

Oxidized and reduced Ni-rich phases in Voorspoed diamonds

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Introduction

Mantle xenoliths reveal a decrease in oxygen fugacity (fO_2) with depth down to ~250 km. This trend coincides with thermodynamic calculations and experimental results, which also predict a further, more modest, decrease in fO_2 following the stabilization of Ni-rich metallic alloy at 250-300 km. However, majoritic garnet inclusions in diamonds from the deep upper mantle and the transition zone record more oxidized conditions, and no Ni-rich alloy was ever reported from these regions to provide natural evidence for the predictions.

Results

Here we report a study of two unique diamonds from the Voorspoed mine, South Africa, ON-VRS-664 and ON-VRS-866. Both diamonds have an inner cloud of microinclusions, while ON-VRS-664 also carries mineral inclusions in the clear rim that surrounds the cloud. FTIR analyses indicate that both diamonds are type-II diamonds, but unknown absorption bands are present in the 900-1350 cm^{-1} range. Carbonate and CO_2 absorption bands were found in spectra of the central zone of diamond ON-VRS-664 (Fig. 1), but unlike other cloudy diamonds that carry high-density fluids (e.g. Kempe et al. 2021), no water was detected.

Nanoinclusions - A thin foil was cut from the cloudy region of each diamond using FIB and the two foils were analysed using TEM. Both carry octahedral nanoinclusions (mainly <80 nm) of solid $\delta-N_2$ (Fig. 2), of which most also hold a tiny (4-8 nm) Ni-Fe-rich phase with Ni# of ~85 (Ni# = $100 \times Ni / (Ni + Fe)$ molar ratio). The presence of $\delta-N_2$ in the cloudy zones was confirmed by Raman and synchrotron-XRD.

Microinclusions - TEM images of the foil cut from diamond ON-VRS-664 also revealed microinclusions (~500 to 1000 nm), that carry a Ni-rich carbonate along with a void. Selected area diffraction patterns taken from a single $(Ni,Fe)CO_3$ microinclusion indicate a trigonal symmetry and cell parameters that agree with those of gaspeite $(Ni,Mg)CO_3$ and ankerite. TEM-EDS yielded atomic proportions of 16% Ni, 3% Fe, 25% C, and 55% O, or $(Ni_{0.84}Fe_{0.16})C_{1.3}O_{2.9}$, not far from $(Ni,Fe)CO_3$. Many shallow subsurface microinclusions were analysed using an EPMA. Only Fe and Ni were detected with an average Ni# of 89 ± 4 (oxygen was observed but not quantified). The position of the carbonate IR bands also agree with those of gaspeite. No CO_2 nanoinclusions were found by TEM and the good correlation between the intensity of the 2390 and 660 cm^{-1} CO_2 peaks and the 1437 cm^{-1} carbonate peak suggests that the CO_2 occupies the voids in the carbonate microinclusions.

Mineral inclusions - Small mineral inclusions (up to 20 μm) were found in the clear outer zone surrounding the central cloud of diamond ON-VRS-664. They were identified by Raman and synchrotron-X-ray diffraction as coesite, Na-Al-rich pyroxene, olivine, Ulvospinel + ilmenite, and two inclusions with composition that is close to that of a NAL phase (with K substituting for Na): $K_{1.55}(Mg,Fe)_{0.68}Al_{4.24}Si_{2.09}O_{12}$ and $K_{1.18}(Mg,Fe)_{1.46}Al_{4.88}Si_{1.18}O_{12}$. The Raman spectrum of the latter shows only limited correlation with the sole Na-rich NAL spectrum available in the literature.

