Investigation of mineral inclusions trapped in lithospheric diamonds with implications for their origin and ascent rate

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INTRODUCTION

Diamonds provide a unique window into the inaccessible regions of the Earth's mantle, preserving information on their mineralogical and chemical composition, oxidation state and volatile budget (Shirey et al., 2013). Through the study of mineral and fluid inclusions, they provide direct constraints on pressure-temperature conditions, redox processes and the role of carbon-, nitrogen- and hydrogen-bearing components during diamond formation and mantle evolution (Stachel et al., 2022). In addition, diamond lattice defects, morphology and microstructures can record residence times, thermal histories and ascent-related mineralogical transformations, making diamonds key archives of both growth and post-growth processes (Gurney et al., 2010).

However, diamond-based records are difficult to interpret because inclusions, defects, metasomatic fluids and redox-sensitive phases may interact during the formation and the mantle residence. For this reason, an integrated approach combining spectroscopy, geochemistry, thermobarometry, oxybarometry and high-pressure experiments is required to reconstruct realistic pressure–temperature–fO_2 pathways for lithospheric diamonds.

This thesis investigates mineral inclusions and lattice defects in lithospheric diamonds from the Amazonian and Siberian cratons. The work combines natural samples, synchrotron micro-FTIR mapping, synchrotron Mössbauer spectroscopy, mineral chemistry and high-pressure experiments to evaluate mantle metasomatism, volatile incorporation, redox heterogeneity and mineral-fluid reactions. Together, these studies show that lithospheric diamonds are not static records, but dynamic archives of deep-Earth processes operating across multiple spatial and temporal scales.

METHODS AND MATERIALS

The samples investigated in this thesis are diamonds from two main localities: Juína, Brazil, and the Siberian Craton, Russia. The Juína area (Mato Grosso State, Brazil) is located within the Amazonian Craton and lies in the Rio Negro–Juruena Province (1.55–1.8 Ga) (Tassinari & Macambira, 1999; Hayman et al., 2005). The Brazilian sample is the lithospheric diamond COMSK3 from the Rio Sorriso area. The locality of Juína is particularly significant because many diamonds from Juína have been classified as sublithospheric, originating from the mantle transition zone or even the lower mantle (Kaminsky, 2017).

The second group of samples includes both peridotitic and eclogitic diamonds from the Nyurbinskaya and Udachnaya mines, located within the Daldyn–Alakit kimberlite field of the Yakutia Province, Sakha Republic, Russia. The Daldyn–Alakit field lies on the Precambrian basement of the central Siberian Craton, overlain by Paleozoic sedimentary rocks and Permian–Triassic flood basalts (Ionov et al., 2010). Among these kimberlites, the Udachnaya and Nyurbinskaya pipes are of Devonian age (367 ± 3 Ma; Yudin et al., 2014) (Fig. 1).

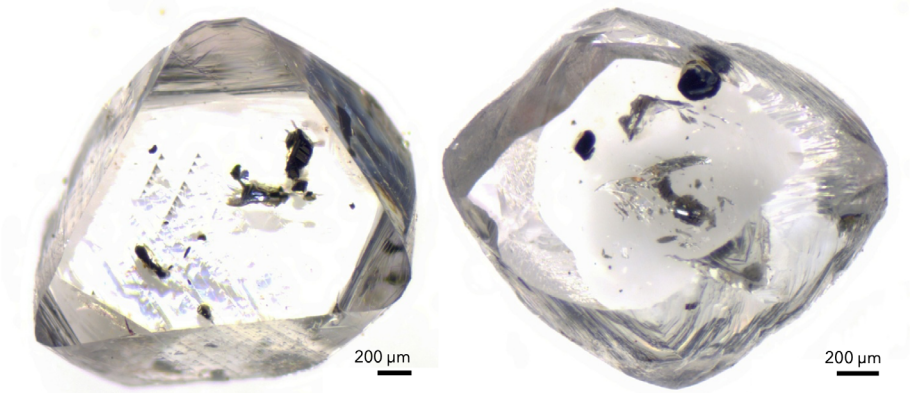

Figure 1 *Two representative peridotitic diamond samples investigated in this thesis.*

A multi-technique analytical approach was adopted for this thesis. Mineral inclusions were characterized using scanning electron microscopy, electron microprobe analysis, LA-ICP-MS, micro-Raman spectroscopy, X-ray diffraction and synchrotron Mössbauer spectroscopy. Diamond lattice defects were investigated by conventional and synchrotron-based micro-FTIR spectroscopy, including point analyses, transects and high-resolution two-dimensional maps. In addition, high-pressure and high-temperature diamond anvil cell experiments were performed to study reactions between natural garnets and carbonate-rich fluids under conditions relevant to diamond formation.

