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Laser-Raman spectroscopic studies on graphite from East Antarctica

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Abstract: We report here the Laser-Raman spectroscopic data on the carbonaceous matter (CM) from Schirmacher Oasis (70°45′S, 11°40′E), East Antarctica for the first time. The sample was collected from the Precambrian rock, which consists of garnet-biotite gneiss. The first order Laser-Raman spectra of the sample shows a strong well-ordered Raman peak (*O*) at 1581 cm^{-1} and a weak broad peak due to disorder (*D*) at 1354 cm^{-1}. The intensity ratio disordered-to-ordered Raman peak $(D/O)_{area}$ has been used to estimate the in-plan crystallite size (L_a) of the graphite. The experimental values of D/O=0.143 and $D/D+O$=0.125 indicate that the CM is well crystallized graphite, thereby indicating the high metamorphic grade of the host rocks. Powder X-ray diffraction studies on the same sample of CM also indicate that the CM is well-crystalline hexagonal graphite with d_{002}=0.3354 nm. The structural parameters obtained by Raman spectroscopic method and the estimated in-plane crystallite size (L_a=298 Å) indicate that the metamorphic grade of the host rock of the studied sample falls in the upper sillimanite zone. The present study suggests that the peak metamorphic temperature of the host rock could be in the temperature range of about 700°C.

key words: Laser-Raman studies, East Antarctica, Schirmacher Oasis, Graphitization, metamorphism

1. Introduction

The occurrence of carbonaceous matter (CM) in sedimentary rocks is common. The structure of carbon changes to well ordered graphite structure systematically with the increase of metamorphic grade (Hamilton *et al.*, 1970; Landis, 1971). The short range order of CM has been used as an indicator of metamorphic grades and peak metamorphic temperatures have been estimated through the study of structural parameters of graphite using spectroscopic techniques (Wang, 1989; Wada *et al.*, 1994; Grew, 1974; Tagiri, 1981; Sharma *et al.*, 1998). Laser-Raman Spectroscopic technique (LRS) on CM is a reliable tool in providing a fast and non destructive micro analysis of short range order parameters of CM. These parameters are used to determine the metamorphic grade, and peak metamorphic temperature of the host rocks (Pasteris and Wopenka, 1991; Wopenka and Pasteris, 1993; Pearson *et al.*, 1994; Yui *et al.*, 1996; Sharma *et al.*, 2000).

Although Satish and Wada (2000) reported stable isotope of graphite in Skallen area, near Enderby Land, East Antarctica, but to our knowledge, there is no previous report

either on Raman spectroscopic investigations or on powder X-ray diffraction (XRD) studies on CM from East Antarctica region. In this study, we present the new results on the Laser-Raman spectroscopic data, along with powder XRD data on the carbonaceous matter (CM) from Schirmacher Oasis, East Antarctica and make an attempt to infer the metamorphic grade and peak metamorphic temperature of the host rock. The results are consistent with the results obtained through the study of mineral assemblages on the same host rock, and using conventional geothermobarometry (Grew, 1984; Sengupta, 1988) and fluid inclusion studies (Rameshwar Rao *et al.*, 1998).

2. Geological setting

The graphite bearing host rock (AM-33) has been collected from the Schirmacher Oasis (70°45′S, 11°40′E) as shown in Fig. 1. The Schirmacher Oasis (lat: 71°44′ to 70°47′S; long:11°22′ to 11°55′E) exposes Precambrian basement crystalline rocks consisting of both acid and basic rocks (Sengupta ,1988). The garnet-biotite gneiss (GBG) occupying the central part of the Schirmacher Hills, which is charcterized by the presence of large elongate dark clots of mafic minerals separated by quartzofeldspathic materials. It is a coarse grained rock that contains mainly quartz, plagioclase, K-feldspar-garnet-biotite, cordierite, sillimanite and accesory graphite (Grew, 1984). The details of the geology, polymetamorphism and the petrological studies of this area have been discussed elsewhere (Grew, 1984; Sengupta, 1988; Hussain and Rao, 1996).

