

Argyle Violet Diamonds

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Figure 1. A collection of violet rough diamonds from Argyle showing their fragmented nature.

Introduction

Knowledge and understanding of violet diamonds from the Argyle diamond mine in Western Australia have taken second place behind the deposit's famous pinks. For much of the mine's life, the stones were referred to as blues. The colour grading system at Argyle assigned them as BL – short for blue – and sales marketing events included a 'Once in a Blue Moon' tender. However, the colour is more accurately described as violet and only in a few instances has an Argyle violet received a primary GIA colour description of blue. Even with this primary colour description, they are invariably accompanied by modifiers of 'grey' or 'greyish' and with 'deep' or 'dark' as additional descriptors. This violet-based colour has been almost uniquely assigned to Argyle diamonds, but in reality a small proportion (~5%) of those with a GIA violet colour are Type II and not from Argyle (Eaton Magaña *et al.*, 2018). For brevity, in this article this range of violet colours will be referred to merely as violet.

GIA noted the unusual colour soon after the Argyle mine started production and the first study of the gems was published in 1992 (Fritsch and Scarratt, 1992). This study revealed that the Argyle violets were characterised by very high levels of both nitrogen and hydrogen as revealed by infrared (IR) spectra, in contrast to conventional blue diamonds that owe their colour to boron in the absence of nitrogen. As a result, the Argyle 'blues' were often referred to in the trade as 'hydrogen blues' with an inference that the cause of colour was from the hydrogen. However, a study in 1998 (Noble *et al.*, 1998) suggested that the defect responsible for the colour was more likely related to nickel. Furthermore, among the Argyle bluish diamonds there have been rare instances of specimens that have relatively low levels of both nitrogen and hydrogen, and owe their colour to irradiation.

Delta Diamond Laboratory in Perth specialises in certifying pink and violet diamonds from Argyle and has been able to record the characteristics of over twenty polished violets ranging in size from 0.05 to 0.2cts.

Several articles in the gemmological literature have been written on Argyle's violet diamonds, the most notable being those in *Gems & Gemology* (Van der Bogert *et al.*, 2009; Eaton Magaña *et al.*, 2018). This article expands on the knowledge base of the Argyle violets by examining their optical characteristics as observed using fluorescence, visible absorption spectra, IR spectra, photoluminescence (PL) spectra and birefringence. These observations were recorded at room temperature with instruments made by Gemetrix except for the IR spectra that were recorded using a Bruker Alpha II FTIR spectrometer. IR spectral fitting was performed with Excel software constructed by the author.

Visual Characteristics

The size distribution of the violets from Argyle is skewed towards smaller sizes compared to other colours from the mine. The largest violet offered was 2.83ct (Rio Tinto, 2016). The smaller size may be on account of the observation that in the rough state the violets look fragmented, being products of larger crystals (Figure 1). The author has seen hundreds of rough violets during his many years working for Argyle Diamonds and has only seen one instance of a natural (octahedral) crystal habit.

Another notable visual characteristic of Argyle violets is that the colour is reasonably uniform throughout the bulk of the stone, with only subtle patchiness and no graining as is commonly seen with Argyle browns and pinks. The clarity of violets tends to be in the higher grades in notable contrast to the profile of clarities in other diamonds, especially those from the Argyle mine.

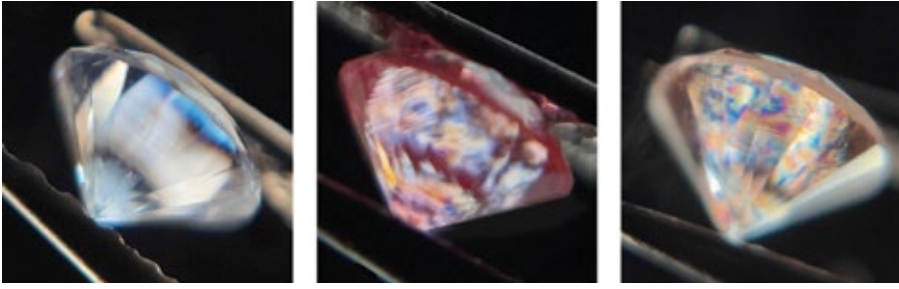


Figure 2. The birefringence pattern of violet diamonds (left) shows very low degrees of strain as seen in this 0.31ct greyish-blue specimen, in contrast to the typical patterns of pink (centre) and colourless (right) diamonds from the Argyle mine.