RESULTS AND DISCUSSION

The main body of this thesis is organized around five interconnected studies, some of which have already been published in peer-reviewed journals. Collectively, these studies investigate lithospheric diamonds as archives of mantle metasomatism, volatile incorporation, redox evolution and mineral-fluid interactions.

These studies combine natural samples from the Amazonian and Siberian cratons with high-resolution spectroscopic mapping, geochemical analyses, synchrotron-based techniques and high-pressure experiments. Together, they provide new insights into the evaluation of how mineral inclusions, nitrogen- and hydrogen-related lattice defects, carbonate-rich fluids and redox-sensitive phases record the origin, evolution and ascent-related modification of lithospheric diamonds.

Lithospheric origin of a diamond from the Rio Sorriso area, Mato Grosso State, Brazil

The Rio Sorriso diamond was investigated to clarify whether this region, commonly associated with sublithospheric diamonds (Hayman et al., 2005), also records lithospheric diamond-forming processes. The diamond sample hosts Na-Cr-bearing diopside, high-Mg olivine and enstatite inclusions, indicating a peridotitic, lherzolitic paragenesis. Thermobarometric estimates from polished and entrapped inclusions constrain diamond formation to approximately 4–5 GPa and 1050–1150°C, consistent with lithospheric mantle conditions (Fig. 2).

Major and trace-element compositions of clinopyroxene indicate interaction between the local peridotitic mantle and an oxidized Na-rich, CO_2-rich carbonatitic, or carbonate-silicate melt. The $Fe^{3+}/\Sigma Fe$ ratio of clinopyroxene, ranging from 0.13 to 0.16, further supports interaction with an oxidizing metasomatic agent. Although a single diamond cannot fully resolve the complexity of lithospheric diamond formation at Juína (Timmerman et al., 2023), this sample provides direct evidence that the region did not produce only sublithospheric diamonds. Instead, it also records diamond growth within a metasomatized lithospheric mantle beneath the Amazonian Craton. This work has been published in Frontiers in Geochemistry (Angellotti et al., 2025a).

