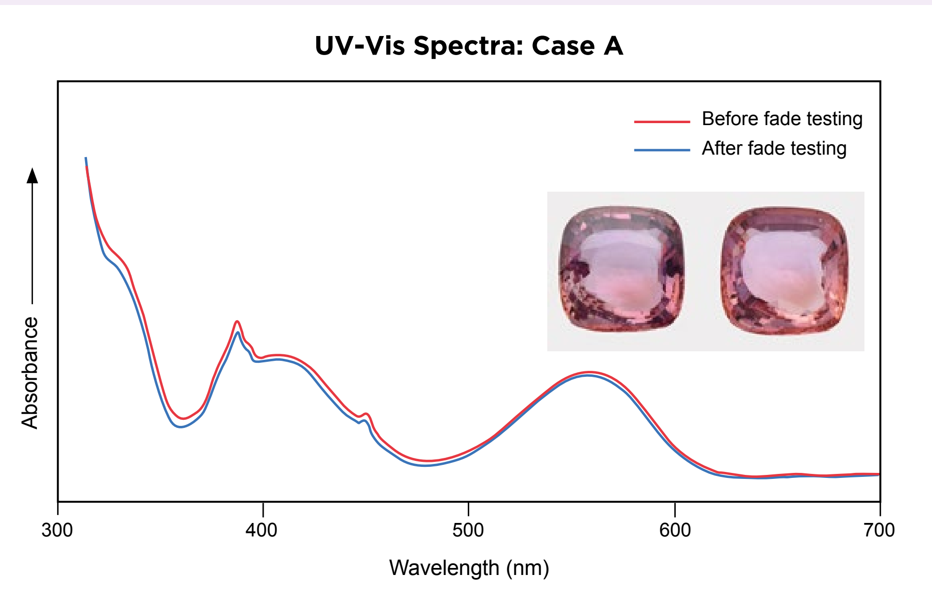

Figure 7: The nearly identical absorption spectra of a 12.02 ct sapphire with a distinct purplish pink colour zone (thus disqualifying it as padparadscha; see LMHC, 2018) are consistent with the lack of a noticeable colour difference before and after fade testing (i.e. case A). Inset photos by M. S. Krzemnicki.

