# TiO₂ exsolution as a cause of ferropericlase inclusion iridescence in diamond

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## Introduction

Ferropericlase, represented by the chemical formula $(Mg,Fe)O$, is the most common inclusion phase found in sublithospheric diamonds (Walter et al., 2022). It often manifests a vivid iridescence that serves as a distinctive visual identifier (Figure 1). The exact cause of this iridescence has previously been unresolved, and suggestions have been made that it may arise at the inclusion-diamond interface due to thin-film interference from graphite (Tappert and Tappert, 2011), trapped fluid, or structural colouration from ultra-fine exsolution of magnesioferrite (Smith and Moe, 2016). Inclusion studies on a suite of sublithospheric diamonds from Candle Lake kimberlite in Saskatchewan, Canada, identified a highly iridescent ferropericlase inclusion as well as unusual slightly iridescent bridgmanite and majoritic garnet inclusions. In situ and ex situ analysis of these iridescent inclusions has provided more definitive insights into the underlying cause of the observed iridescence.



**Figure 1:** Visually striking photomicrographs of the irridescent colours of a ferropericlase inclusion as revealed through different facets of the host diamond. Field of view 1.99 mm. Photomicrographs: Evan M. Smith/© GIA. Reprinted with permission.

## Inclusion Analysis

In situ Raman spectroscopic analysis of the highly iridescent Candle Lake ferropericlase diamond inclusion (Figure 2a) generated a spectrum markedly distinct from previously published Raman spectra related to ferropericlase (e.g., Smith et al., 2022; Smith 2021 and references therein), with main Raman bands at 150 cm⁻¹ and ~1135 cm⁻¹ and poorly resolved minor bands at ~340 cm⁻¹, ~420 cm⁻¹, ~650 cm⁻¹ and ~740 cm⁻¹ (Figure 2b). The slightly iridescent bridgmanite and majoritic garnet inclusions yielded analogous, but less intense, Raman spectra. Extraction and ex situ re-analysis of the ferropericlase inclusion (which fragmented on extraction and lacked the iridescence observed when it was in situ) yielded a different Raman spectrum

that, in contrast, does resemble certain published spectra associated with ferropericlase (Figure 2c). The unusual in situ spectra obtained for the highly iridescent ferropericlase (and slightly iridescent bridgmanite and majoritic garnet inclusions) is therefore interpreted to reflect the signature of the iridescence causative.
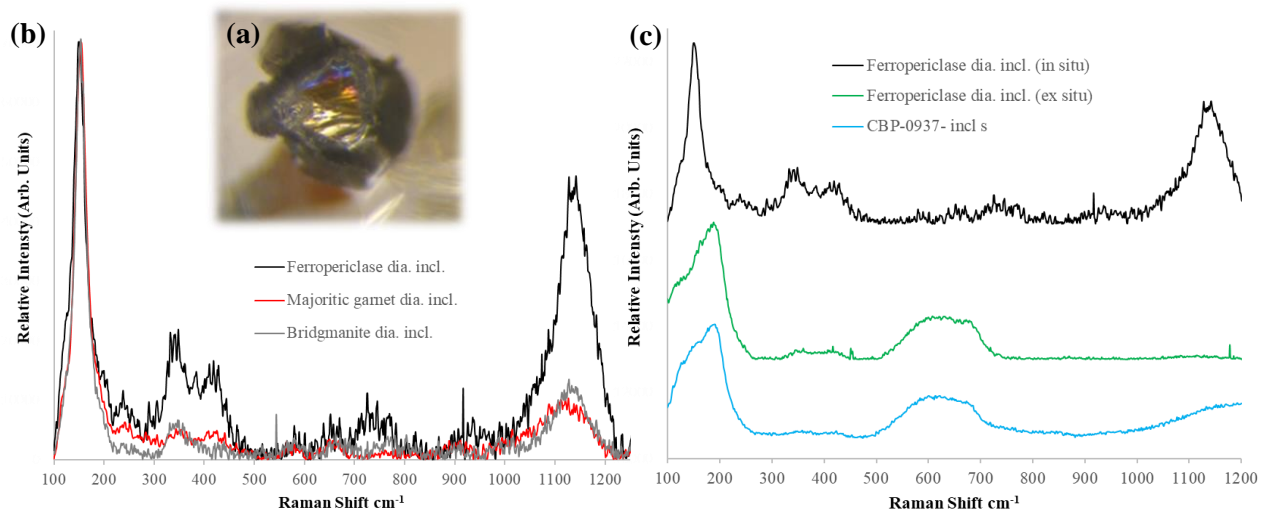


**Figure 2:** (a) Photomicrograph of in situ highly iridescent Candle Lake ferropericlase diamond inclusion (field of view 300 μm). (b) Normalised and baselined in situ Raman spectra of highly iridescent Candle Lake ferropericlase inclusion as well as unusual slightly iridescent bridgmanite and majoritic garnet inclusions. (c) Comparative in situ and ex situ Raman spectra for Candle Lake ferropericlase inclusion and published Raman spectrum for ferropericlase inclusion "CBP-0937- incl s" (from Smith, 2021).

As extraction and fragmentation resulted in the loss of the iridescent phase of the ferropericlase inclusion, the slightly iridescent bridgmanite and majoritic garnet inclusions were left in situ to ensure preservation of their equivalent causatives. The slightly iridescent bridgmanite inclusion was carefully exposed by polishing of the host diamond. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was undertaken on the exposed inclusion, during which the ablation pit was advanced through the entire thickness of bridgmanite and into the host diamond on the other side of the inclusion. As the ablation pit advanced from inclusion to host diamond it passed through and ablated the iridescent phase between the inclusion and the underlying diamond, providing a valuable glimpse at the chemical composition of this enveloping material.