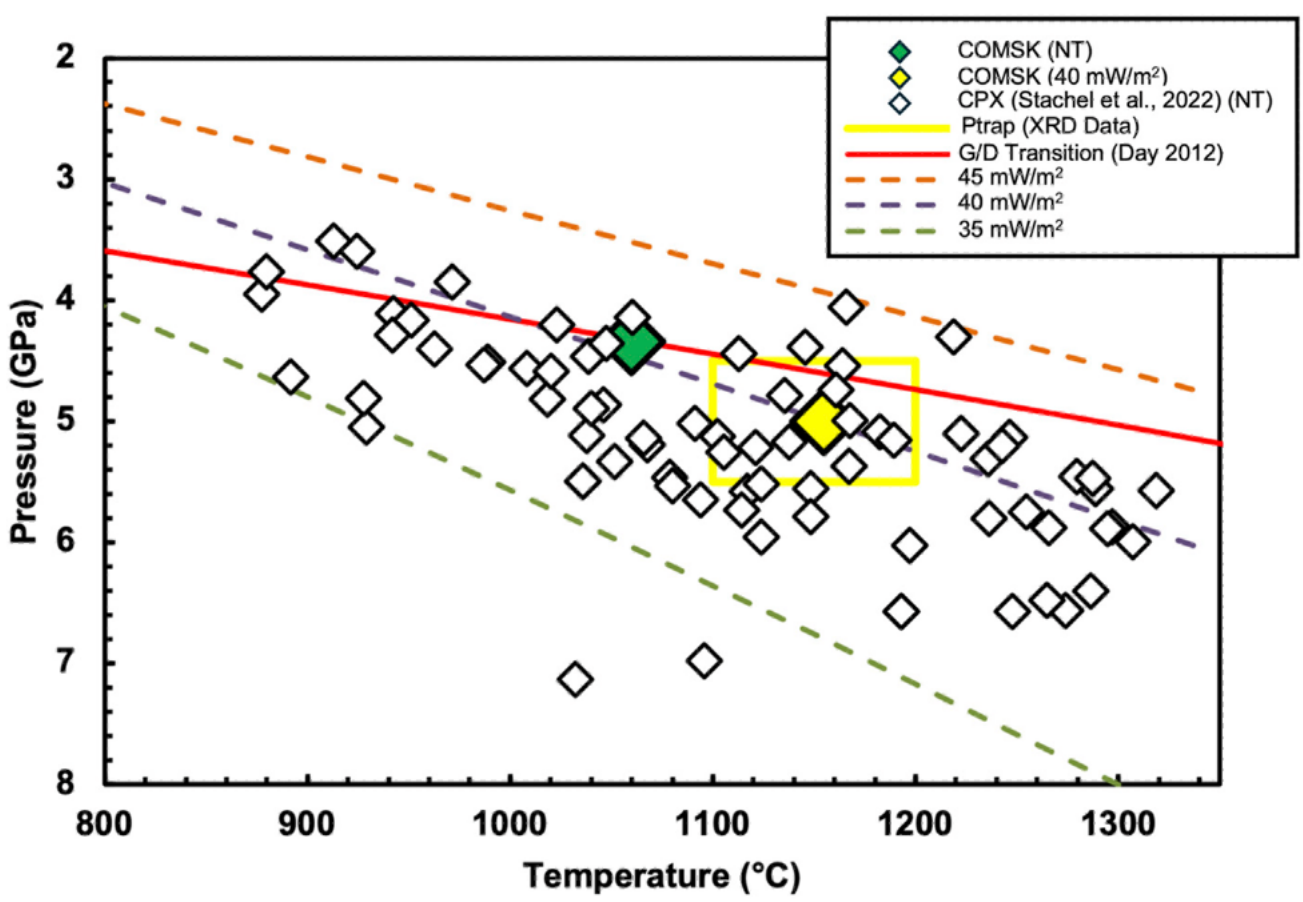

Figure 2 *P–T conditions determined for inclusions of COMSK3 diamond using the cpx-thermobarometer. Further details are reported in Angellotti et al. (2025a).*

Spatial distribution of nitrogen and hydrogen in natural lithospheric diamonds by in situ synchrotron infrared microspectroscopy

Synchrotron-based micro-FTIR mapping was used to investigate the spatial distribution of nitrogen- and hydrogen-related defects in two Type IaAB peridotitic diamonds from the Siberian Craton. The synchrotron-FTIR-based approach (Cinque et al., 2017) and the high-resolution dataset, comprising more than 1500 spectra, allowed the evaluation of micrometre-scale variations in the total nitrogen, nitrogen aggregation state and H-related infrared bands.

The results show a spatial relationship between H-related absorption bands, particularly those at 1405 and 3107 cm^{-1}, and A-centre nitrogen (Fig. 3). This suggests that the distribution of hydrogen-related defects may not be exclusively controlled by the composition of the diamond-forming medium, but is also linked to nitrogen aggregation, residence conditions and possibly local perturbations induced by mineral inclusions. These patterns are difficult to identify using conventional FTIR spot analyses.

Overall, this study, published in Diamond and Related Materials (Angellotti et al., 2025b), highlights the ability of synchrotron micro-FTIR mapping to resolve subtle defect heterogeneities in natural diamonds. The observed relationship between nitrogen aggregation and hydrogen-related defects provides new constraints on volatile incorporation, defect evolution and the possible influence of inclusions during diamond growth and mantle residence.

Interplay between the distribution of nitrogen and hydrogen and mineral inclusions in E-type diamonds from Yakutia, Siberian craton

High-resolution synchrotron micro-FTIR mapping was used to investigate the spatial relationship between mineral inclusions and nitrogen- and hydrogen-related lattice defects in four eclogitic diamonds from the Siberian Craton. The investigated diamonds host graphite, sulfide and garnet inclusions, allowing the effect of different mineral phases on defect distribution to be evaluated.

