

## Nano and sub-micro inclusions as probes into the origin and history of natural diamonds

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### ABSTRACT

Five natural faceted diamond samples, considered to have inherent submicroscopic and nanometric inclusions, were studied using various techniques such as Raman spectroscopy, Raman microscopy, scanning electron microscopy (SEM), and energy dispersive analysis of X-rays (EDAX). The principal focus was to find out the chemical nature of the inclusions and their distribution. As a confirmative tool, laser desorption ionization mass spectrometry (LDI MS) was used for the characterization of the inclusions. Our study suggests that the inclusions in diamond belong to the pyroxene group of silicate minerals with Fe, Mg, Ca, Ru, and Cr as the major elements. As evidenced by the absence of alkali, aluminum, and rare earth elements in the inclusion, the diamond can be of peridotitic origin. Interestingly, we found that chromium scavenges Ru, a platinum group element (PGE), and other metals such as Nb, Co, and Ni, entrained into the pyroxene inclusions. We established that the diamond sample in which inclusions are found is of Kimberlitic origin.

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### 1. Introduction

Among various gem stones, diamond is considered as the prince of solids, since it is relatively inert, unreactive and hard. Due to this reason, its formation, genetic history and environment at which it formed have been looked at in great detail. Since purest diamonds, free from any inclusions, do not shed any light on their history, the studies of primary mineral inclusions [1] such as those crystallized and encapsulated during (syngenetic) or before (protophenetic) the growth of the gems throw light on their genesis as well as its physical and chemical history. These mineral inclusions are important indicative sources of information on the composition of continental lithospheric mantle at depths exceeding 120–150 km and deeper, from where the genesis of diamond is now traced [2]. They also point out a vital knowledge of the mass balance and depth dependant distribution of certain elements such as carbon and sulfur. The existence of metals like Au, Pt, Pd, etc., as inclusions in diamond can give an idea about the potential areas and deposits of such elements, and may have important implications to the mining industry.

The host rocks of diamonds have been investigated extensively over the past few decades in search of their origin and genesis [3]. Formation of diamond occurs in the interior of Earth from the peridotite or eclogite mineral assemblages [4]. Peridotites are predominantly made up of silicates of magnesium and iron and they

are derived from Kimberlitic rocks (xenoliths), whereas eclogites are derived from lamproite related xenoliths which are made up of garnetiferous (aluminous ferromagnesian silicate) mineral assemblages. Isotopic dating method reveals that many diamonds are older than their host kimberlite or lamproite [5]. Prospective regions of diamondiferous provinces or more appropriately termed as provenances were hitherto inferred based on geochemistry [6]. In recent years, a new geophysical method called magnetotelluric [7] technique, a cost-effective and rapid method, has been used to look into the mantle and detect the diamond-prospective regions [8].

Raman spectroscopy is a useful tool to study the chemical/molecular composition of the materials, their bonding, crystal and electronic structure, phases as well as strain at micron and sub-micron sizes [9]. The technique is highly useful for the identification of inclusions [10] with its paragenesis because each carbon allotrope displays a clearly identifiable Raman signature, which can easily be distinguished from that of the inclusions. It therefore provides a clear fingerprint by which the material can be identified even from a micron or nanoscale sample area or volume under analysis [11]. Internal pressure inside the diamond can be monitored from the inclusions, since diamonds are capable of sustaining high internal confining pressure on its inclusions. This internal pressure reflects as a shift in the peak position of the Raman features of the inclusions. Raman spectroscopic data when combined with scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDAX) can give a very clear picture of the inclusions present inside diamonds and thereby the history of the host. In several earlier reports, fragmentation and combustion of the host have been used to liberate

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the inclusions for the analysis [12]. In the case of diamonds with inclusions of different parageneses, this method is not effective as the spatial relationships between the mineral grains themselves and the different growth zones of the host diamond will be lost upon crushing [12c,13]. Herein, we demonstrate the characterization of sub-micron or nanometric inclusions inside the diamonds in a non-destructive manner by using a wide range of spectroscopic and microscopic techniques. An attempt to image inclusions using Raman microscopy in conjunction with electron microscopy and elemental imaging is the principal focus of this paper.