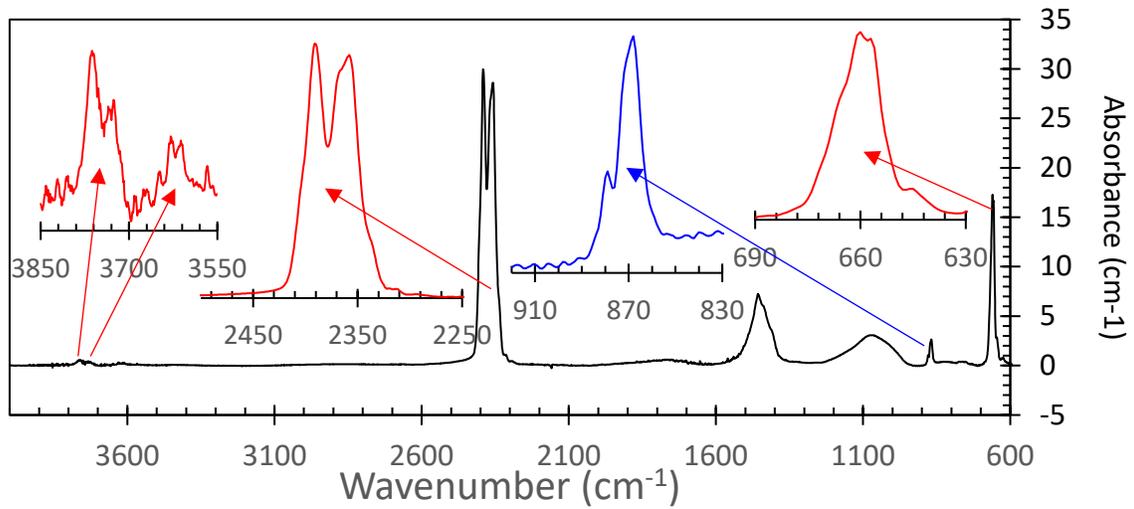


Figure 1: Residual spectrum (after subtraction of a type II diamond spectrum and baseline correction) collected from the central cloud of diamond ON-VRS-664 (black line). The bands at ~ 660 , 2360 , 2390 , 3615 , and 3760 cm^{-1} are attributed to solid molecular CO_2 under pressure. They are expanded (red spectra) to reveal their complex nature. The lines at 870 and 1440 cm^{-1} are due to carbonate absorption and fit the spectrum of $(\text{Ni},\text{Mg})\text{CO}_3$ gaspeite. The spectrum of the narrow band of carbonate at ~ 870 cm^{-1} (in blue) reveals an additional small peak at ~ 880 cm^{-1} .