The results reveal localized enrichments in H-related infrared absorption bands, particularly those at 3107, 1405 and 3236 cm^{-1}, in proximity to mineral inclusions. These enrichments commonly extend for several to tens of micrometres from the inclusion-diamond interface. Sulfide inclusions are frequently associated with local increases in both nitrogen and hydrogen, whereas graphite inclusions mainly correlate with enhanced hydrogen-related absorbance (Fig. 4). Garnet inclusions show less systematic effects, suggesting that their influence depends on mineral chemistry and the specific solubility of volatiles.

These observations indicate that inclusions are not passive markers but can define localized microdomains where hydrogen and nitrogen defects may be preferentially stabilized. Hydrogen-related defects therefore appear to be more sensitive tracers of local perturbations than nitrogen aggregation state or calculated residence temperatures. This work has shown the potential of synchrotron micro-FTIR mapping for resolving defect-scale heterogeneities in diamonds linked to diamond growth, inclusion entrapment and post-growth modification.

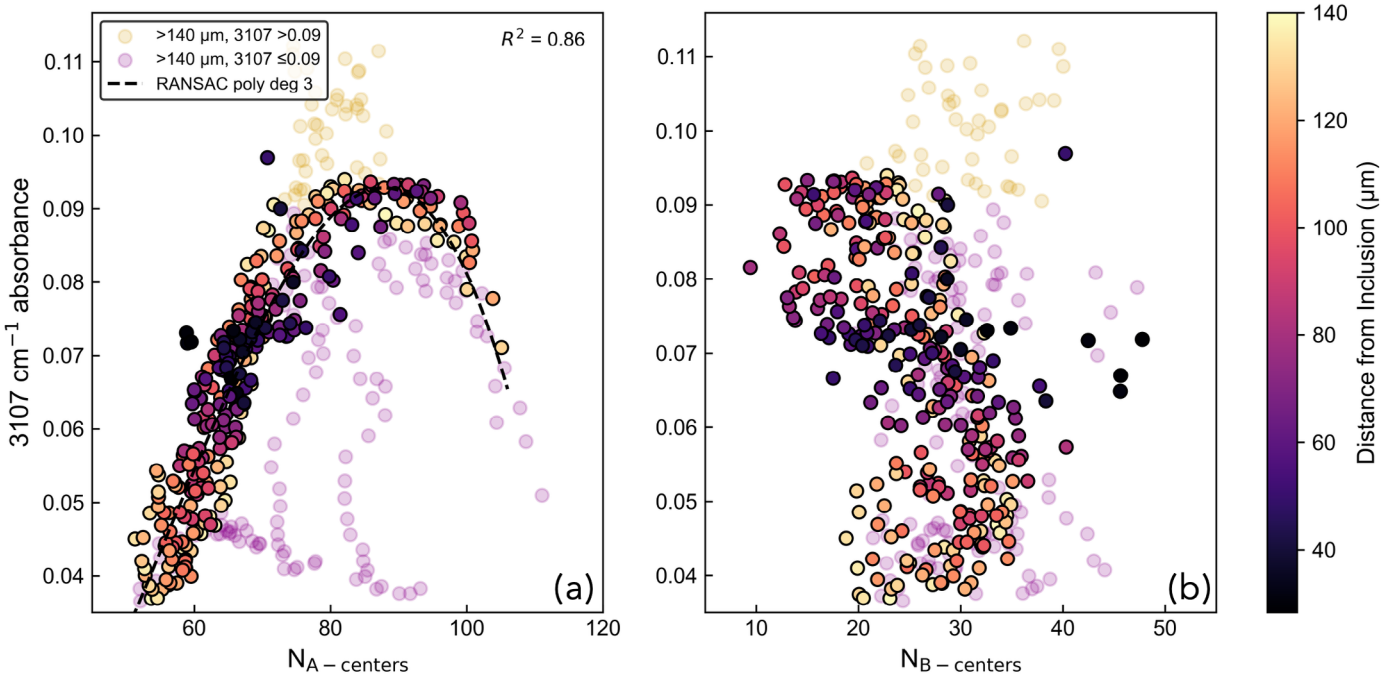

Figure 3 Scatter plots showing the absorbance of the 3107 cm^{-1} peak versus ***a)*** *$N_{A\text{-}centers}$ and* ***b)*** *$N_{B\text{-}centers}$ (in ppm) from Map 1 of Dia8. Color scale indicates the distance from the inclusion used as spatial reference points. Data points are filtered to include only the spectra located within 140 µm from the inclusion.*