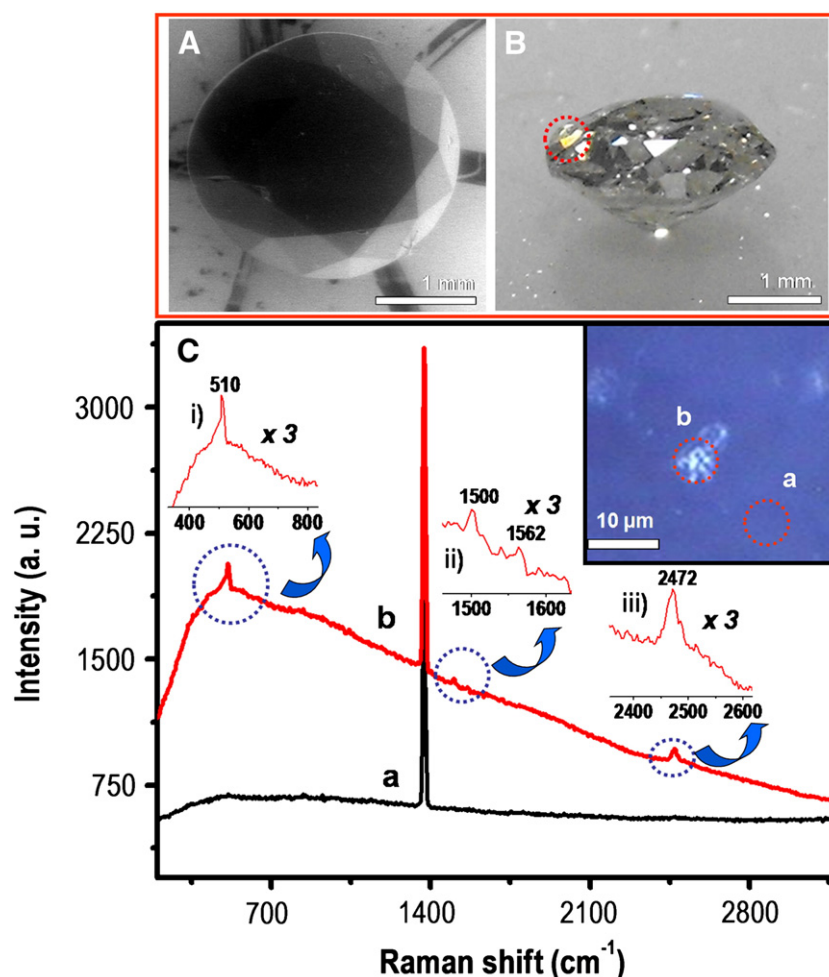
## 2. Experimental

Five natural well faceted diamond samples, ranging between 0.75 and 1.35 carats, were cleaned with distilled water and ethanol for removing all physisorbed impurities such as dust, grease, etc. Each cleaned diamond specimen was anchored with its culet (pointed cone) sticking on a conducting carbon tape which in turn was stuck on an indium tin oxide (ITO) glass substrate for observation. The optical and Raman measurements were done using a Witec GmbH confocal Raman spectrometer equipped with a 532 nm laser. For measuring Raman images of the inclusions, the diamond samples, anchored on the ITO plate, were mounted on a piezo-equipped scan stage of the Raman spectrometer. The signals were then dispersed using a 600 grooves/mm grating. The back-scattered light was collected by a 20× objective at an integration time of 50 ms and sent to the spectrometer through a multimode fiber. The dispersed light was

