

## Formation of unusual yellow Orapa diamonds

Suzette Timmerman<sup>1</sup>, Ingrid L. Chinn<sup>2</sup>, David Fisher<sup>3</sup>, Gareth R. Davies<sup>1</sup>

<sup>1</sup>Vrije Universiteit, Amsterdam, Netherlands, [suzette.timmerman@anu.edu.au](mailto:suzette.timmerman@anu.edu.au), [g.r.davies@vu.nl](mailto:g.r.davies@vu.nl)

<sup>2</sup>De Beers Exploration, Southdale, South Africa, [ingrid.chinn@debeersgroup.com](mailto:ingrid.chinn@debeersgroup.com)

<sup>3</sup>De Beers Technologies, Maidenhead, United Kingdom, [david.fisher@debeersgroup.com](mailto:david.fisher@debeersgroup.com)

### Introduction

Complex growth structures in monocrystalline diamonds accompanied by changes in N and/or  $\delta^{13}\text{C}$  reflect episodic growth and changes in the C-H-O-S rich diamond-forming media. Determining the nature of different types of diamond growth is important to build an understanding of the conditions of diamond formation in the mantle. Recent changes to processing at Orapa have significantly increased the yield of unusual yellow diamonds. These diamonds have an uneven yellow colour owing in part to the presence of relict unaggregated nitrogen defects (C defects) rather than the N3 defect that gives rise to the more common “Cape yellow” colour. They represent a previously undocumented eclogitic diamond-formation event at a mine dominated by eclogitic diamonds. The diamonds studied were sizeable; of  $\frac{3}{4}$  to 1 carat, underlining the economic importance of understanding the formation of these particular diamonds. To this end, we present a detailed FTIR, carbon isotope and inclusion major element study of 20 of these unusual eclogitic diamonds from Orapa.

### Results

In general, all the diamonds have an uneven yellow to orange colour and an irregular morphology, with trigons present on some faces. The internal growth structure of central plates, as revealed by DiamondView<sup>TM</sup> fluorescence imaging, shows complex intergrowth of zones with green fluorescence and non-fluorescent to blue zones. Growth sector zonation was identified in the green fluorescent zones that are directly related to the yellow colour in normal transmitted light (Fig. 1). The non-fluorescent to blue zones correspond with colourless zones in transmitted light. Most diamonds show a clear resorption boundary (Fig. 1b) between the green fluorescent zones and non-fluorescent to blue fluorescent zones. More examples of the growth structure of these Orapa diamonds can be found in the supplementary information of Timmerman et al. (2017).

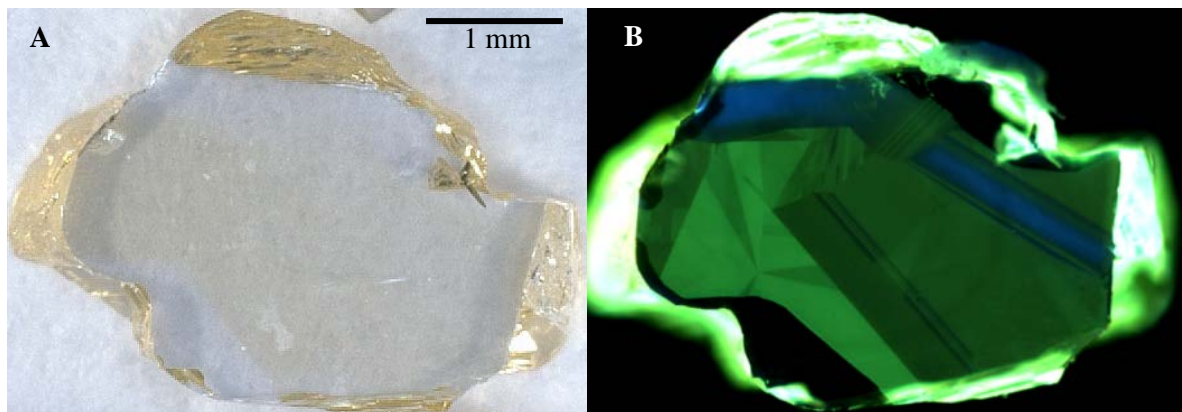


Figure 1: A) Normal transmitted light image, and B) DiamondView<sup>TM</sup> image of diamond OR19. The yellow section in transmitted light corresponds to the green luminescence in DiamondView.

FTIR spectra show that all growth zones are characterized by low nitrogen concentrations (<125 ppm) and a hydrogen peak at  $3107\text{ cm}^{-1}$  (Fig. 2). Some spectra contain platelet peaks, marking the start of aggregation from A to B centres. Relict unaggregated nitrogen defects are present in the yellow growth zones. The nitrogen peak at  $1344\text{ cm}^{-1}$  of single substitutional nitrogen is very low corresponding to 0.2 to 1.1 ppm (Fig. 2) and absorption at  $1332\text{ cm}^{-1}$  is partially caused by  $\text{N}^+$ . The single phonon region

does not generally fit well to the usual C, A and N<sup>+</sup> components and the nature of the defects causing the additional absorption is presently unknown.