Birefringence

Using crossed polar filters, all the violet samples showed very low strain (Figure 2). Such a result is unexpected from a deposit that is characterised by diamonds that generally exhibit high levels of plastic deformation and strain producing the pinks and browns for which the deposit is noted. While these pinks and browns all show obvious strain, even Argyle's colourless diamonds show prominent strain, so the strain-free nature of violets is unique within the Argyle population.



Figure 3. A variety of violet colours spanning different saturations and balances of grey, violet and blue hues.

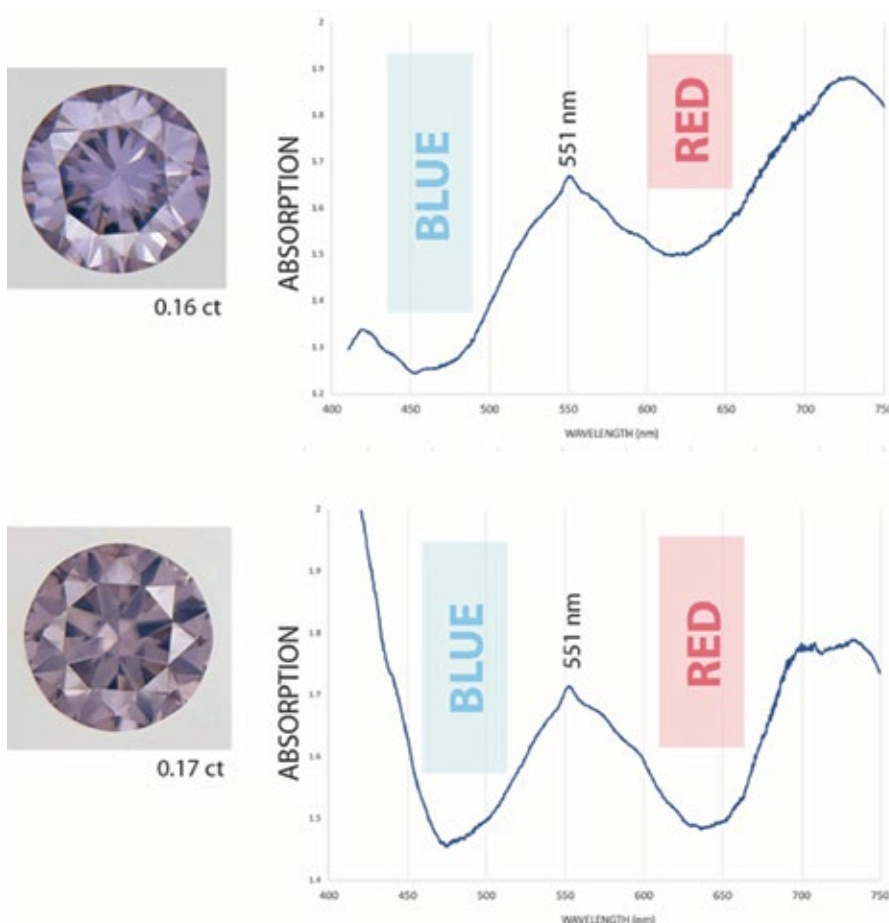


Figure 4. Typical absorption spectra of two fancy grey-violet diamonds with transparency windows in the blue and red regions. The upper spectrum has a relatively lower transparency in the red and so imparts a higher blue component to its appearance.

Visible Absorption

The range of violet hues spans different levels of grey and violet, from greyish-violet to violet-grey and with saturations from light to intense (Figure 3). The Argyle grading system assigned one of four colour grades – BL1, BL2, BL3 and BL3+ – based on the saturation of colour (BL3+ being the most saturated) without reference to the dominant hue, grey or violet. Such broad classifications are likely a result of the lower attention given to violets in the early days of the mine. Nowadays, these coloured diamonds sell for several hundred thousand dollars per carat.

A typical absorption spectrum is shown in Figure 4, with transmission in the blue and red regions flanked by absorptions in the ultraviolet (UV), green (centred at 540nm) and near-IR regions (centred at 740nm). A small but distinctive peak is also observed at 551nm, although in some instances it is subtle or absent (see Figure 7).