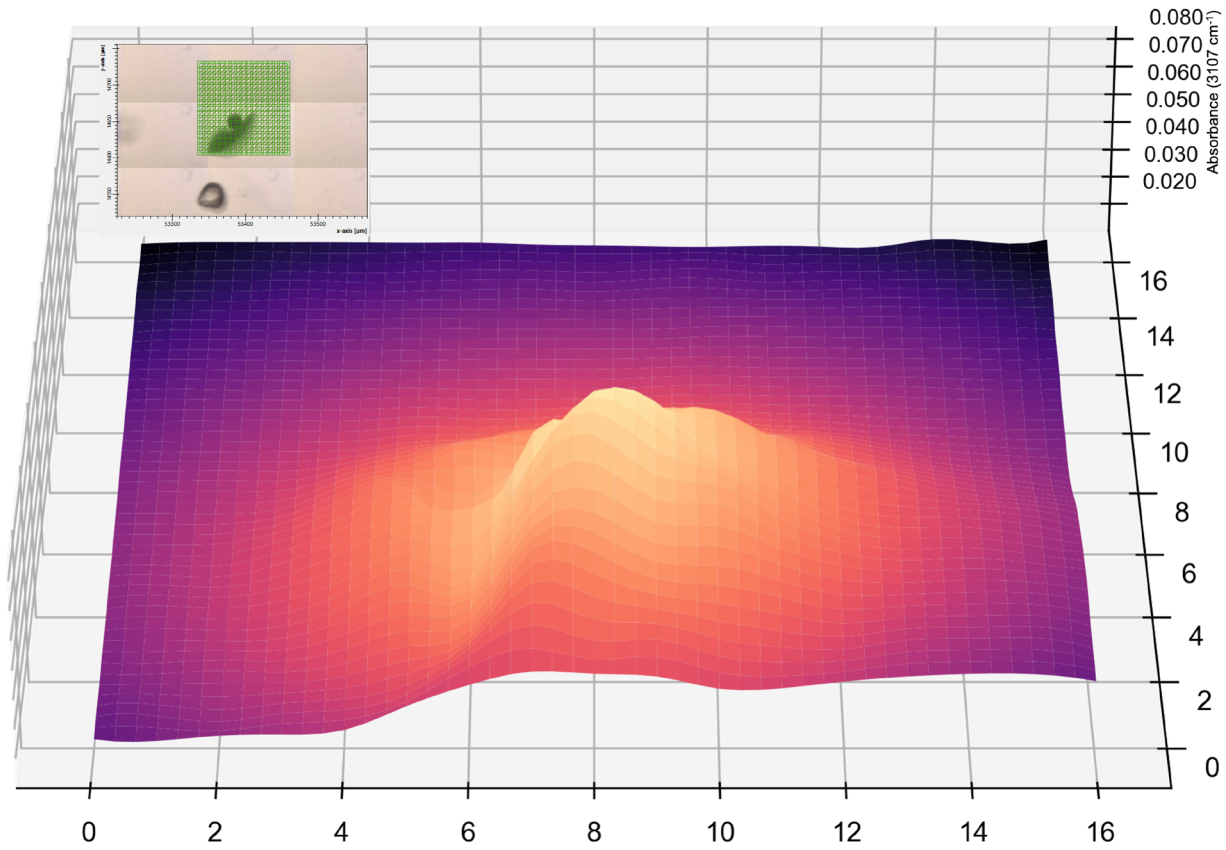

Figure 4 *LGM12 Map2 data presented as a 3D map color-coded by distance from the center of the graphite inclusion, with elevation corresponding to the absorbance of the 3107 cm⁻¹ peak. An inset shows the sampling position on the LGM12 diamond.*

