Doctoral School of Geosciences

FACTORS CONTROLLING DIAMOND PRESERVATION IN KIMBERLITES: A STUDY OF PERIDOTITE XENOLITHS FROM KAAPVAAL CRATON

PhD Dissertation

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Introduction and Aims

Kimberlites are igneous rocks with significant economic importance, primarily due to their potential to host diamonds. The exploration and sampling processes for finding a kimberlite and determining its profitability are expensive, but the majority of kimberlites are uneconomical, and only a small fraction contains diamonds in quantities sufficient to support commercial mining operations. The economic viability and complexity of the mantle cargo sampled by a kimberlite over its journey from > 150km depths in the mantle to emplacement on the surface has garnered attention from the scientific community. The decades of research on kimberlite formation and diamond potential have demonstrated the many factors that cause diamond dissolution in kimberlites and the complexity of the various processes affecting a kimberlite.

One of the main challenges in understanding the processes that lead to diamond loss is the bias in research on economic kimberlites. The few studies focused on the uneconomic kimberlites and their evolution to help understand the local processes affecting them. One such locality is the northern Lesotho kimberlite field, where many economic kimberlites (Kao, Letšeng-le-Terae, Mothae, and Liqhobong) lie close to many other uneconomic kimberlites. In this study, we focus on the mantle xenoliths from three uneconomic kimberlites (Matsoku, Thaba Putsoa, and Pipe 200) from northern Lesotho and compare them with two classic economic kimberlites (Bultfontein and Frank Smith) from the Kaapvaal Craton. The significance of these uneconomic kimberlites is that they lie at the edge of Kaapvaal Craton and may provide a better understanding of the role of tectonic settings as compared to the kimberlite emplaced in the interior of the Kaapvaal Craton.

The PhD research focuses on the factors controlling diamond destruction in kimberlites. The aims of this thesis are the following: 1) detailed petrological and geochemical identification of the local evolution of the xenoliths from one uneconomic kimberlite (Pipe 200); 2) determine the composition of secondary melt inclusions in xenolith olivine from economic and uneconomic kimberlites and its role in diamond destruction, if any; 3) analyses the distribution of H^+ and calculated water concentration in the different nominally anhydrous minerals (NAMs) in the economic and uneconomic kimberlites; 4) identify the role of tectonic setting/ location of kimberlites on their diamond potential.

Applied Methods

In understanding the factors that may have led to the diamond destruction in uneconomic kimberlites, we employed conventional techniques like microscopic petrography and different spectroscopic methods to analyze the mineral-scale major and trace element geochemistry and carried out statistical analysis of the obtained data on the peridotite xenoliths. This study uses the limited thin and thick sections made by Hilchie et al. (2011) on the mantle xenoliths collected by Barrie Clarke during the 1st International Kimberlite Conference. The research emphasises the differences between the xenolith and economic and uneconomic kimberlites to assess their role in diamond destruction. The applied techniques are briefly explained below.

Following the petrographic analysis of all thin and thick sections, Pipe 200 xenolith thin sections were studied in detail and classified into five types. The major element mineral chemistry of the different xenolith minerals and micro-textures was investigated using a Quantax75 EDS–silicon drift detector combined with a Hitachi TM4000Plus microscope in the Faculty of Science Research and Instrument Core Facility, Eötvös Loránd University (ELTE), Budapest. The analyzed mineral composition of olivine, pyroxene, and garnet was used to calculate the equilibration pressure-temperature conditions of the different xenolith types. Additional measurements were carried out using a JEOL JXA 8,200 electron microprobe analyzer (EPMA) at the Chair of Resource Mineralogy, Montanuniversität, Leoben on xenoliths from all kimberlites to estimate the equilibration pressure-temperature conditions better.

Geothermobarometric modelling was performed using Theriak-Domino (de Capitani and Petrakakis 2010) along with the HoPomelt database to mimic the different observed micro-textures to understand the evolution of the xenoliths from Pipe 200. Energy-dispersive (EDS) multi-element μXRF mapping was performed on the xenolith thin and thick sections at the Department of Mineralogy, Geochemistry, and Petrology, University of Szeged, Hungary, using a Horiba Jobin Yvon XGT-5000 X-ray fluorescence (XRF) spectrometer equipped with a Rh X-ray source to determine the elemental distribution between the different minerals and often to estimate the modal mineralogy better.