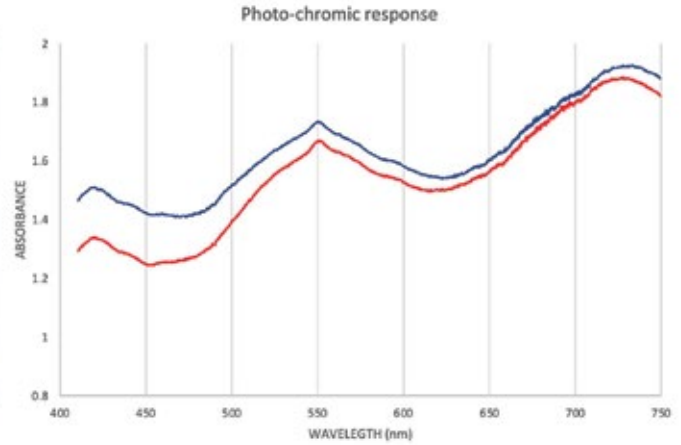


Figure 5. A 0.14ct Fancy Greyish-Violet diamond appears darker after illumination by SWUV light. The change is greater towards the blue end of the visible spectrum as seen in the before (red graph) and after (blue graph) absorption spectra of the diamond.

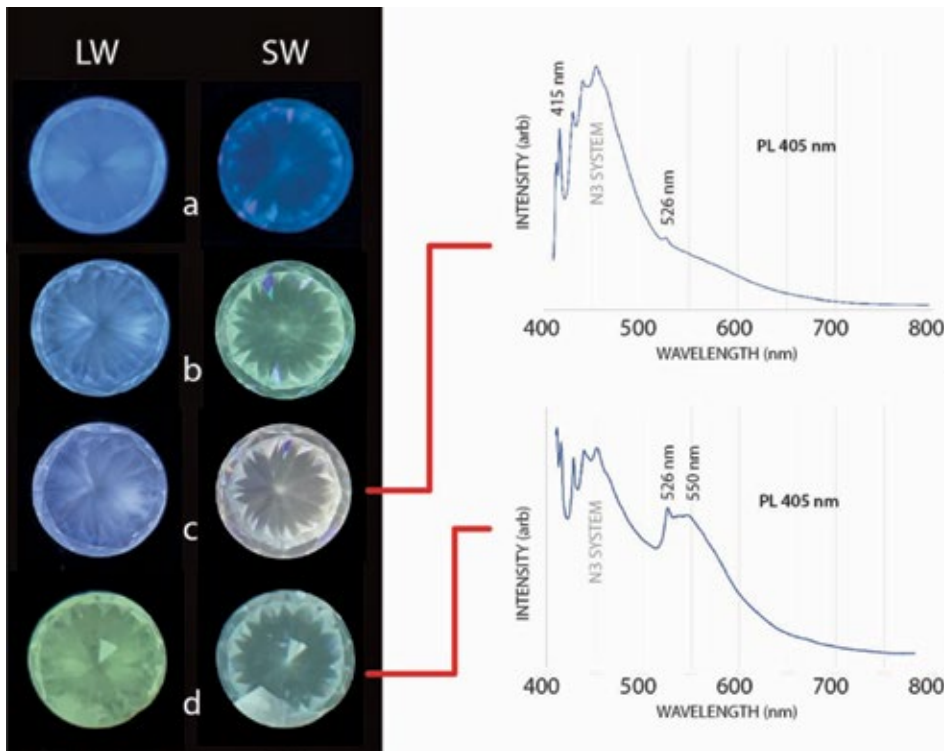
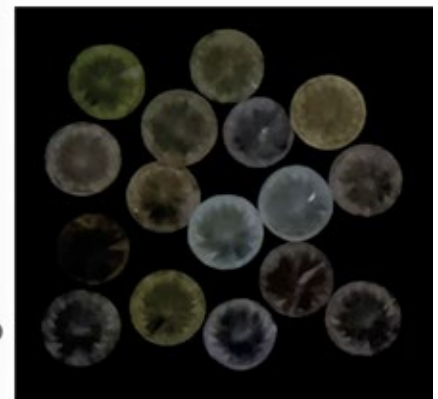


Figure 6. A selection of 0.1–0.2ct violet diamonds showing different fluorescence characteristics under LW and SW UV light (left). The PL spectrum of stone (d) from 405nm excitation shows a yellow band with a peak at 550nm, while most PL spectra of violets show a peak at 526nm. The right hand photo shows phosphorescence of some melee diamonds after exposure to SWUV.