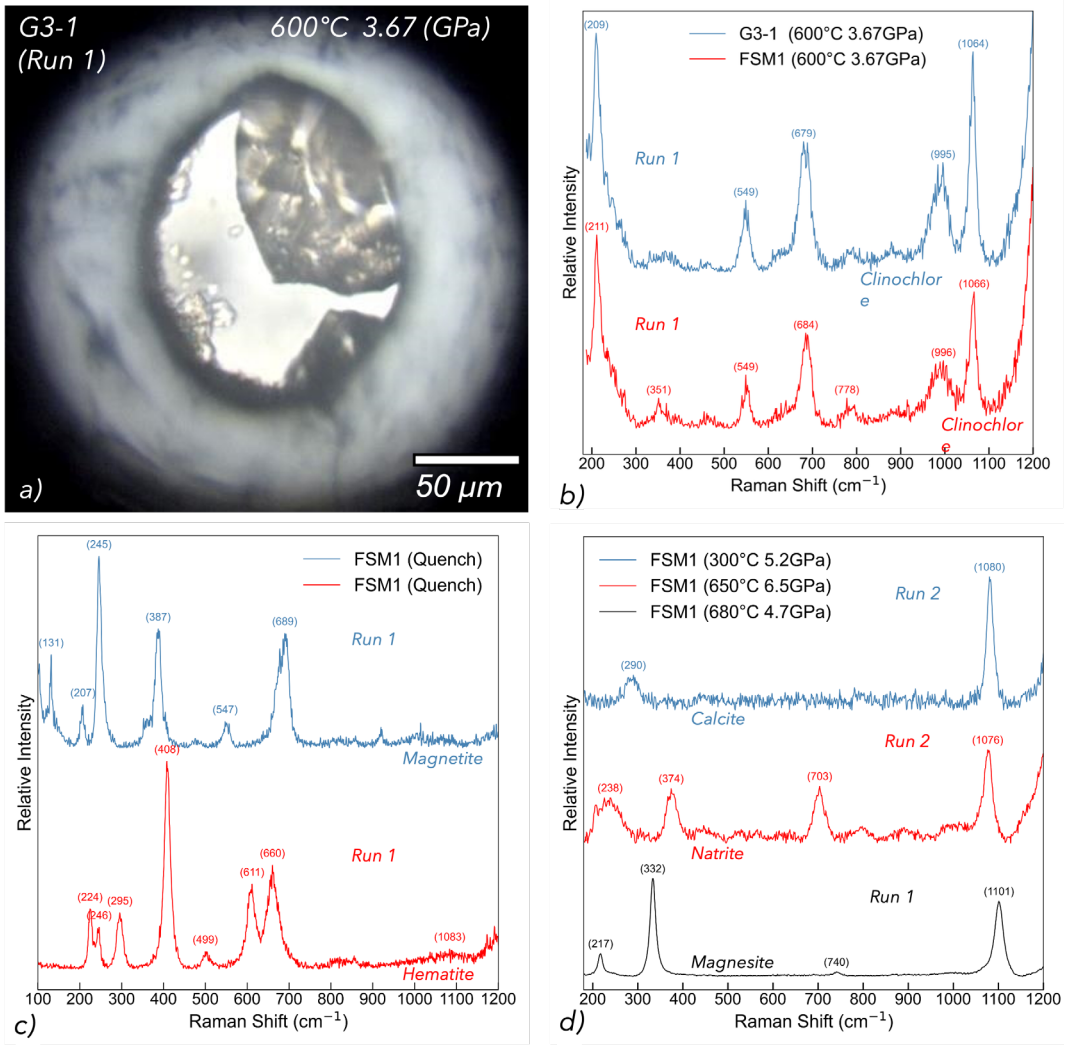

Figure 5 *View of the garnet G3-1 during the experiment and Raman spectra of minerals formed during the DAC experiments.* ***a)*** *Top-view photograph of the DAC showing the formation of clinochlore during Run 1.* ***b)*** *Raman spectrum of clinochlore measured during the experiment.* ***c)*** *Raman spectrum of iron oxides collected after quenching of Run 1.* ***d)*** *Raman spectra of carbonate minerals observed during Runs 1 and 2.*

Garnet and carbonated fluid reactions at high pressure and temperature with implications for the lack of garnets in fibrous diamonds

Garnet-carbonated fluid reactions were investigated to evaluate how CO_2-rich fluids may modify mantle minerals during diamond formation (Weiss et al., 2022). High-pressure and high-temperature experiments were performed in diamond anvil cells using natural peridotitic and eclogitic garnets reacted with Na_2CO_3- and $CaCO_3$-rich aqueous solutions at 4.7–6.8 GPa and 700–800°C. The experiments were monitored by in situ Raman spectroscopy and complemented by synchrotron Mössbauer analyses to assess changes in the Fe oxidation state of garnet (Potapkin et al., 2012).