FTIR spectroscopy was carried out on the thick sections of the xenolith from four kimberlites to study the hydrogen distribution and calculate the water contents. The analyses were first conducted at the Institute of Geological and Geochemical Research, Budapest, using a Bruker FTIR Vertex 70 spectrometer equipped with a Globar light source. Later, additional measurements were carried out using an MCT-A detector coupled to a Bruker Hyperion 2000 microscope at the Budapest University of Technology and Economics, using the Perkin Elmer Spectrum 400 infrared spectrometer and a coupled Spotlight 400 FTIR imaging system. OPUS software was used for the absorbance integration. A statistical analysis of the raw FT-IR spectra of peridotite olivine crystals from this study and that of economic kimberlites from Peslier et al. (2010) and Peslier et al. (2008) was carried out after standardization using SPSS software.

Lastly, confocal Raman spectroscopy was used to identify the daughter minerals in secondary melt inclusion trails in olivine in the xenolith thin sections from five kimberlites at the Department of Mineralogy, Geochemistry, and Petrology at the University of Szeged using a Thermo Scientific DXR Raman microscope equipped with a diode-pumped frequency-doubled Nd–YAG laser. The RRUFF project database (Downs, 2006) and OMNIC for Dispersive Raman 8.3.104 software were used to identify minerals from the Raman spectra.

New Scientific Results

The study of the peridotite xenoliths from economic and uneconomic kimberlites has yielded new results concerning the diamond destruction of the uneconomic kimberlites from northern Lesotho. They are:

T1: The metasomatism of the mantle by a melt enriched in K_2O, CaO, and possibly H_2O may have caused diamond destruction in the uneconomic kimberlites at northern Lesotho. The main petrological difference between the economic and uneconomic kimberlites lies in the breakdown of garnet and crystallization of an assemblage made up of phlogopite, chromite, and diopside. The suggested possible source of this kimberlite is an alkaline silico-carbonatite melt. The metasomatism by melts at mantle depths is corrosive for diamonds and may have caused diamond destruction in the mantle sampled by uneconomic kimberlites.

T2: Slow ascent or stalling of kimberlite may have caused diffusion of hydrogen, disturbed the water concentration of xenoliths, and led to diamond destruction. The FT-IR analysis profiles across olivine are flat due to the diffusion of hydrogen to the surrounding media, probably the kimberlite itself. This is reflected in the flat diffusion profile and low integrated absorbance in olivines from this study compared to the rare bell-shaped hydrogen diffusion profiles recorded for the same xenoliths by Hilchie et al. (2014). The flat diffusion profile of re-equilibration due to residence in the kimberlite magma, low calculated olivine water concentration when combined with micro-textures of uplift to shallower depths (<90 km) partial melting and kelyphitization observed in Pipe 200 xenoliths suggests slow ascent of kimberlite magma. The diamonds, if sampled from the mantle source, can be destroyed during the slow ascent of the kimberlites.

T3: Composition of melt trapped by secondary melt inclusions in olivine is similar in both economic and uneconomic kimberlite and does not affect diamond dissolution. The secondary melt inclusions in olivine contain daughter minerals of Ca-Mg (±Na, K, P, Cl)-bearing carbonates, alkali (±Ca, Ba, Cl, F, H2O, CO2)-bearing sulfates, phosphates, oxides, silicates, etc. The similar composition of identified minerals and estimated melt in the melt inclusions from both economic and uneconomic kimberlites suggest the absence of their role in diamond destruction. Our findings further suggest their late-stage entrapment at shallow depths, and the diamond grade of these kimberlites is affected by mantle metasomatism before kimberlite emplacement with kimberlite ascent.

T4: The xenoliths from the margin of the Kaapvaal Craton are less hydrated than those from the interior. The water concentration of olivine and orthopyroxene is higher in the xenoliths from the interior of the craton than those from the margin. In addition, the uneconomic kimberlite xenoliths from the margin of the Kaapvaal Craton affected by mantle melt metasomatism have lower water concentration in olivine and higher water concentration in orthopyroxene than the unaffected ones. It highlights the better preservation of water by pyroxene compared to the faster diffusive loss of water by olivine to the surrounding media, possibly the melt.

T5: The statistical analysis of olivine spectra for discriminating economic and uneconomic kimberlites suggests bands associated with high water activity and oxygen fugacity. The hydrogen bands at 3540, 3624, 3638, and 3672 cm^{-1} identified with the discriminant analysis indicate the role of Si-related defects in determining the diamond potential of a kimberlite. The bands associated with hydrous defects linked to the metasomatism-associated process and the F-rich system played a significant role in altering the diamond potential of the xenoliths. The band at 3638 cm^{-1} suggests stabilization at high water activity and oxygen fugacity.

T6: The carbonate melt traversing and metasomatizing mantle in shear zones at craton margins dehydrates the NAMs by diffusion and causes diamond destruction. The narrow shear zones, formed by lithospheric deformation at the margin of the Kaapvaal Craton, provide pathways for CO_2-rich alkaline silico-carbonatite melts metasomatizing the mantle. These CO_2-rich melts can decrease the water concentration of olivine by diffusion and cause diamond destruction in the mantle at the craton margins, like in northern Lesotho. The high oxygen fugacity of H_2O-rich melts of carbonate composition is aggressive for diamond resorption at mantle temperatures, which is also reflected in the high-water activity and oxygen fugacity of the 3638 cm^{-1} band.