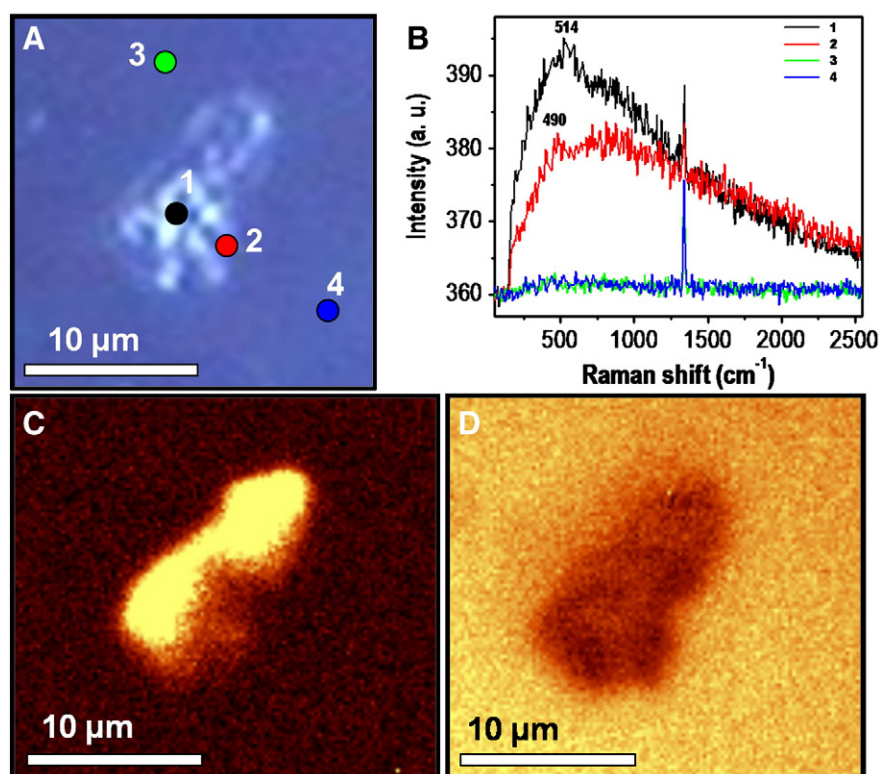
collected by a Peltier cooled charge coupled device (CCD) detector. Spectra from various parts of the Raman image were collected and analyzed. For spectral imaging, the desired area was partitioned into 10,000 squares (an imaginary  $100 \times 100$  matrix drawn over it), with each square representing a sampling point and consequently a pixel for the image. Intensities of the desired portion of the spectra, collected over all the pixels, were compared by Scan CTRL Spectroscopy using the Version 1.32 software to construct a color-coded image. Spectral intensities acquired over a predefined area were automatically compared to generate color-coded images. Laser desorption/ionization mass spectrometric (LDI MS) studies were conducted using a Voyager DE PRO Biospectrometry Workstation (Applied Biosystems) matrix assisted laser desorption/ionization-time of flight-mass spectrometer (MALDI-TOF-MS). A pulsed nitrogen laser of 337 nm was used (maximum firing rate: 20 Hz, maximum pulse energy: 300  $\mu$ J) for the LDI MS studies. Spectra were collected in the positive ion mode. SEM and EDAX studies were done in a FEI QUANTA-200 SEM. In order to minimize the charging effect, SEM measurements were done at low vacuum mode using a large field detector.

## 3. Results and discussion

For studying the nano/micro inclusions in the diamonds, we selected five different diamond samples from various sources. Out of these five samples, results from one sample in which the inclusions were of a definite nature, and observed with characteristic signatures,



**Fig. 1.** SEM image (A) and corresponding photograph (B) of the diamond sample containing inclusions. (C) Raman spectra collected from two different areas of the diamond, marked 'a' and 'b' in the optical image, shown in the inset. Weak Raman features are expanded. The optical image is from a face marked in B. The impurity features in Raman are marked in C.