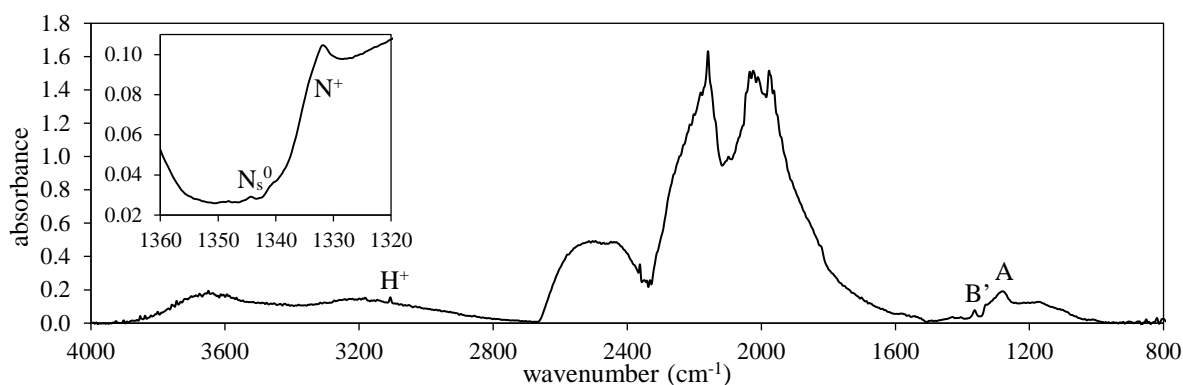


Figure 2: FTIR spectrum of diamond OR07, showing the small nitrogen A-centre peak relative to the diamond absorbance, and the platelet peak at 1363 cm<sup>-1</sup> (B'). The inset shows the presence of the N peaks at 1344 and 1332 cm<sup>-1</sup>.

The  $\delta^{13}\text{C}$  values of these Orapa diamonds show a limited range of -5.7 to -10.6 ‰. Yellow and colourless zones exhibit a similar variation in carbon isotope composition of -5.7 to -10.6 ‰ and -6.8 to -10.4 ‰ respectively (Fig. 3a). One heavier composition of -2.9 ‰ was found for the blue fluorescent inner zone of diamond OR12. Most diamonds show no significant change in their carbon isotope composition throughout the diamond (Fig. 3a). Similar to the limited variation in carbon isotope composition and nitrogen content, the major element compositions of the mineral inclusions show limited variability. Mineral inclusions all occur in colourless zones and none were observed in zones with yellow body colour. Garnet inclusions show a range in calcium content of 3.46 – 6.89 wt%, with one calcium-poor outlier (1.73 wt%; Fig. 3b). Both calcium and iron decrease with increasing magnesium content and the data form a single population in bi-variant diagrams suggesting that there is only one garnet population. Clinopyroxenes show limited variation in Mg<sup>#</sup> and Cr<sup>#</sup>, apart from 3 clinopyroxenes in diamond OR18. Based on the fluorescence images four non-touching garnet-clinopyroxene pairs were considered to be in equilibrium and yielded temperatures of 1105-1191 °C at an assumed pressure of 5 GPa, calculated with the Fe-Mg exchange thermometer of Krogh (1988). These temperatures are ~100 °C higher than the temperatures of  $\pm 1000$ -1100 °C previously reported for eclogitic diamonds from Orapa (Deines and Harris 2004).

