

Analytical techniques

Selected diamonds were investigated for their carbon and nitrogen isotopes, nitrogen content and inclusions. Prior to SIMS analysis for their C isotopes, N abundances and N isotopic compositions, the diamonds were mounted in epoxy, polished and then imaged by cathodoluminescence (CL) using a Zeiss EVO scanning electron microscope (SEM; CAGS). Carbon isotope ratios ($^{13}\text{C}/^{12}\text{C}$), nitrogen abundances and nitrogen isotope ratios ($^{15}\text{N}/^{14}\text{N}$) were determined using the CAMECA 1280-HR large geometry Secondary Ion Mass Spectrometer (SIMS) at the GeoForschungsZentrum (GFZ), Potsdam, Germany. Prior to analysis, the diamond mounts were again polished for 10 minutes and twice cleaned for 5 minutes using high-purity ethanol (purity >99.8%) in an ultrasonic bath. Diamond mounts were sputter coated with a 35-nm-thick, high-purity gold film to assure electric conductivity, and then placed in a low magnetic susceptibility SIMS sample holder, being held in place with tension springs. Carbon isotope measurements were performed using an ~ 2 nA $^{133}\text{Cs}^+$ primary beam with a total impact energy of 20 KeV, which was focused to an ~ 10 μm diameter Gaussian spot on the polished sample surface. The target area on the sample was pre-sputtered for 90 s using a 20 μm square raster to remove the gold coat and to suppress any surface contamination. A 10 μm raster (in conjunction with the dynamic transfer to compensate for the raster) was applied during analyses in order to assure a more uniform primary beam and a flat-bottom sputter crater. Low energy electron flooding (diameter ~ 100 μm ; 1.5 μA current flow from the sample holder) was used to suppress charge build up on the

sample surface at the point of primary beam impact. The electron cloud was carefully centred under the secondary ion extraction optics at the beginning of the session.

Negative secondary ions were extracted at 10 kV and these ions were guided into the mass spectrometer, which was operated in multi-collection mode, using a mass resolution of $M/\Delta M \approx 4004$. The $^{12}\text{C}^-$ and $^{13}\text{C}^-$ were collected using Faraday cups at the L'2 and FC2 positions using $10\text{E}+10 \ \Omega$ and $10\text{E}+11 \ \Omega$ resistors, respectively. The $^{12}\text{C}^-$ count rate on the diamonds was typically 1.4 billion ions per second. A single analysis consisted of 20 cycles of 4 s each. In order to assure maximum stability, the 1280-HR magnetic field was monitored throughout using a nuclear magnetic resonance-controlled feedback loop. All data were filtered for analytical outliers at the 3 standard deviation (SD) level. A single carbon isotope analysis, including the pre-sputtering and centering routines, lasted around 190 s.

N contents and isotope ratios were measured adjacent to the locations of the carbon isotope analyses. Nitrogen isotope measurements were acquired following a procedure similar to that used for carbon isotope ratio determinations, but with some minor differences. Nitrogen isotope measurements used a 10 pA $^{133}\text{Cs}^+$ primary beam current and the sample was pre-sputtered for 200 s using a 20 μm square raster. The mass spectrometer was operated in mono-collection mode, with a mass resolution of $M/\Delta M \approx 8880$. The $^{12}\text{C}^{14}\text{N}$ and $^{12}\text{C}^{15}\text{N}$ were collected using an ETP 133H electron multiplier, to which a synthetic 46.2 ns dead time was applied to the preamplifier circuit. Each nitrogen isotope analysis consisted of 25 cycles of 1 s for $^{12}\text{C}^{12}\text{C}^-$ (1 s

integration), $^{12}\text{C}^{14}\text{N}$ - (4 s), and $^{12}\text{C}^{15}\text{N}$ - (15 s). A single nitrogen isotope analysis, including the pre-sputtering and centering routines lasted around 12 min.

Internal features of the diamonds and their inclusions were investigated using transmission electron microscopy (TEM) at the Helmholtz Centre, Potsdam. Seven electron-transparent foils from five of the diamonds were prepared using the focused ion beam (FIB) technique: foils 5006 and 5015 from grain E180-1; foil 5008 from grain E180-2; foil 5013 from grain E180-3; foil 5012 from grain E180-4; and foils 5010 and 5017 from grain E180-5. Details of the FIB sample preparation are given in Wirth (2004, 2009). The electron-transparent foils were studied with a TECNAI F20 XTWIN transmission electron microscope operated at 200 kV with a field emission gun electron source. The TEM was equipped with a Gatan imaging filter (GIF) TridiemTM, a Fishione high-angle annular dark-field (HAADF) detector and an EDAX GenesisTM X-ray analyzer. Electron diffraction, bright-field and dark-field imaging, lattice-fringe imaging, X-ray analysis and electron energy-loss spectroscopy (EELS) were used to investigate the foils.

EELS was performed in the diffraction mode at a camera length of 700 mm. The spectrometer entrance aperture was 2 mm, and the spectrum dispersion was 0.1 eV/channel. The resolution using the zero-loss peak was determined at full width at half intensity to be 0.9 eV. The spectrum was background subtracted using a power-law background model. Plural scattering was removed from the original spectrum by applying the Fourier ratio method.