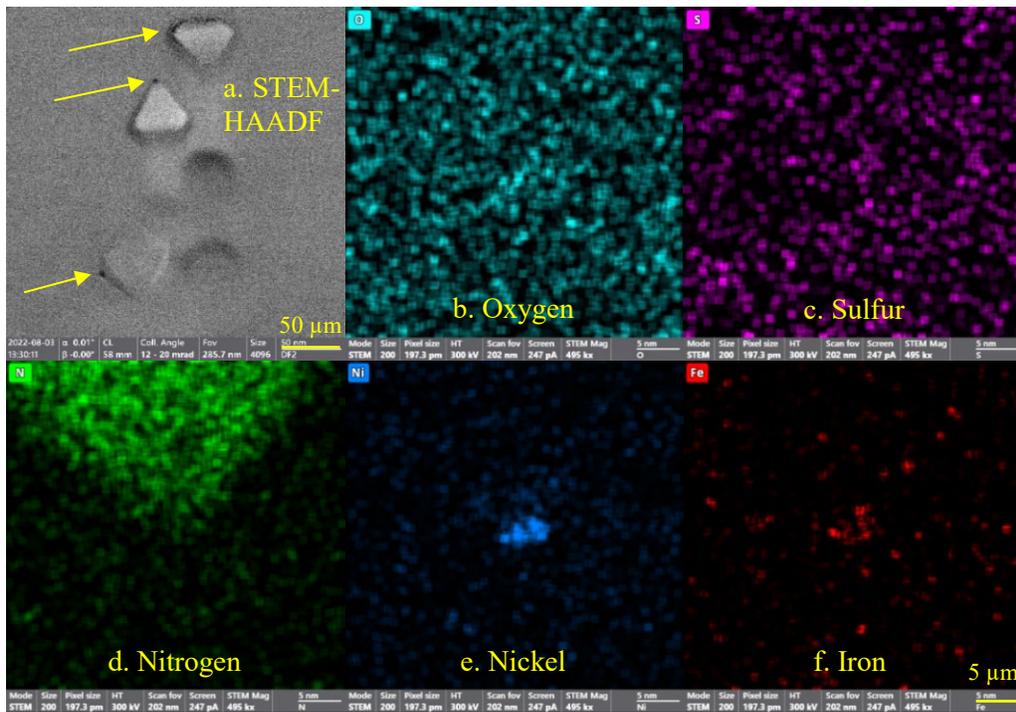


Figure 2: TEM of nano-inclusions. a. An image showing two open and three closed octahedral nano-inclusions, ~ 35 - 50 nm in size. Small dark spots (pointed by arrows) in the apexes of two inclusions mark the presence of high electron-density material. b-f. TEM-EDS maps of the apex of a similar inclusion. Nitrogen is the main constituent of the nano-inclusion and its high concentration (in bright green) reveals the border of the inclusion. Nickel and, to a lesser degree, iron are the main constituents of the dense phase at the apex. The size of this phase is ~ 5 nm. Oxygen and sulfur are present, at noise level, all over the map. We suggest that the Ni-Fe phase is metallic with $\sim 85\%$ Ni, but the possibility of a carbide cannot be excluded due to the high carbon background from the diamond.

Pressure indicators and depth of origin

Various pressure indicators confirm a source within the deep upper mantle or the shallow transition zone. The $\delta\text{-N}_2$ is under pressure of 8-9 GPa at room temperature and originated from pressures above 14 GPa at mantle temperatures (see Navon et al., 2017). The ν_3 CO_2 IR absorbance at 2390 cm^{-1} fits the single peak of solid $\text{CO}_2\text{-I}$ at 8 GPa (Hanson et al., 1981), and extrapolation to mantle temperatures suggests origin at 11 or 17 GPa (the double peak at $\sim 2360\text{ cm}^{-1}$ remains unexplained). Of the various mineral inclusions, coesite Raman lines indicate a minimum mantle entrapment pressure of ~ 9 GPa, and the possible presence of K-rich NAL-phase inclusions suggests pressures of ≥ 16 GPa. Together, the nitrogen and the CO_2 in the cloud, and the coesite and NAL phase in the outer zone suggest a pressure of origin between 9-16 GPa, corresponding to a depth range of 280-470 km in the deep upper mantle to the shallow transition zone.

Discussion

Such rare coexistence of a Ni-rich metallic phase and a carbonate phase indicates a metasomatic reaction between an oxidized carbonatitic melt that penetrated a reduced metal-bearing peridotite and led to reaction and diamond growth. The Ni# of both phases is higher than predicted at the Ni-saturation depth (Ni# \approx 50-60; Frost and McCammon, 2008). We propose that the carbonatitic melt induced a transient, higher $f\text{O}_2$ environment, where iron in the alloy was preferentially oxidized to Fe^{2+} (relative to Ni) and entered the silicate phases. As a result, the residual metallic phase evolved towards a high Ni#, and the Ni-rich carbonate was formed. Diamond formation also took place as part of such a reaction: $2\text{Ni}_{(\text{metal})} + 3\text{MgCO}_{3(\text{carbonatitic melt})} + 3\text{MgSiO}_{3(\text{pyroxene})} = \text{C}_{(\text{diamond})} + 2\text{NiCO}_{3(\text{carbonate})} + 3\text{Mg}_2\text{SiO}_4(\text{olivine})$.

The outcome of such a reaction is the formation of oxidized zones in the deep upper mantle and the shallow transition zone. Majoritic garnet inclusions in diamonds from Jagersfontein (Kiseeva et al., 2018) also record such oxidizing conditions. Thus, carbonatitic metasomatism may lead to the formation of oxidized zones in the deep upper mantle. The extent of such zones is likely limited due to the very small melt fraction and small volume of the melts. However, we suggest that over time, recurring of such carbonatitic metasomatism may lead to an overall increase in the $f\text{O}_2$ of the upper mantle.

The Ni-rich phases may contribute to the formation of Ni-rich basalts. Indeed, they are transient reaction products. In the scenario we described, the nickel comes from the mantle and, over time, the Ni-rich metallic phase or the Ni-carbonate would equilibrate with the dominant silicate fraction and would take more Fe. However, due to their less refractory nature and while they exist, they may be incorporated preferentially into the melt phase during a melting event or into a passing, ascending deeper magma.

References

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