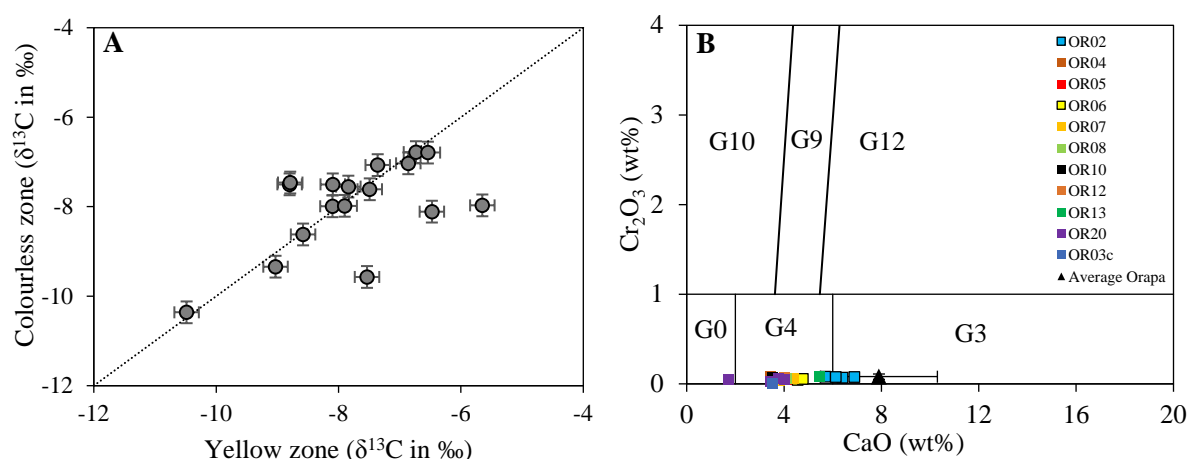


Figure 3: A) Carbon isotope compositions for yellow and colourless zones of the studied Orapa diamonds. B) Limited variation in major element composition of garnet inclusions in the Orapa diamonds, with on average lower calcium contents compared to the average eclogitic population reported by Deines et al. (1993). Classification diagram after Grütter et al. (2004).

## Discussion

Despite a distinct difference in growth structure and fluorescence between yellow and colourless zones, the nitrogen concentration and carbon isotope composition are indistinguishable. The restricted range in N and  $\delta^{13}\text{C}$  within the diamonds suggests that the different zones formed from similar fluids. Furthermore the presence of only one compositional population of eclogitic silicate inclusions in all 20 studied diamonds shows that the colourless zones formed from similar fluids. The source of the fluid and conditions of growth can be further constrained based on the nitrogen contents and composition of the inclusions. Nitrogen aggregates from single nitrogen to nitrogen pairs to four nitrogen around a vacancy, and is dependent on time, temperature and nitrogen concentration (Taylor et al. 1996). The relict unaggregated nitrogen defects present in the studied diamonds therefore suggest young diamond formation, formation in a cool environment, and/or low aggregation rates due to the low nitrogen concentration. A dating study of silicate inclusions derived from the colourless outer zones of these same unusual yellow Orapa diamonds yielded isochron ages of  $140\pm 93$ ,  $1096\pm 230$ , and  $1699\pm 340$  Ma (Timmerman et al. 2017). This implies that some of the yellow inner zones are likely to be  $\geq 1699$  Ma and indicates that the diamonds did not have an unusually short mantle residence time. The equilibration temperatures of  $1105\text{--}1191^\circ\text{C}$  for four non-touching garnet-clinopyroxene pairs suggest that the unaggregated nitrogen defects are not associated with diamond formation at unusually low temperatures. It is possible, however, that diamond formation took place during a thermal perturbation associated with hot upwelling mantle material resulting in a higher equilibrium temperature recorded in the mineral inclusions. Subsequent cooling to ambient mantle conditions would result in a lower average residence temperature. The unaggregated nitrogen defects are more likely a consequence of the difficulty of aggregation at low N concentrations. In addition, the lack of aggregated nitrogen may be explained by the formation of hydrogen-nitrogen complexes instead of nitrogen aggregates.

The distinct characteristics of these diamonds compared to other diamonds from Orapa suggest they were formed in a different environment and growth event to the majority of Orapa diamonds. The  $^{87}\text{Sr}/^{86}\text{Sr}$  composition of the silicate inclusions in the colourless zones of the diamonds showed large variations (0.7033-0.7084; Timmerman et al. 2017), and coupled to the limited range in  $\delta^{13}\text{C}$  it was suggested to be caused by mixing fluids from a depleted mantle and a post-Archaeon subducted sediment source (Timmerman et al. 2017). In summary, the similarity of all twenty diamonds in terms of morphology, growth structure and the limited range in nitrogen concentration, aggregation state, inclusion major element composition, formation temperature, and carbon isotope composition indicate that these complexly zoned diamonds formed from fluids mixed from depleted mantle and post-Archaeon subducted sediment sources that have restricted carbon isotope compositions.

## References

- Deines P, Harris JW (2004) New insights into the occurrence of  $^{13}\text{C}$ -depleted carbon in the mantle from two closely associated kimberlites: Letlhakane and Orapa, Botswana. *Lithos* 77(1):125-142
- Deines P, Harris JW, Gurney JJ (1993) Depth-related carbon isotope and nitrogen concentration variability in the mantle below the Orapa kimberlite, Botswana, Africa. *Geochimica et Cosmochimica Acta* 57(12):2781-2796
- Grütter HS, Gurney JJ, Menzies AH, Winter F (2004) An updated classification scheme for mantle-derived garnet, for use by diamond explorers. *Lithos* 77(1):841-857
- Krogh EJ (1988) The garnet-clinopyroxene Fe-Mg geothermometer—a reinterpretation of existing experimental data. *Contributions to Mineralogy and Petrology* 99(1):44-48
- Taylor WR, Canil D, Milledge HJ (1996) Kinetics of Ib to IaA nitrogen aggregation in diamond. *Geochimica et Cosmochimica Acta* 60(23):4725-4733
- Timmerman S, Koornneef JM, Chinn IL, Davies GR (2017) Dated eclogitic diamond growth zones reveal variable recycling of crustal carbon through time. *Earth and Planetary Science Letters* 463:178-188