**Fig. 2.** (A) Optical image of the diamond sample. (B) Raman spectra collected from different regions marked in A. (C) and (D) are corresponding Raman images created by collecting the intensities in the range of  $100\text{--}750\text{ cm}^{-1}$  and  $1300\text{--}1400\text{ cm}^{-1}$ , respectively.

on several faces of the sample, are presented here. To locate the regions with defects, samples were examined in detail using optical microscopy. Potential locations at which inclusions are possible were examined in detail using SEM, EDAX, LDI MS, and confocal Raman microscopy (CRM). A large area SEM image and corresponding photograph of the sample used for this study are shown in Fig. 1A and B, respectively. Optical images from different locations were collected at suitable magnifications in search of inclusions. We observed that certain areas were looking much brighter than others in reflected white light. These areas had inclusions and are shown in the inset of Fig. 1C. Two important locations identified as 'a' and 'b', are marked in the optical image. In order to check their chemical nature, Raman spectra were collected from these positions (traces in Fig. 1C). There are three significant Raman features in the spectra collected from the brighter portions (location 'b'). A sharp and intense line at  $1332 \pm 2\text{ cm}^{-1}$  is due to the oscillation of two interpenetrating Bravais lattices of tetrahedrally bonded carbon atoms in diamond [14]. In addition to this first order Raman feature, we find yet another Raman peak around  $2472\text{ cm}^{-1}$ , which is attributed to the second order Raman feature of diamond [15]. The second order Raman features of diamond are normally considered about 250 times weaker than the first order peak, is found in the range of  $2200\text{ to }2700\text{ cm}^{-1}$  with several bands depending upon the degree of its crystallinity [15,16]. Obviously these are regions of diamond in which the tetrahedral structure is affected. Two tiny Raman peaks observed at  $1500$  and  $1562\text{ cm}^{-1}$  can be attributed to the first order spectra of carbonaceous matter present inside diamond [17,18].

Besides these two Raman features, a third less pronounced peak with a broad band around  $510\text{ cm}^{-1}$  was observed in the spectrum collected from location 'b'. This sits on a broad feature. This signature can only be caused by non-carbonaceous inclusions in diamond. Raman spectrum from position 'a' did not show any features other than the prominent diamond feature at  $1332\text{ cm}^{-1}$ . This observation points towards the fact that the brighter areas in the sample may be due to nano/micron sized inclusions. Such kind of brighter areas in the

image were not seen over the entire sample but were highly localized. The rare nature of these inclusions was further confirmed by collecting the Raman image of the brighter area.

Optical and corresponding Raman images collected from position 'b' are shown in Fig. 2. From the Raman images, we were able to identify and delineate clearly two different zones, brighter and darker in nature. To check the existence of inclusions in diamond or other similar features inside diamond, we selected the broad Raman features appearing in the range of  $100\text{ to }750\text{ cm}^{-1}$ , to generate a Raman image (Fig. 2C). Interestingly, we found a difference in the intensity of the Raman signals only at the brighter area seen in the optical image. Qualitatively, this region with an orange–yellow tinge is recognized as the inclusion and the darker region as the non-inclusion zone. We also created the Raman image by collecting the intensities ranging from  $1300\text{ to }1400\text{ cm}^{-1}$  (Fig. 2D), where the vibration due to C–C bond in diamond appears. In this case, we found that the Raman intensity was less at the brighter portion as shown in Fig. 2C. This indicates that a substantial amount of diamond is replaced by impurities which appear as dark regions in the Raman image (Fig. 2D). The inclusion features are accompanied by the second order feature at  $2472\text{ cm}^{-1}$ , as seen by the brighter intensity of that image (Fig. 1C). Similar kind of Raman features was seen from other areas as well (Supplementary data Fig. S1).