Photochromism

Illuminating a violet diamond with 255nm short wave UV (SWUV) light results in a noticeable enhancement of the grey component from an increasing absorption towards UV wavelengths. Figure 5 shows the before and after absorption spectra from such illumination for a particular greyish-violet specimen and the corresponding spectral change. The colour could be restored by extended time in ambient light.

Luminescence and PL

The long wave UV (LWUV) fluorescence for the violet family is usually of a moderate blue hue typical for N3 centres, sometimes with a green or yellow undertone; however, under SWUV the colour varies between blue to bluish-green to white. Most commonly, the SWUV colour is bluish-green (Figure 6, stone b), but there is a variety of fluorescence reactions under LW and SWUV. In almost all specimens, orangey-yellow or white phosphorescence (Figure 6, right) lasting a few seconds was observed after SWUV illumination and in some instances after LWUV illumination.

Using a 405nm laser, the emission spectrum is dominated by the N3 system for those diamonds that fluoresce blue under LWUV, whereas the greenish emissions (as in Figure 6, stone d) correspond to an N3 band in combination with a yellow band peaking at 550nm and an additional prominent peak at 526nm. This peak is also present in the blue fluorescing samples, but in some instances the peak is absent. When the PL peak is absent, the 551nm absorption peak is also absent as seen in Figure 7 (right).

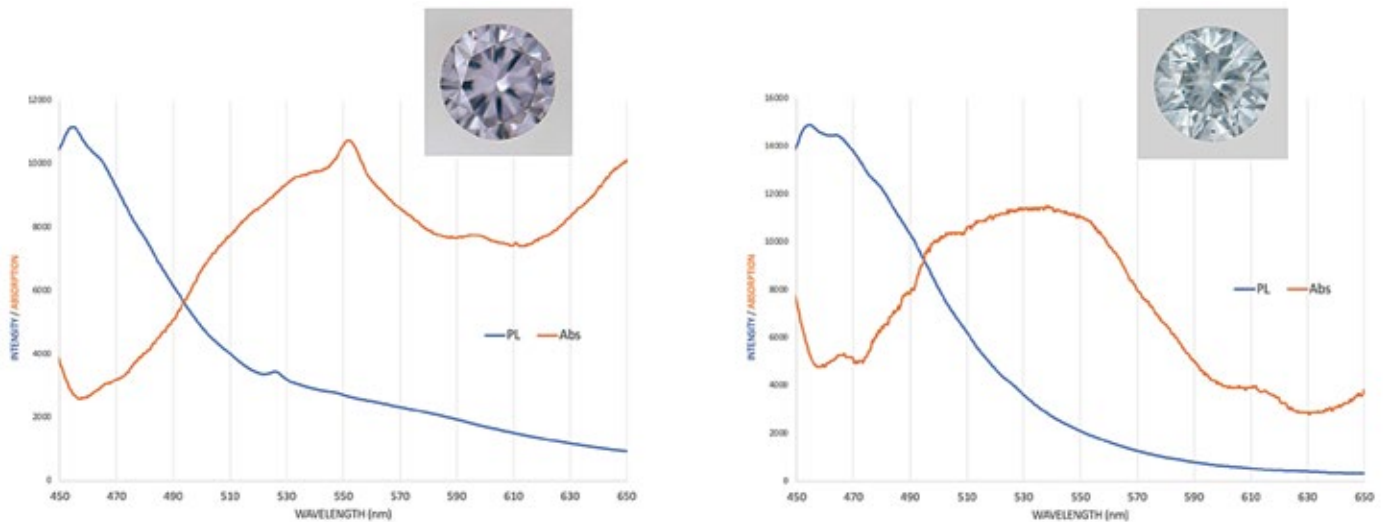


Figure 7. Examples of absorption and PL spectra that indicate a correlation between the 551nm absorption peak and the 526nm PL peak in the violet diamond (left) with the two peaks being absent in the bluish violet stone (right).

