

## Mineral inclusions in E-type diamonds from the Siberian craton: witnesses of Archaean mantle redox heterogeneities and eclogite buffering capacity

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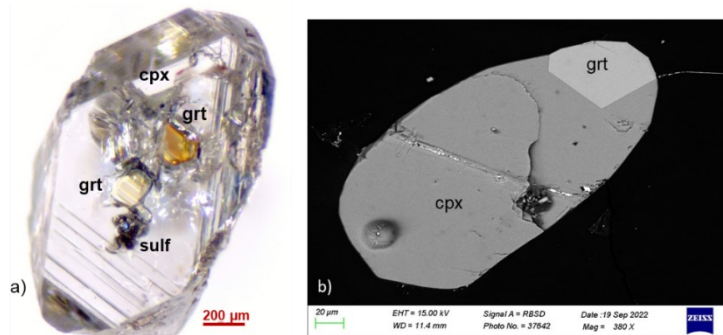
### Introduction

Kimberlite-borne eclogites originated as ancient oceanic crust (protolith) that underwent subduction, and they are considered fertile source rocks for diamonds. Cratonic eclogites distributed worldwide show redox conditions expressed in oxygen fugacity ( $f_{O_2}$ ) that vary from -6 to -0.1 log units normalized to the Fayalite-Magnetite-Quartz (FMQ) buffer, suggesting their equilibration with fluids from CH<sub>4</sub>-H<sub>2</sub>O to H<sub>2</sub>O-CO<sub>2</sub> dominated. However, during the residence in the lithospheric mantle, the  $f_{O_2}$  of the eclogite source could be shifted by the interaction with circulating metasomatic fluids, some of which likely served as growth media for diamonds. Due to the inert nature of diamonds, the mineral inclusions can provide pristine information about the chemistry, mineralogy and redox state of the eclogite source at the time of entrapment.

In this study we investigated a suite of 19 eclogitic diamonds (E-type) from the Siberian craton with inclusions of garnet and clinopyroxene. The aims of this work are to i) shed light on the  $f_{O_2}$  recorded by inclusions in E-type diamonds compared to Udachnaya eclogitic xenoliths; ii) reconstruct the nature of the igneous protoliths and retrieve the  $f_{O_2}$  of the convecting mantle source; iii) track the chemical and redox evolution of the eclogites emplaced in lithospheric mantle over time.

### Material and methods

The selected nineteen E-type diamonds were sampled from diverse kimberlitic pipes in the Yakutian province (Siberian craton) such as Udachnaya, Komsomolskaya, Nurbinskaya, Inter and Mir, which host a large variety of fresh diamondiferous eclogitic xenoliths (e.g., Mikhailenko et al. 2020). The observed mineral inclusions are coexisting garnet and clinopyroxene (touching and non-touching; Fig. 1a-b) either exposed (after polishing) or still enclosed within the diamond, with sizes ranging from 20 to 200  $\mu$ m. Garnet and clinopyroxene grains hand-picked from the host eclogite of one diamond (sample LGM15) were also analyzed. The crystal chemistry (major and minor elements including vanadium) was determined by electron microprobe analyses on the exposed inclusions, while the  $Fe^{3+}/\Sigma Fe$  of both exposed and encapsulated inclusions was measured by synchrotron Mössbauer



**Figure 1 :** a) E-type diamond with paired clinopyroxene and garnet non-touching inclusions associated with sulfide. b) Back-scattered electron image of exposed touching garnet and clinopyroxene.

source spectroscopy. Finally, Raman spectroscopy was employed to identify additional tiny inclusions still trapped within the diamond.