In order to study the chemical composition, Raman spectra from different regions of the inclusions were studied. A uniform Raman feature throughout the entire area of the inclusion was expected if the composition is the same everywhere and the object is a single piece of micron size. But the Raman data suggest that composition of the inclusion is not uniform. Fig. 2B shows the single Raman spectra (without averaging, collected with  $50\text{ ms}$  integration time; a collection of such spectra constitute the image) collected from various regions of the diamond marked in the optical image. Apart from the characteristic Raman signal of diamond at  $1332\text{ cm}^{-1}$ , a peak at  $514\text{ cm}^{-1}$  was also observed. Along with this, a broad band was observed around  $800\text{ cm}^{-1}$ . Careful investigation of the Raman



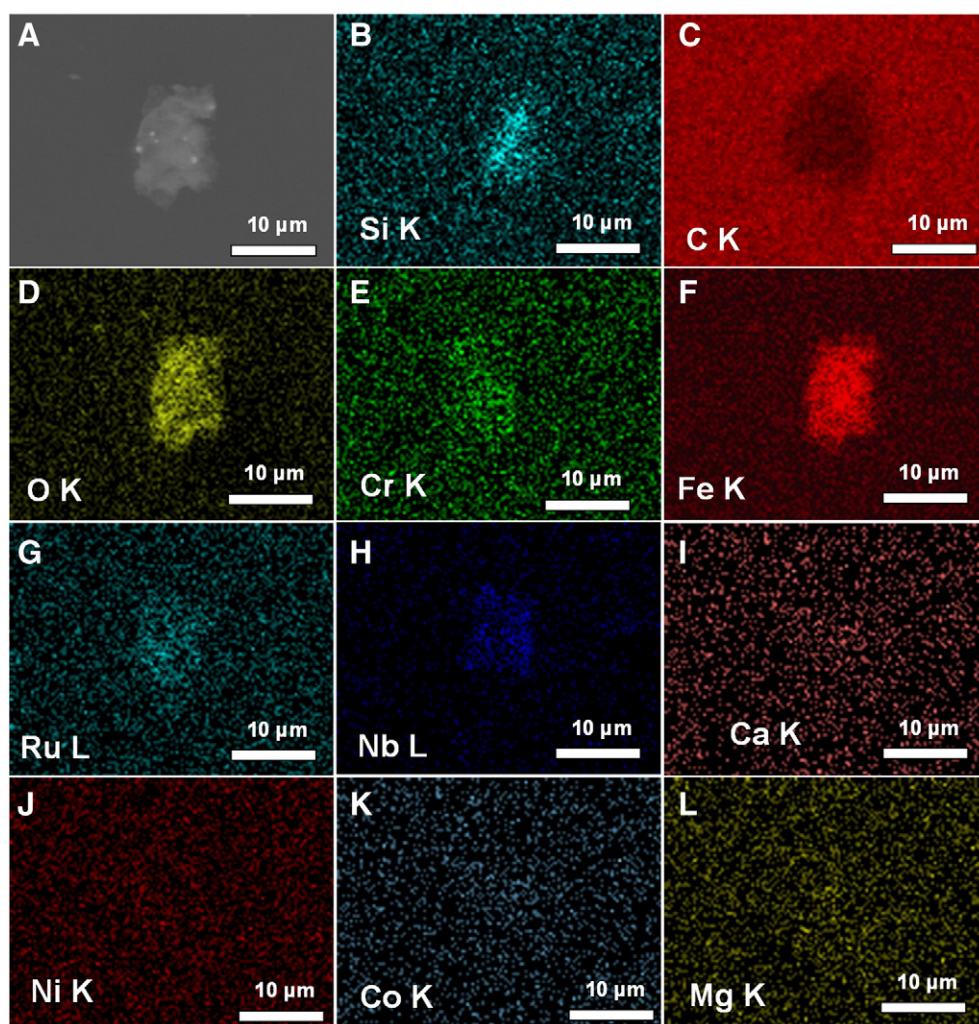


Fig. 3. SEM image (A) and corresponding EDAX maps (B–L) of the diamond containing inclusions.