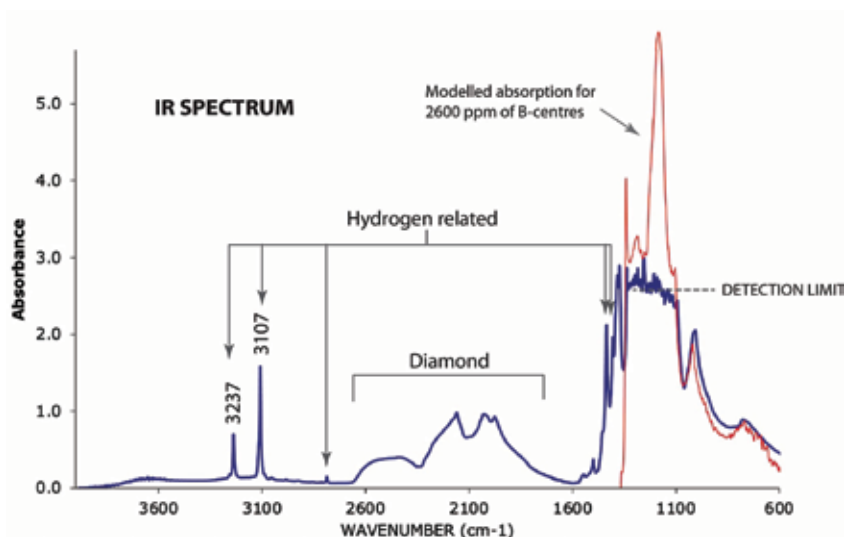


Figure 8. A typical IR spectrum of an Argyle violet showing high concentrations of nitrogen in the 600–1350 cm^{-1} band and hydrogen in the 3100–3240 cm^{-1} region.

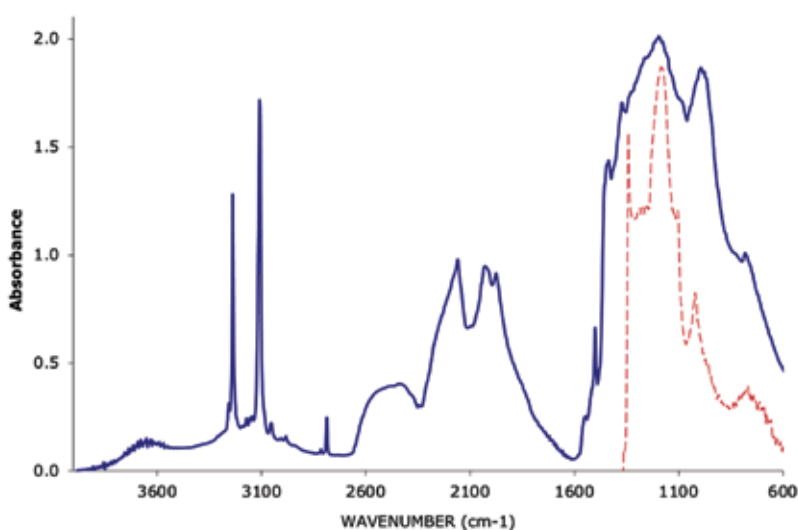


Figure 9. An IR spectrum of a violet diamond showing a 1-phonon profile that does not conform to that of a B-centre (red graph). Note also the high intensity of the 3237 cm^{-1} peak.

Infrared Spectra

Argyle violets have been noted for their high nitrogen and high hydrogen contents (Fritsch and Scarratt, 1992) as observed in their IR absorption spectra that feature very strong nitrogen peaks in the 1100–1300 cm^{-1} band (1-phonon region) and two hydrogen related lines at 3107 cm^{-1} and 3237 cm^{-1} . One of the difficulties of measuring the nitrogen content and aggregation state in violets has been that the absorption in the nitrogen region exceeds the detection limit of spectrometers. Figure 8 shows a typical IR spectrum (blue graph) with a superimposed curve in the 1-phonon region (red graph) corresponding to 2600ppm of nitrogen B-centres.

Estimates relating to the nitrogen content therefore need to be based on fitting modelled curves to those areas within the instrument's detection range as performed in the example above.

With the samples measured, the nitrogen concentrations ranged from 1000–3000ppm of which a very high proportion is in the B-aggregate state. With such high absorption in the spectra it is very difficult to estimate the A-centre concentrations, but it was established from some of the spectra to be between 0 and 100ppm.

With some samples, by using many scans on a small stone it was possible to produce a spectrum within the detection limits of the spectrometer, however these spectra were found not to lend themselves to conventional fitting of model curves for A and B centres, as shown in Figure 9.

The other notable feature in IR spectra is the relatively intense 3237 cm^{-1} peak that is associated with hydrogen. In some samples the absorbance of this peak was as high as 80% that of the 3107 cm^{-1} peak. Other coloured and colourless diamonds can show this 3237 cm^{-1} peak, however its height is only a small fraction of the 3107 cm^{-1} peak.