The chemical composition of the inclusions was determined by analytical electron microscopy (AEM). AEM was performed with an X-ray analyzer with an ultra-thin window. EDX analyses were performed by scanning a pre-selected area, thus avoiding mass loss. The size of the window depended on the size of the object and was generally 50×50 nm. The sample was tilted 20° towards the detector prior to data acquisition. Acquisition time was 60 s at an average count rate of approximately 60–100 counts/s. EDX spectra were usually acquired in the scanning transmission mode (STEM) using the TIA™ software package of the TEM and used for qualitative and standard based quantitative chemical analysis (Wirth 2009). The NiMnCo alloy was calculated in at% with uncertainty estimates of ± 3%. The calculated diffraction patterns (fast Fourier transform, or FFT) from high-resolution lattice-fringe images were used for phase identification as well as electron diffraction patterns that were acquired on image plates. The d_{hkl} -spacing calculated from the FFT was compared with the calculated d_{hkl} -spacing based on lattice parameters for the respective mineral or compound from literature data. Additionally, the measured angles between adjacent diffraction vectors were compared with the calculated angles. Only a good agreement of both measured angles ($< 1^\circ$) and d_{hkl} -spacing with calculated data was used for the identification of phases.

REFERENCES

- Wirth, R. (2004) Focused Ion Beam (FIB): A novel technology for advanced application of micro- and nanoanalysis in geosciences and applied mineralogy. *European Journal of Mineralogy*, 16, 863-876.

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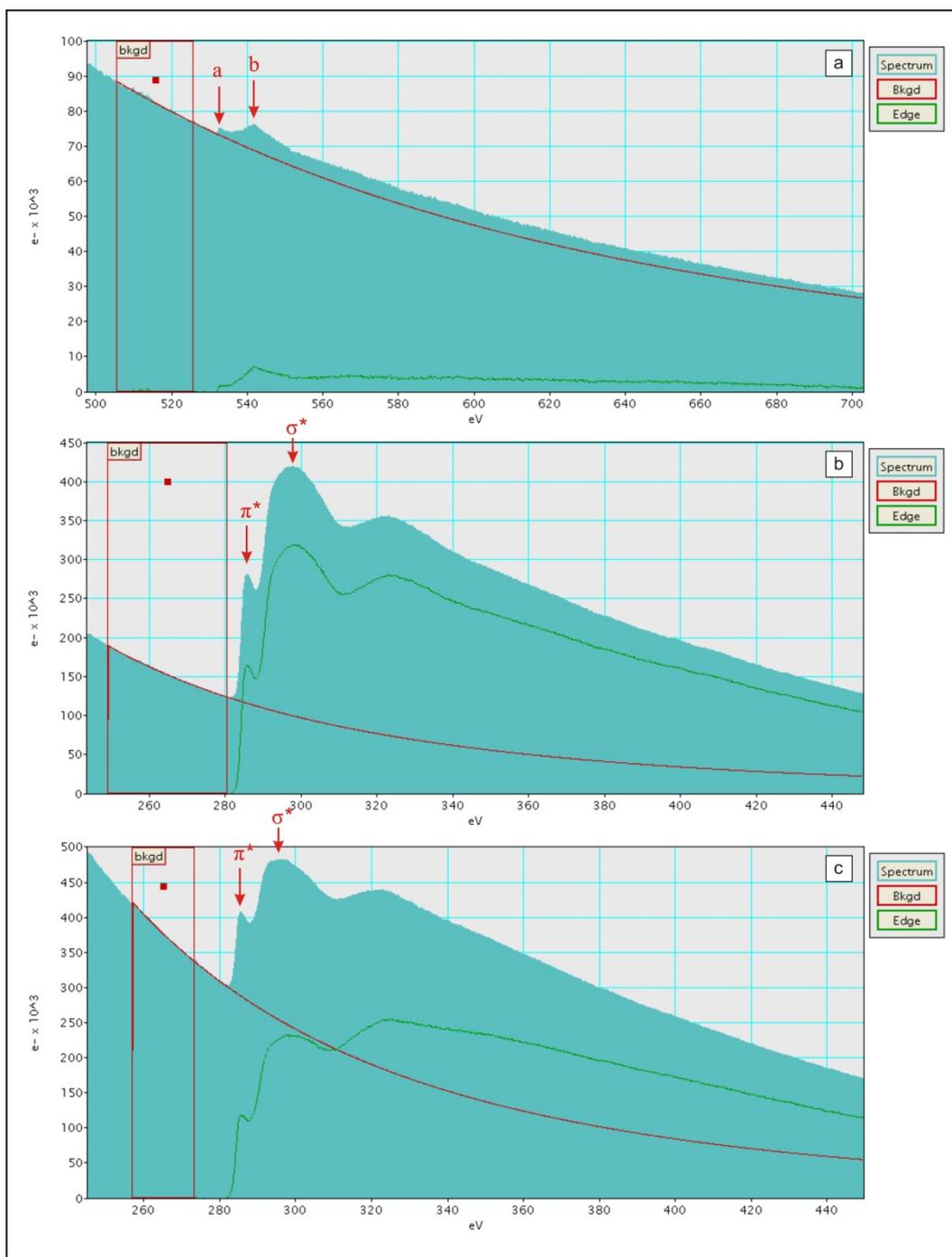


FIGURE A1. (a) Electron energy-loss spectrum (EELS) showing the O K-edge of inclusion 2. **(b)** and **(c)** EELS spectra showing the C K-edge of the inclusions 1 and 2, respectively. The broad, featureless σ^* peak, indicating many randomly oriented bonding configurations, is typical of amorphous material.