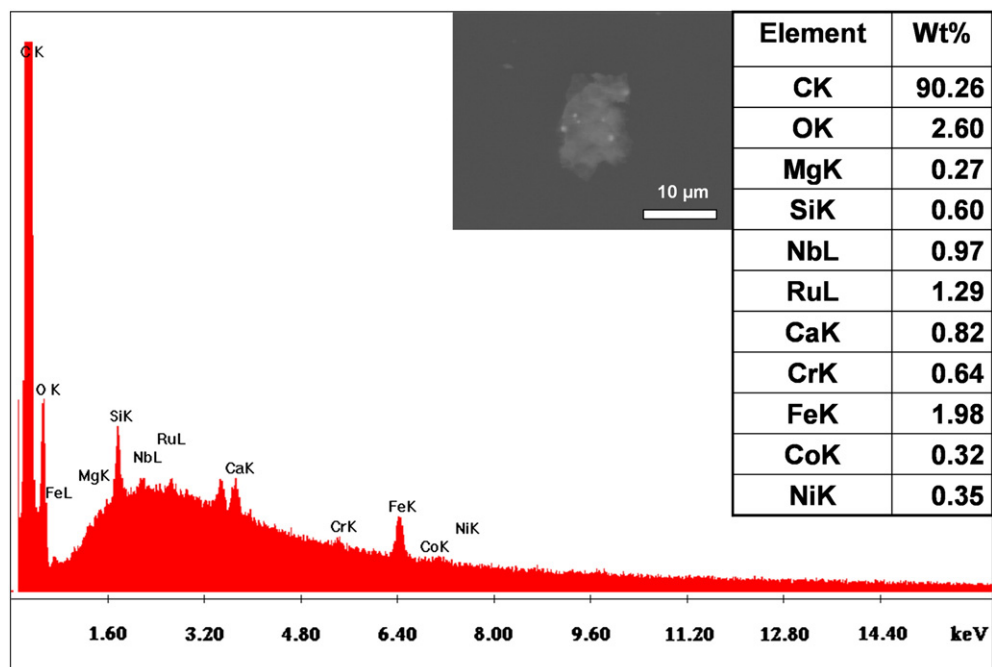


Fig. 4. EDAX spectrum and quantification data collected from the inclusion shown in the inset.

spectra suggests that the vibration observed around  $514\text{ cm}^{-1}$  at position 1 got shifted to  $\sim 490\text{ cm}^{-1}$  at position 2 of the same inclusion (Fig. 2B). A substantial increase in the intensity of the shoulder band around  $800\text{ cm}^{-1}$  was observed at position 2, compared to 1. The variations in the Raman spectral features at different locations of the same inclusion suggest that they are aggregates of smaller nanograins of distinct composition, which appeared as a micron-size structure. This was confirmed by the EDAX images.

It is known that the Raman spectral features of oxides of iron occur near to those of silicate minerals, which contribute to the wide band around  $500\text{ cm}^{-1}$  [19]. In our case also, a broad feature was found near  $500\text{ cm}^{-1}$ . From the mantle geochemistry, it is known that carbonates and silicates of ferromagnetic minerals (pyroxenes) are the major raw materials for the nucleation and growth of diamond. Hence, smaller quantities of these minerals are safely protected and well shielded as inclusions in the host diamond [20]. Therefore, the observed Raman feature in this specific case may be due to the pyroxene group.

In order to further understand the chemical composition of the inclusion, EDAX analysis was carried out. SEM and corresponding EDAX images of the inclusion are shown in Fig. 3. The same region, examined by Raman was probed here. EDAX spectrum and quantification data collected from the inclusions are shown in Fig. 4. The EDAX data also corroborate with the chemistry of pyroxene with a ternary perovskite structure with Fe, Mg, and Ca silicates. From these data, we came into a conclusion that the broad Raman feature observed around  $510\text{ cm}^{-1}$  can be attributed to the collective vibrations of the isostructural members of the pyroxene group of silicate minerals. Also, we saw the presence of Cr in the inclusion which is of peridotitic origin. We observed the presence of a platinum group element (PGE) ruthenium, and other metals such as niobium, cobalt and nickel, as can be seen in the elemental analysis of the sample (Figs. 3 and 4). Careful investigation of the EDAX images also suggests that the composition of the inclusions is not uniform throughout, which was confirmed by the Raman study. Some of the characteristic peaks of pyroxenes were masked by the fluorescence