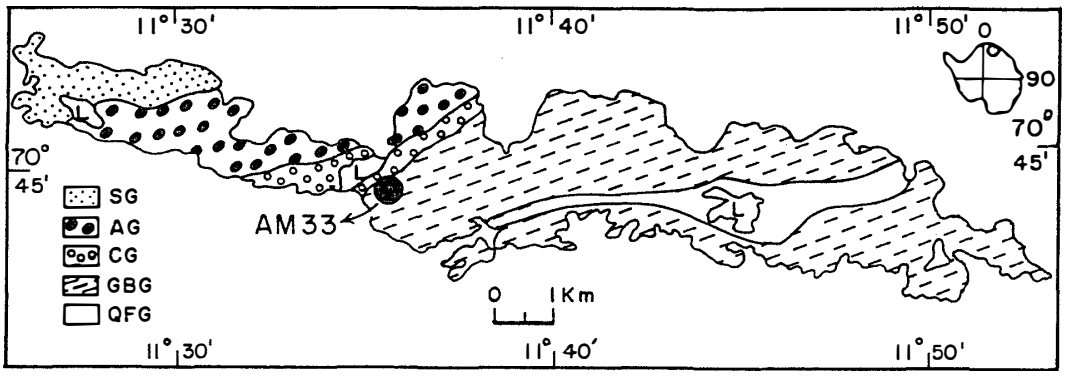

Fig. 1. Simplified geological map of Schirmacher Oasis, East Antarctica (after Sengupta, 1988) and location of host rock sample. SG, streaky gneiss; AG, augen gneiss; CG, calc-gneiss; GBG, garnet-biotite gneiss; QFG, quartzo-feldspathic gneiss; L, lake.

3. Experimental methods

The carbonaceous matter (CM) was extracted from the host rock by adopting the standard acid-digestion technique (Wedeking *et al.*, 1983). The content of carbonaceous matter (CM) in the rock sample is estimated to be about 2 wt% of the total rock sample. About 20 g of the rock samples were finely ground to ~120 mesh. The powdered samples were treated with the acid mixtures of 60% HF and 37% HCl in the ratio 5:2 for 18 hours to dissolve acid soluble minerals .The resultant residue was washed with 1000 m*l* of double distilled water. The carbon-rich residue was dried in the oven at 80°C for 3

hours. Fluorides were normally not observed in the X-ray diffraction pattern of the acid digested residues. In case fluorides were detected by XRD, the samples should be treated with 1.2 M $AlCl_3$ for 24 hours at 25°C, which would remove any observable quantities of fluoride complexes (Wedeking *et al.*, 1983). Rock sample does not contain pyrite.

The Laser-Raman studies on carbonaceous matter sample AM33 (Fig. 1) was carried out by using a computer controlled double monochromator made by SPEX Instruments Ltd, USA, equipped with photon counting detection system and 488 nm line of argon-ion laser was used as the excitation source. The laser intensity was maintained at 100 mW to avoid any laser induced heating effect on the sample (Kagi *et al.*, 1994). The scattered light was detected using cooled photomultiplier tube operated in the photon counting mode. We have also carried out powder X-ray diffraction (XRD) , and differential thermal analysis (DTA) studies on highly oriented pyrolytic graphite (HOPG), for comparison with the natural graphite (Parthasarathy and Sharma, 2001). Powder X-ray diffraction studies on the purified carbonaceous matter, using two independent X-ray diffractometer with Cu$K\alpha$ radiation (λ=1.54060 Å). A SIEMENS D-5000 diffractometer at Indian Institute of Chemical Technology, Hyderabad was used. Vertical slits were used with 1 mm width size at the source side and three slits with 1 mm, 0.6 mm, and 0.1 mm width at the detector side. Ni-filter was used in the experiments. Typical powder XRD pattern for the sample AM33 is shown in Fig. 2.