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List of Publications

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Journal Articles Used in the PhD Thesis

Khan, S., Kovács, I. J., Fedortchouk, Y., Feichter, M., Szabó, C., & Tóth, T. M. (2024). Multistep evolution of harzburgitic mantle underneath pipe 200 kimberlite, northern Lesotho: a study on xenoliths and their implication on diamond-barren nature of pipe 200 kimberlite. *International Journal of Earth Sciences*, 1-25 (Scimago Journal Rank in 2024: Q1 - Impact Factor: 1.8).

Khan, S., Fedortchouk, Y., Feichter, M., & Toth, T. M. (2024). Confocal Raman spectroscopic study of melt inclusions from peridotite xenoliths in economic and barren kimberlites from Kaapvaal Craton. *Journal of Raman Spectroscopy*, 1 (Scimago Journal Rank in 2024: Q2 - Impact Factor in 2024: 2.6).

Khan, S., Liptai, N., Kovács, I. J., Fedortchouk, Y., & Tóth, T. M. (2024). Heterogeneous water distribution in between peridotite xenoliths from Kaapvaal Craton kimberlites: constraints on diamond barren nature of kimberlites. *Gondwana Research* (in press) (Scimago Journal Rank in 2024: Q1 - Impact Factor in 2024: 7.2).

Other publications

Khan, S., Dongre, A., Viljoen, F., Li, Q. L., & Le Roux, P. (2019). Petrogenesis of lamprophyres synchronous to kimberlites from the Wajrakarur kimberlite field: Implications for contrasting lithospheric mantle sources and geodynamic evolution of the eastern Dharwar Craton of southern India. *Geological Journal*, 54(5), 2994-3016.

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Khan, S., Fedortchouk, Y., Feichter, M., & Tóth, T. M. (2024). Raman study of melt inclusions in peridotite xenoliths from economic and uneconomic kimberlites from Kaapvaal craton. *14. Kőzettani és Geokémiai Vándorgyűlés*, Telkibánya, 2024.

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Khan, S., Liptai, N., Kovács, I. J., Fedortchouk, Y., & Tóth, T. M. (2023). Water content of peridotite xenoliths from Kaapvaal craton kimberlites: implications on barren nature of kimberlites. 13. Kőzettani és Geokémiai Vándorgyűlés, Szekszárd, 2023.

Khan, S., Tóth, T. M. & Fedortchouk, Y., (2022). Heterogeneous mantle tapped by Pipe 200 kimberlite and implications on diamond content. *12. Kőzettani és Geokémiai Vándorgyűlés*, Miskolc, 2022.

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Co-author statements

I, Tivadar M. Tóth, hereby declare that the role of Sahroz Khan, the doctoral candidate, in the publication of

Khan, S., Kovács, I. J., Fedortchouk, Y., Feichter, M., Szabó, C., & Tóth, T. M. (2024). Multistep evolution of harzburgitic mantle underneath pipe 200 kimberlite, northern Lesotho: a study on xenoliths and their implication on diamond-barren nature of pipe 200 kimberlite. *International Journal of Earth Sciences*, 1-25.

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was decisive and that I have not used it to obtain a scientific degree and will not do so in the future.

Szeged (Hungary), 14.10.2024

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I, Yana Fedortchouk, hereby declare that the role of Sahroz Khan, the doctoral candidate, in the publication of

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Leoben (Austria), 14.10.2024

Monika Feichter

Declaration of the supervisor

I hereby confirm that the content of the dissertation is based on the independent work of the doctoral candidate and that he has contributed decisively to the results through his independent creative activity. I consider the entire dissertation to be eligible for support from a professional and academic point of view and recommend its acceptance.

Szeged (Hungary), 14.10.2024

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Declaration of the supervisor

I hereby confirm that the content of the dissertation is based on the independent work of the doctoral candidate and that he has contributed decisively to the results through his independent creative activity. I consider the entire dissertation to be eligible for support from a professional and academic point of view and recommend its acceptance.

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Your submission GWR-D-24-00064R1- Accepted

Prof. M. Santosh <santosh@cugb.edu.cn> Thu, Oct 10, 2024 at 2:42 AM
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Dear Sahroz,

Based on the recommendation of Dr. Sebastian Tappe, Associate Editor, I am pleased to confirm that your paper "Heterogeneous water distribution in between peridotite xenoliths from Kaapvaal Craton kimberlites: constraints on diamond barren nature of kimberlites." has been accepted for publication in Gondwana Research.

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