### Chemistry and Fe oxidation state of E-type inclusions

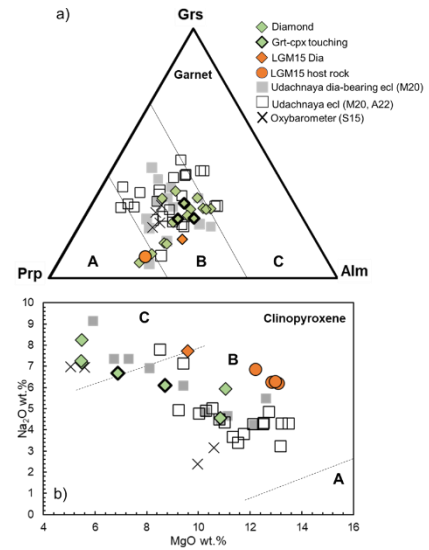
Garnets are solid solutions of pyrope (30-65%), almandine (23-40%) and grossular (6-35%; Fig. 2a), with V concentration varying between 53 and 477 ppm. Clinopyroxenes are omphacites with jadeitic content ranging from 23 to 65%. Na<sub>2</sub>O and MgO contents are 4.5-8.2 and 5.5-11.1 wt%, respectively (Fig. 2b) while V concentrations are 297-407 ppm. Generally, the compositions of garnet and clinopyroxene inclusions agree with those from Udachnaya eclogites, some of which are coesite- and diamond-bearing (Mikhailenko et al. 2020; Aulbach et al. 2022), and synthetic samples used for the calibration of the eclogite oxy-thermobarometer (Stagno et al. 2015; Fig. 2). In addition, Raman spectra collected on a ~30 μm diameter inclusion revealed the presence of coesite. The Fe<sup>3+</sup>/ΣFe ratios of inclusions were determined by fitting the collected Mössbauer spectra. Fe<sup>3+</sup>/ΣFe in garnet inclusions ranges between 0.02 and 0.07 (± 0.01-0.02; Fig. 3), while in clinopyroxene it varies from 0.11 to 0.20 (± 0.03). Fe<sup>3+</sup>/ΣFe ratios of garnets from the host eclogite show no variations between rim and core and are similar to those from inclusions (0.06 and 0.04, respectively), while an increase is observed for clinopyroxene (0.20 for the inclusion and 0.24-0.28 for the host eclogite crystals). Different garnet or clinopyroxene inclusions measured in the same diamond exhibit similar Fe<sup>3+</sup>/ΣFe ratios.

### Geothermobarometry

For seven samples having both garnet and clinopyroxene exposed, T was calculated by the Krogh (1988) thermometer and projected onto the Udachnaya geotherm (35 mW/m<sup>2</sup>) to determine the P of equilibration. The resulting T-P range from 840 to 1170 (± 60) °C and from 4.3 to 6.9 (± 0.4) GPa, respectively. In the case of those samples where the composition of clinopyroxene was unknown, the linear correlation between TiO<sub>2</sub> and T, linked to the increasing solubility of rutile in garnet with T (Aulbach 2020) was utilized to infer the equilibrium T. This extrapolation was based on the regression of 143 data points from recent literature data for Siberian craton eclogites. The obtained T-P are 914-1038 °C and 4.9-5.9 GPa, respectively. The retrieved T-P conditions overlap with those of diamond-bearing Udachnaya eclogite xenoliths. The host eclogite appears to have re-equilibrated at lower T-P compared to the non-touching inclusions in the diamond it hosts. Touching inclusions are expected to have equilibrated to the same geotherm as xenoliths, while non-touching inclusions would reflect the T-P conditions at the time of entrapment. If the cratonic lithosphere of Udachnaya cooled to its current geotherm relatively early (Nestola et al. 2019), the lower xenolith T-P would indicate decompression and cooling.

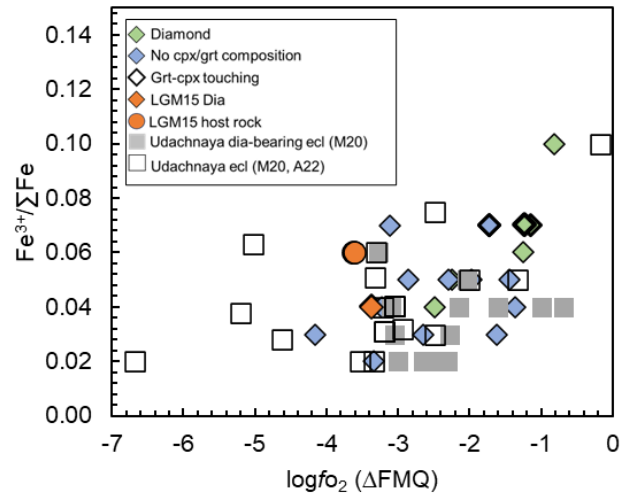
### Implications and Conclusions

The reconstructed bulk rock composition allowed to infer the protolith nature based on TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO versus MgO contents. The subducted protoliths are diverse and likely formed through low-P