background observed in the Raman spectra. Fluorescence is an obvious phenomenon in such a case, where pyroxene is a major inclusion. Our studies confirm that the inclusion is a silicate of pyroxene group, a vestige or an exhumed reaction product from the parental pyroxene group of minerals. It is important to note that a few of the elements labeled are below the quantitation limits of EDAX (0.5 wt.%). Among a few other possibilities, chemically acceptable elements, considering the geochemistry of the region are chosen. Also, the spot EDAX taken from certain regions of the inclusion showed the presence of these elements in considerable quantities, well above the detection limit of EDAX.

EDAX data collected from other locations of the same sample showed the presence of the same elements (Supplementary data Fig. S2). We found an interesting platinum group element Ru, attached to chromium, along with Ni and Co, which is part of the pyroxene mineral group. We did not see any other elements and Raman features other than those presented. The studies showed that the kind of inclusions present throughout this particular diamond is the same, although the composition is different.

We have also analyzed thoroughly four other diamond samples using Raman spectroscopy. But we could not find any definite signatures of inclusions in them. Raman spectra collected from these different samples at various locations and their optical images are presented in the Supplementary data Fig. S3.

We made an attempt to confirm the presence of various elements using LDI MS. This was important as many of the elements suggested by EDAX are near the detection limit. For LDI measurements, the diamond sample was fixed on a slot, made for this purpose on a LDI MS sample plate, and spectra were collected from various regions of the diamond. The mass spectrum collected in the linear positive mode from the sample is shown in Fig. 5A. As expected, distinct elemental features were obtained only from specific regions of the diamond and not from the entire sample, which suggest the localized existence of the inclusion. The spectrum shows too many peaks as shown in Fig. 5A, and a wide

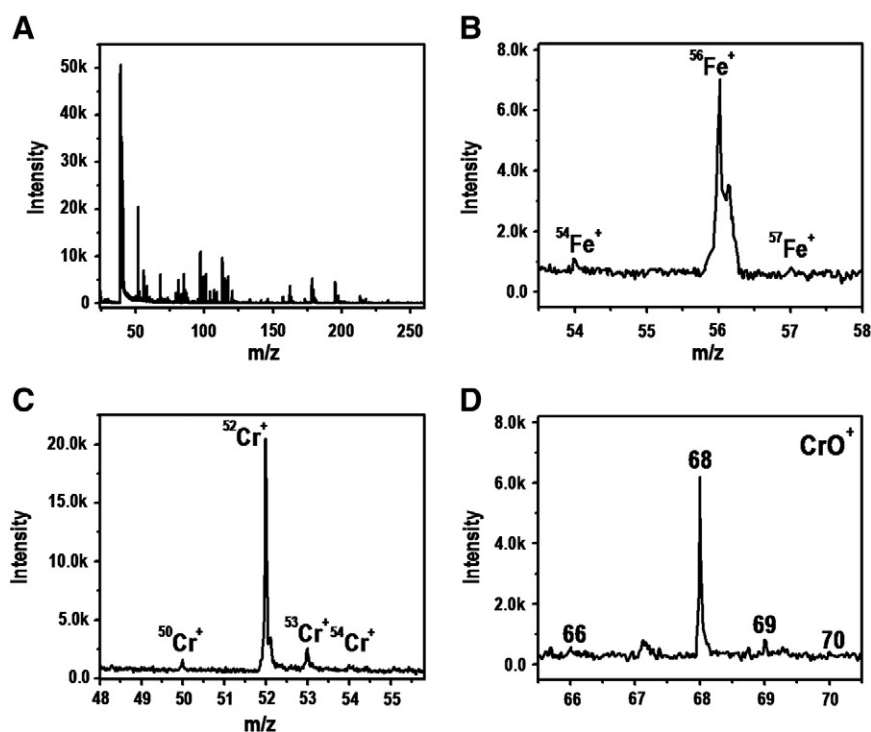


Fig. 5. (A) LDI mass spectra of diamond collected in the positive mode. B–D are the expanded view of the mass spectra showing the mass peaks due to Fe, Cr, and CrO, respectively. All the three mass spectra show good isotopic distribution, which are in agreement with the theoretical distribution.