Discussion

Research performed by Noble *et al.* (1998) and confirmed by others suggested that nickel is the elemental impurity that may be responsible for the violet colouration in Argyle diamonds, and observations described in this article support the hypothesis that high levels of nitrogen and hydrogen are not the cause of colour. The 3237cm^{-1} peak is not recorded in other (coloured) diamonds at the level observed in violets. The structure for this defect hasn't been characterised and it can be speculated that it might comprise nickel and hydrogen in combination with one or more nitrogen atoms. An observed general correlation of violet colour saturation and the 3237cm^{-1} peak lends credence to the associated defect incorporating nickel.

The difficulty in fitting model A- and B-centre curves to those spectra where the nitrogen absorption doesn't exceed the detection limit of the spectrometer (for example in Figure 8) may suggest that other nitrogen complexes are present having a different spectral signature.

With any diamond, a high concentration of B-centres would be expected to be accompanied by a high concentration of N3 defects. These N3 defects are considered a by-product of the aggregation process from pairs of nitrogen atoms (A-centres) to clusters of four nitrogen atoms (B-centres), however with the violets, despite the high concentrations of B-centres, N3 is barely perceptible in the absorption spectrum and of weak strength in PL spectra. A possible reason for this low presence is N3 defects being 'mopped up' by hydrogen to produce the significant 3107cm^{-1} peak. This peak is believed to be an N3 centre coupled to a hydrogen atom (Goss *et al.*, 2014).

The 526nm PL peak observed is distinctive and of similar profile to the 551nm absorption peak and, from the samples analysed, these two peaks appear to be correlated. Figure 7 shows extreme examples, with one spectrum without the peaks and one with the peaks. No correlation was found between the 551nm peak and any H-related IR spectral feature. A PL peak has been observed (Lawson *et al.*, 1993) at 527nm in synthetic diamonds grown using nickel catalysts and the authors proposed it relates to a defect containing a nickel atom bound to a nitrogen A-aggregate. Such structure would be consistent with what might be expected in nickel and nitrogen-rich diamonds represented by violets.

For those spectra that do not show the 551nm absorption peak, they may have low concentrations of A-centres, however this explanation is difficult to confirm in the absence of IR spectra that allow deconvolution to resolve

the A-centre component. This 526nm peak appears to be the same as a 524nm peak that was observed with 488nm excitation by Van der Bogert *et al.* (2009).

The observations of violet diamond fluorescence contrast with those reported in the literature. Van de Bogert (2009) noted that all fluoresced blue; Eaton-Magaña *et al.* (2018) remarked that 61% fluoresced yellow under LWUV; and Fritsch and Scarratt (1992) also noted yellow to orangey-yellow for the four violets stones investigated. A yellow component is observed in the PL spectra to varying degrees, however, the author has not seen any violet diamonds that could be described as fluorescing yellow and he is unable to offer an explanation for the stark difference between recorded observations.

Some authors (eg. Noble *et al.*, 1998) have noted the similarity between the absorption peak at 550nm with that of pink diamonds sharing the same peak wavelength and width. This may be coincidental, however, the requisite of plastic deformation for pinks is inconsistent with the near strain-free structure observed with violets. Additionally, the 550nm band in pinks is photochromic and this behaviour is not observed with the same 550nm band in violets. Photochromism is the result of an exchange of electrons between one defect responsible for a colour and another defect. It is possible that the lack of 550nm photochromism could be due to the absence of the defect with which the pink colour centre exchanges electronic charge and hence the pink defect may still be present, but unable to interact with any nearby defect.

In the case of violets, the photochromism observed indicates one of the defects participating in the electron exchange adds a grey tone to the stone. With the two dominant colours being violet and grey, the interplay between the charge states of a violet and grey defect could determine whether a stone is violet-grey or grey-violet.

The Argyle violets have characteristics quite different to other diamonds in the Argyle deposit which typically have low nitrogen, high strain and low clarity. Such differences suggest a different growth environment providing higher nitrogen and nickel content, less plastic deformation, and fewer inclusions. With research (Smith *et al.*, 2017) finding type II (nitrogen-free) diamonds were formed at greater depth than type I diamonds, it could be speculated that shallower depths are associated with higher nitrogen contents, lower temperatures and lower pressures for which nickel serves as a catalyst to enable diamond growth.

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Editor's Note: The author has a commercial interest in Delta Diamond Laboratory and Gemetrix.