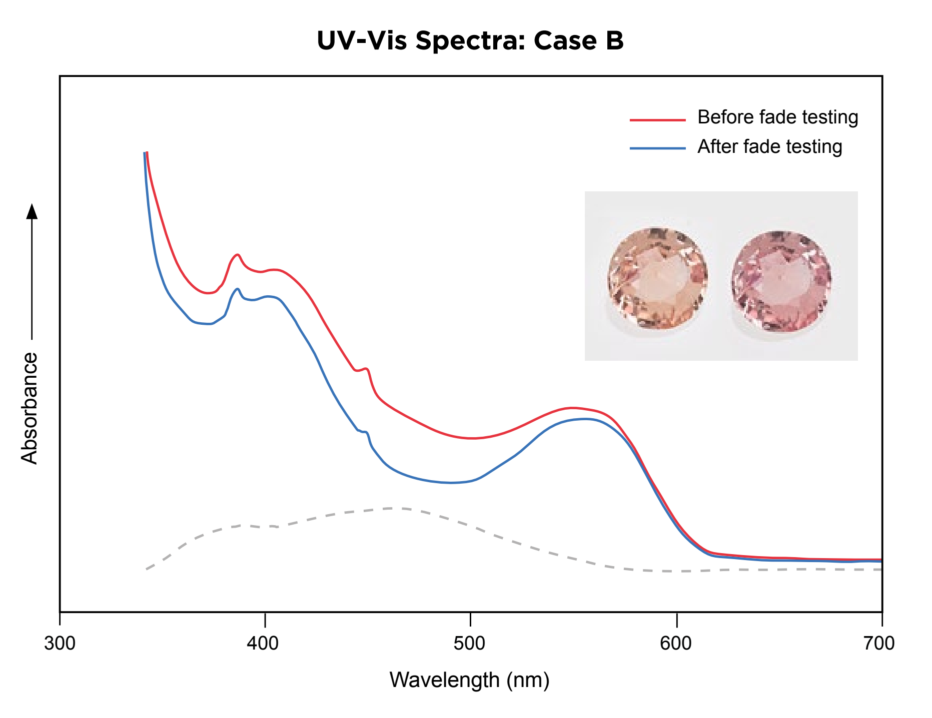

Figure 8: A 1.05 ct sapphire with a moderate change of colour before (left) and after (right) fade testing—but within the range of padparadscha; i.e. case B—yielded these absorption spectra. The dashed grey line shows the result of subtracting one trace from the other, representing the spectral contribution from the unstable orange or yellow colour centre. Inset photos by M. S. Krzemnicki.

Their absorption spectra before and after fade testing were characterised by a notable change due to variations in the strength of an unstable orange or yellow colour centre superposed on an existing stable yellow colour centre (possibly a trapped hole involving Mg^{2+} associated with an Fe^{3+} chromophore; see Emmett et al., 2017). The presence of this unstable orange or yellow colour centre is visualised by the grey dashed line in Figure 8, which represents a subtraction of the absorption spectra before and after fade testing.

Case C. Samples with Distinctly Unstable Colour: Most interestingly, 14 of the stones showed a distinct change in appearance, with a padparadscha-like orange-pink colour seen only after being activated by long-wave UV radiation (unstable colour) and a more-or-less pure pink hue after fade testing. As shown in Table I, most of the case C sapphires were from Ambatondrazaka (nine samples), compared to those from Ilakaka (three), from Sri Lanka (one) and of unknown origin (one).

Similar to the stones in case B, the absorption spectra of the case C samples were characterised by the presence of an unstable colour centre (represented by the grey dashed line in Figures 9 and 10) that pushed their colour towards pinkish orange when activated by UV radiation. However, in contrast to the abovementioned case B, these fancy-colour sapphires completely lacked or had only a very weak stable yellow colour centre, as can be seen by their lack of absorption, and thus a distinct transmission window, at ~480 nm after fade testing (Figure 11). The contrasting colour behaviour of case B can be explained by the presence of a stable yellow colour centre that is discernible by the greater absorption in the transmission window region at ~480 nm and therefore is less affected by fade testing (again, see Figure 11). This absence of a stable yellow colour centre in case C samples results in a more-or-less pure pink colour after fade testing. This 'stable' colour is thus distinctly out of the padparadscha colour range (Figure 12).

CONCLUSIONS

This study shows that metamorphic sapphires of padparadscha-like colour do not always have stable colouration, very similar to that of some yellow sapphires. Instead, they may show a tenebrescent behaviour in which the yellow/orange colour component is developed by long-wave UV exposure and is faded by exposure to daylight over time. While most of the studied samples from 'classic' sources in Sri Lanka and Ilakaka in Madagascar showed no change in appearance or a slight-to-moderate colour difference after colour-stability testing, sapphires from the recently discovered deposit near Ambatondrazaka in Madagascar often showed a distinct colour instability, shifting from pinkish orange (when 'activated' by a long-wave UV lamp) to pure pink