The iridescent phase is very thin and appears as an isolated peak on the isotope counts recorded by the LA-ICP-MS. Only a single isotope from a list of 42 trace elements being analysed recorded the ablation of this phase – $^{47}$Ti – suggesting the iridescence is primarily a result of exsolution of Ti from the inclusion mineral phase. This compositional information provides valuable direction for the interpretation of the Raman spectra of the iridescent phase.

**Interpretation of Raman Spectra**

Assignment of the iridescent phase Raman modes is assisted by the LA-ICP-MS results that identified the presence of $^{47}$Ti in a thin layer around the slightly iridescent bridgmanite inclusion. The main Raman band at 150 cm$^{-1}$ is interpreted to represent an orthorhombic/$\alpha$-PbO$_2$-type TiO$_2$ Eg mode (Figure 3). This likely reflects decompression of exsolved nanophase TiO$_2$ from a primary high-pressure monoclinic/baddeleyite structure, with the ~30 cm$^{-1}$ line width (FWHM) of the intense Eg mode preserving a record of exposure to pressures of ~20 GPa (based on the experimental results of Hearne et al., 2004). This should be considered a minimum pressure estimate as pressure-related broadening of the nanophase TiO$_2$ Eg mode is known

from experimental studies to be at least partially reversable on decompression (Hearne et al., 2004). The secondary modes at ~340 cm$^{-1}$, ~420 cm$^{-1}$, ~650 cm$^{-1}$ and ~740 cm$^{-1}$ are poorly defined but based on a comparison to nanophase TiO$_2$ pressure evolution spectra reported in Hearne et al. (2004) likely reflect pressure-related transformations of nanophase TiO$_2$ with associated secondary mode shifts, with the broad line widths again preserving an indication of exposure to high pressure conditions. The broad mode at ~1135 cm$^{-1}$ is not accounted for in a pure TiO$_2$ phase, and this mode is open to interpretation from a range of possible causes.
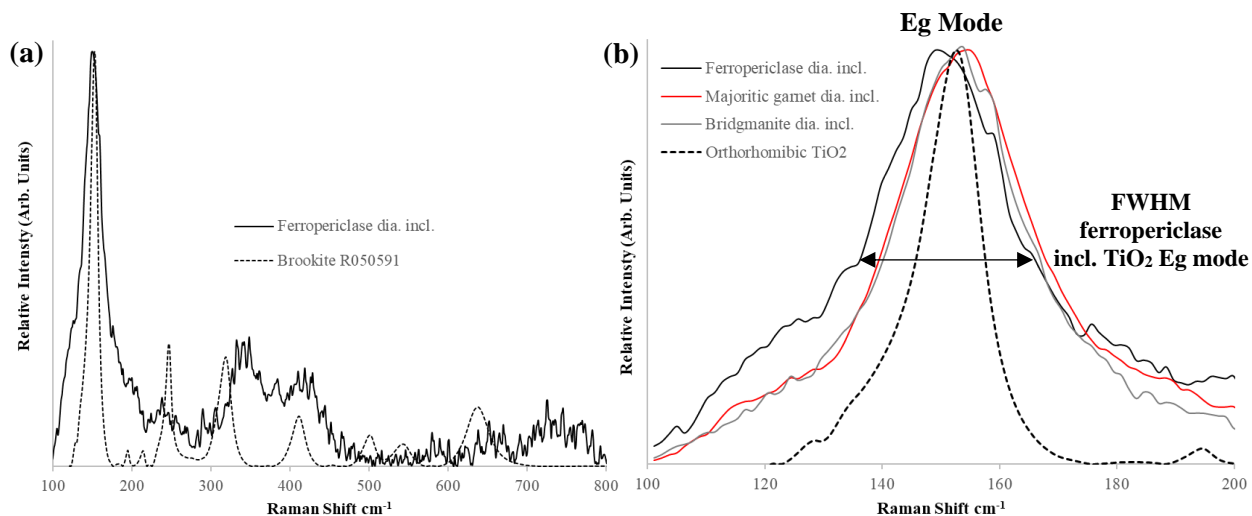


**Figure 3:** (a) Comparative Raman spectra for Candle Lake ferropericlase inclusion iridescent phase and orthorhombic TiO$_2$ (Brookite, RRUFFID R050591). (b) Ferropericlase, bridgmanite and majoritic garnet inclusion iridescent phase main Raman bands compared to the Eg mode of orthorhombic TiO$_2$ (Brookite, RRUFFID R050591).

## Conclusions

Ferropericlase inclusion iridescence is interpreted as arising from a thin enclosing TiO$_2$ rich nanophase. This TiO$_2$ nanophase likely exsolved from the inclusion, and in the case of the Candle Lake diamonds preserves a record of exposure to sublithospheric pressures. Thin-film interference through semi-transparent nanometer-scale TiO$_2$ is a well-known phenomenon, resulting in titanium being christened the "peacock metal" due to the consequent colourful iridescence. This effect would account for the vivid iridescence of ferropericlase inclusions in diamond, with the presence or absence of iridescence dependent on the presence or absence of nanophase TiO$_2$ exsolution.

## References

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