In Na_2CO_3-bearing systems, garnet underwent partial dissolution, accompanied by the formation of clinochlore, newly formed carbonates and Fe oxides, including magnetite and hematite (Fig. 5). In contrast, the $CaCO_3$ run promoted redox reactions without clear garnet breakdown, producing methane and graphite. The decrease in $Fe^{3+}/\Sigma Fe$ ratios indicates reduction of ferric iron during interaction with carbonate-rich fluids. Preliminary data suggest that garnet can act as a redox mediator controlling carbon speciation. These experiments may provide an explanation for the scarcity of common silicate inclusions and the occurrence of uncommon phyllosilicates, carbonates and carbon-bearing phases in fibrous diamonds (Schrauder & Navon, 1994).

Redox Heterogeneity of the Lithospheric Mantle Revealed by $Fe^{3+}/\Sigma Fe$ Variability in Mg-Chromite Inclusions from Udachnaya Diamonds

As shown before, mineral inclusions in lithospheric diamonds can provide direct constraints on the pressure, temperature and redox conditions prevailing during diamond formation. In this study, we focused on a complete suite of Mg-chromite inclusions hosted by ten peridotitic diamonds from the Udachnaya kimberlite pipes (Siberian Craton). We investigated the inclusions to assess the redox state of the subcontinental lithospheric mantle. Inclusion chemistry and textures were characterized by electron microprobe analysis and SEM, while $Fe^{3+}/\Sigma Fe$ ratios were determined in situ by synchrotron Mössbauer spectroscopy.

The Mg-chromite inclusions show significant chemical and redox variability, with $Fe^{3+}/\Sigma Fe$ ratios ranging from 0.06 to 0.22. Oxygen fugacity estimates indicate relatively reduced conditions, extending to approximately two log units below the fayalite-magnetite-quartz buffer (ΔFMQ -1 to -3). These data reveal localized redox heterogeneities within the peridotitic lithospheric mantle beneath Udachnaya. The occurrence of Mg-chromite at depths (Nestola et al., 2019; Faccincani et al., 2022) exceeding the classical spinel-peridotite stability field further shows how Cr-rich spinels can form and persist under higher-pressure conditions (Ziberna et al., 2013).

Overall, these results, when they reach the completion of the research, will enable us to obtain a more complete view of redox variations present under the Siberian Craton and their key role in chromite stability and diamond formation processes.

FINAL REMARKS

This thesis shows that lithospheric diamonds are complex and dynamic archives of mantle processes. Their mineral inclusions, nitrogen- and hydrogen-related lattice defects, and redox-sensitive phases preserve complementary information on diamond formation, mantle metasomatism, volatile incorporation and growth modification. The integration of natural samples with high-resolution spectroscopic mapping, geochemistry, synchrotron-based techniques and high-pressure experiments provides a multi-scale view of the physical and chemical evolution of the lithospheric mantle.

The results show how diamond formation can occur in metasomatized lithospheric domains affected by oxidized Na-rich carbonated melts, as shown by the Rio Sorriso diamond from Juína. In Siberian diamonds, synchrotron micro-FTIR mapping revealed that nitrogen and hydrogen defects are heterogeneously distributed at the micrometre scale, with hydrogen-related bands being particularly sensitive to local perturbations caused by mineral inclusions. The experimental data further show that carbonate-rich fluids can destabilize or modify garnet, promote redox reactions and influence carbon speciation, providing a possible explanation for the occurrence of peculiar phases in fibrous diamonds. Finally, Mg-chromite inclusions from Udachnaya record reduced and heterogeneous redox conditions within the Siberian lithospheric mantle.

This thesis highlights that diamonds and their inclusions must be interpreted as coupled systems rather than isolated records. By combining inclusion mineralogy, defect chemistry, redox constraints and experimental petrology, this thesis contributes to a more realistic model of lithospheric diamond formation, mantle metasomatism and ascent-related modification.

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