**Figure 2:** a) Garnet and b) clinopyroxene inclusions compositions (this study) compared with literature Udachnaya eclogites and synthetic garnet and clinopyroxene used for the calibration of the eclogite oxy-thermobarometer (see the text).

differentiation of a basaltic melt. The  $f_{O_2}$  of the convecting mantle source from which the peridotite-derived protoliths formed, was estimated by comparing the reconstructed bulk V vs MgO relationship with models (Aulbach and Stachel 2022), with results indicating values between -2 and -1 log units  $\Delta FMQ$ , in agreement with the view of a slightly more reduced Archean ambient mantle compared to today. Here, the similar bulk V concentration for the host eclogite and inclusions (about 190 ppm) implies that V is a reliable proxy for retrieving the redox conditions of the protolith since the V concentration in the eclogite source, as sampled by the xenolith, was not modified by metasomatic processes. The  $Fe^{3+}$ -based calculated  $f_{O_2}$  for the eclogitic inclusions (i.e., the metamorphic minerals) ranges between -4 and -1 log units ( $\Delta FMQ$ ; Fig. 3), with similar  $f_{O_2}$ s recorded by inclusions in diamond LGM15 and the corresponding host eclogite (Fig. 3). This evidence indicates that the eclogitic mineral assemblage might, on average, preserve its redox state even during diamond formation processes, and thus can efficiently act as a redox buffer over time. Moreover, our results provide evidence of heterogeneous redox conditions at a local scale, likely related to the different nature of the former protoliths. The recorded  $f_{O_2}$ s suggest that diamonds grew from diverse fluids, from  $CH_4$ - $H_2O$  to  $CO_2$ - $H_2O$  dominated.



**Figure 3:**  $Fe^{3+}/\Sigma Fe$  ratio of garnet versus calculated  $\log f_{O_2}$  (FMQ) for E-type diamonds from this study and literature Udachnaya eclogites (see the text).

## References

- Aulbach, S. (2020). Temperature-dependent rutile solubility in garnet and clinopyroxene from mantle eclogite: implications for continental crust formation and V-based oxybarometry. *J Petrol*, 61(6), ega065.
- Aulbach, S., & Stachel, T. (2022). Evidence for oxygen-conserving diamond formation in redox buffered subducted oceanic crust sampled as eclogite. *Nature Communications*, 13(1), 1924.
- Aulbach, S., Woodland, A. B., Stagno, V., Korsakov, A. V., Mikhailenko, D., & Golovin, A. (2022).  $Fe^{3+}$  Distribution and  $Fe^{3+}/\Sigma Fe$ -Oxygen Fugacity Variations in Kimberlite-Borne Eclogite Xenoliths, with Comments on Thermobarometry. *J Petrol*, 63(8), egac076.
- Krogh, E. J. (1988). The garnet-clinopyroxene Fe-Mg geothermometer—a reinterpretation of existing experimental data. *Contributions to Mineralogy and Petrology*, 99(1), 44-48.
- Mikhailenko, D. S., Stagno, V., Korsakov, A. V., Andreozzi, G. B., Marras, G., Cerantola, V., & Malygina, E. V. (2020). Redox state determination of eclogite xenoliths from Udachnaya kimberlite pipe (Siberian craton), with some implications for the graphite/diamond formation. *Contrib Mineral Petrol*, 175, 1-17.
- Nestola, F., Jung, H., & Taylor, L. A. (2017). Mineral inclusions in diamonds may be synchronous but not syngenetic. *Nature Communications*, 8(1), 14168.
- Purwin, H., Lauterbach, S., Brey, G. P., Woodland, A. B., & Kleebe, H. J. (2013). An experimental study of the Fe oxidation states in garnet and clinopyroxene as a function of temperature in the system  $CaO-FeO-Fe_2O_3-MgO-Al_2O_3-SiO_2$ : implications for garnet-clinopyroxene geothermometry. *Contrib Mineral Petrol*, 165(4), 623-639.
- Stagno, V., Frost, D. J., McCammon, C. A., Mohseni, H., & Fei, Y. (2015). The oxygen fugacity at which graphite or diamond forms from carbonate-bearing melts in eclogitic rocks. *Contrib Mineral Petrol*, 169, 1-18.