range of elements are possible. Nevertheless, we could see the mass features of iron and chromium clearly in the LDI MS spectra (Fig. 5B–D). From Fig. 5B it is clear that the mass peak observed at  $m/z$  56 is due to iron. The isotope pattern also confirms it. Fig. 5C shows the expanded mass region for chromium ( $m/z$  52). Well defined isotope distribution clearly suggests the presence of chromium within the inclusion. We could also see the mass feature due to CrO at  $m/z$  68, which also showed the expected isotope pattern, which was in good agreement with the spectra from such materials [21]. Even though we could see the mass features of certain other elements, which were observed in the EDAX, the isotope pattern could not be resolved due to the overlap of other mass peaks. The difference in LDI and EDAX data could also be due to the difference in the surface sensitivity of the techniques. Nevertheless, the existence of Cr, which functions as a scavenger to all the available PGEs, substantiates the possible existence of PGEs in the inclusion.

The essential mineral assemblages for the host rock of diamond during its nucleation are two types of ultra basic suite of rocks known as peridotite and eclogite which have definite index minerals for each type [22]. As evidenced by the absence of characteristic eclogitic mineral assemblages such as aluminum, alkali, and rare earth elements (REE) in the inclusion, the diamond can be of peridotitic origin. The essential associated constituent mineral assemblages of the primary ferromagnesian silicate of pyroxene were found in our sample which reveals that our sample clearly belongs to peridotite (P-type) and not to the eclogite (E-type) source materials. Besides, we found the presence of chromium in our sample, which is known to be predominantly reflected in peridotite type of diamond host. Interestingly, we found that Ru, a PGE, is present in the inclusion. Platinum group metals have inherent affinity to chromites [23]. Here, chromium plays an important role of scavenging the available PGEs and got attached into the silicate inclusions (pyroxene) in diamond. The occurrence of Ru-bearing platinum group mineral (PGM) within chromite deposit has already been established [24]. Due to the high melting point, PGEs such as Os, Ir, and Ru will undergo crystallization from the magma before chromite [25]. Afterwards, at the time of crystallization of chromite, these PGEs may get entrapped into the chromite grains.

Though the inclusions of silicate as pyroxene in a diamond are known, the presence of chromium, its role as a scavenger to all the available PGEs in mantle is an interesting finding, which can be correlated to the chromite complex with PGMs as Bushveld complex [26], found in the north eastern part of South Africa [27]. In view of the presence of peridotitic mineral assemblages and the absence of characteristic eclogitic source minerals in the inclusion, the origin of the diamond sample can be related to the source of diamonds from the Kimberley mines. Our studies open up a large possibility of finding the genesis of various gemstones other than diamond, by looking at the nano/micron inclusions.

#### 4. Conclusion

In summary, we studied the existence of inclusions in diamond samples using Raman spectroscopy and elemental mapping. Also, we made use of LDI MS for the characterization of the inclusion. It was found that the inclusions in diamond belong to the pyroxene group of silicate minerals with Fe, Mg, Nb, Ca, Ru, and Cr as the major elements. Studies reveal that the inclusions can be traced to the peridotitic parental source rock and not eclogitic group, as evidenced by the absence of alkali, aluminum, and REE, which are all the index minerals of eclogitic origin. Besides, we found Cr scavenges a platinum group element, Ru with these pyroxenes as inclusions. From the above data, we believe that the diamond sample in which we found inclusion is of Kimberlitic origin. These studies can be extended to look for inclusions in gemstones other than diamond along with their origin,

geochemistry and associated properties. The existence of metal like Ru as an inclusion in diamond can give an idea about the potential areas and deposits of PGEs and other noble metals and may have important implications to the mining industry.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.diamond.2011.06.003.

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