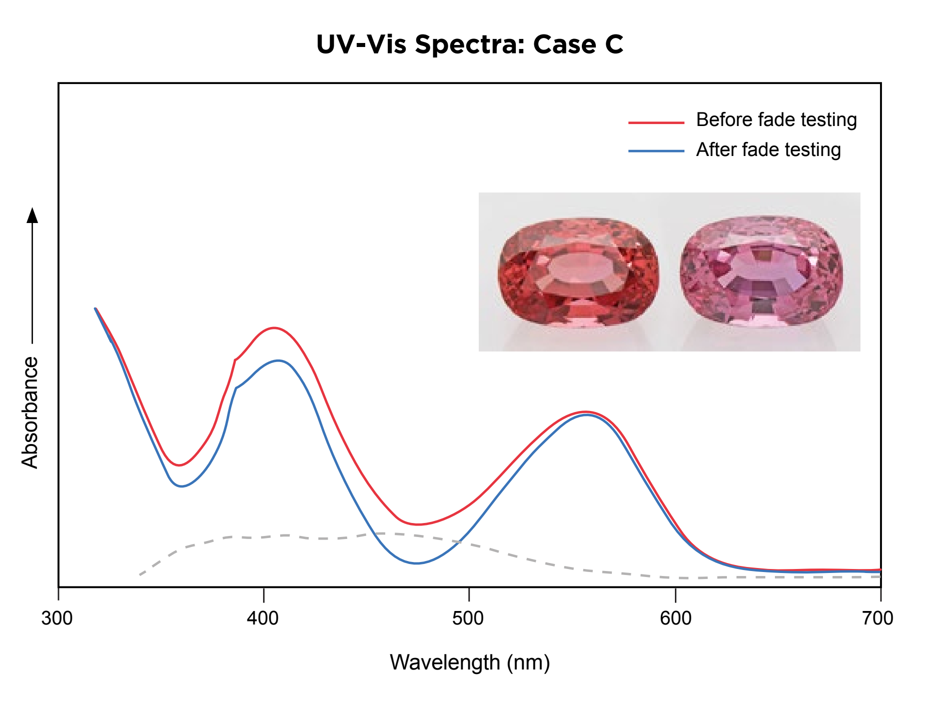

Figure 9: The 9.1 ct fancy-colour sapphire in Figure 1 displays a distinct difference in appearance before (left) and after (right) fade testing (i.e. case C), and yielded these absorption spectra. The dashed grey line representing subtraction of the two spectra shows the spectral contribution from the unstable orange or yellow colour centre. Conversely, there is no evidence of a stable yellow colour centre, which explains why the difference in appearance is so distinct. Inset photos by M. S. Krzemnicki.

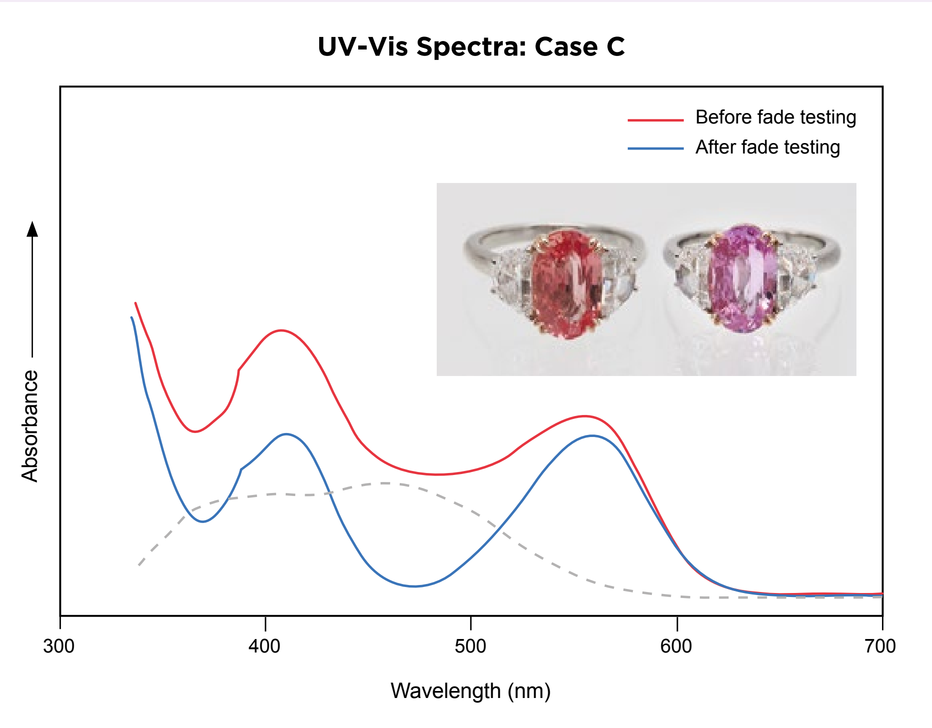

Figure 10: The absorption spectra of a ring-mounted fancy-colour sapphire (declared weight of 4.00 ct) show a distinct difference in appearance after fade testing (i.e. case C). The spectra demonstrate the contribution of an unstable orange or yellow colour centre (represented by the dashed grey line) that is even stronger than that in Figure 9. Inset photos by M. S. Krzemnicki.

after several weeks (or hours under fade-testing conditions) in daylight. Such stones that shift to a colour that is out of the padparadscha range should not be assigned the coveted varietal name 'padparadscha', which historically refers to pinkish orange to orangey pink stones that are colour-stable within this range (see LMHC, 2018).

The results of this study highlight the need to carefully test the colour stability of any corundum showing a yellow to orange colour component before an identification report is finalised.

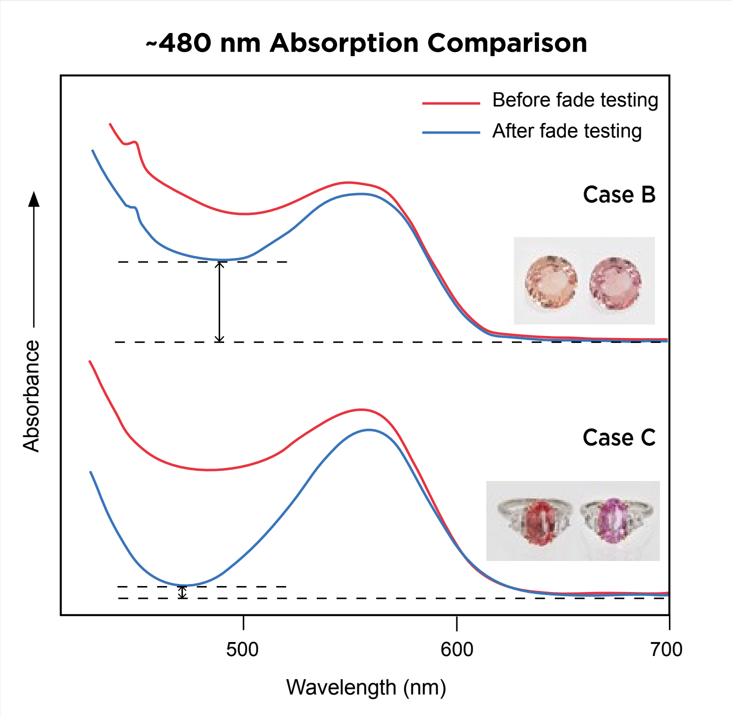

Figure 11: The main criteria that separate padparadscha sapphires with a slight to moderate shift in colour (case B) from fancy-colour sapphires with a distinct change in appearance (case C) after fade testing is not only the presence and strength of an unstable orange or yellow colour centre (see dashed grey lines in Figures 8–10), but mostly the prevalence of a stable yellow colour centre, which is visualised here by the large (top) or small (bottom) absorption step at ~480 nm before and after fade testing. The examples shown here are excerpted from Figures 8 and 10.

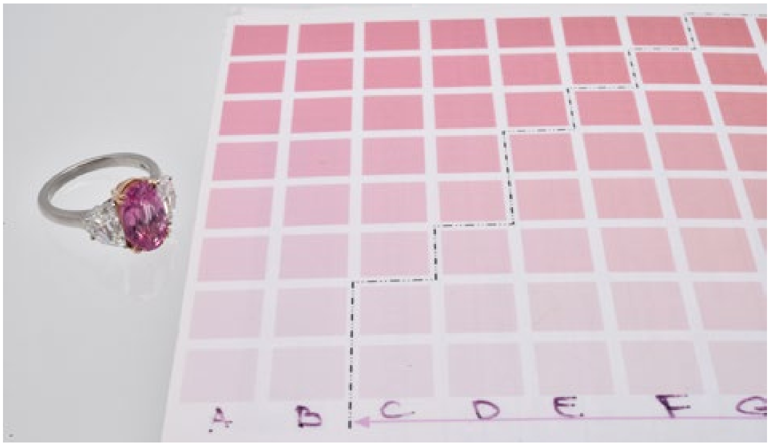

Figure 12: A fancy-colour sapphire ring (also seen in Figures 10 and 11) is shown next to a small portion of a chart proposed by Notari (1996) to represent padparadscha colour space (starting to the right of the dashed line). The pink colour of the sapphire shown here after fade testing falls outside of the padparadscha range. Photo by Luc Phan, SSEF.

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