It is well known that spectroscopic grade graphite shows Raman band E_{2g} mode only at 1582 cm^{-1} (Kawashima and Katagiri, 1995). The first order Raman spectrum of micro-crystalline graphite shows additional bands at around 1360 cm^{-1} and 1620 cm^{-1} (Kawashima and Katagiri, 1995). Tuinstra and Koenig (1970) have attributed the 1360

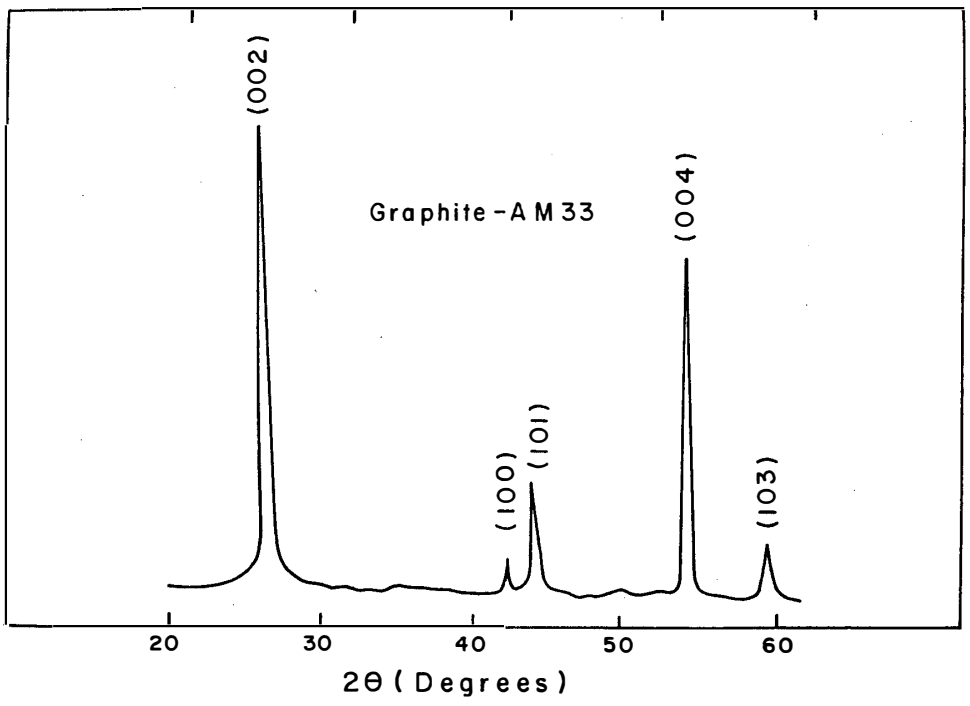

Fig. 2. X-ray powder diffraction pattern of the carbonaceous material sample from the host rock. All the Bragg peaks are indexed to a hexagonal cell of well-crystalline graphite.

cm^{-1} band to the crystallite size effects. The present experiments were carried out by focussing the laser beam in the middle of the scaly or flaky graphite (typical diameter of the laser beam 5 micro meter). The edge-effect of the laser beam would result an appearance of Raman forbidden band at 1620 cm^{-1} which is ascribed to the existence of specific vibrations due to C-O or C=C groups of surface oxidized species (Lespade *et al.*, 1982; Kawashima and Katagiri, 1995). In present studies we have scanned in the wave number region from 1200 to 1700 cm^{-1} for the first order spectrum.

4. Results and discussion

Figure 2 shows the powder XRD pattern of the CM sample (AM33), exhibiting five distinct diffraction peaks, all of them can be indexed to the conventional hexagonal graphite cell (JCPDS card No: 13–148). The value of the d_{002} Bragg peak=0.3354 nm and full width at half maximum $\beta(002)$=0.0148 nm , indicating the sample is well-crystallized graphite. It is evident from Fig. 2 that the acid insoluble residue did not contain any detectable amount (few ppt) of either neo-formed fluorides or pyrite .

The first order Raman spectrum is specially sensitive to the extent of the two dimensional graphite ordering. For a well ordered synthetic (spectroscopic grade) pyrolytic graphite the first order Raman spectra shows a strong peak at 1582 cm^{-1} (ordered or O peak), which is attributed to the $E_{2g}(2)$ vibration mode of graphite with D^4_{6h} crystal symmetry. In polycrystalline graphite and additional band (disordered or D) was observed at 1355 cm^{-1} and attributed to crystalline size (Tuinstra and Koenig, 1970; Pasteris and Wopenka, 1991). In highly disordered graphite compared with the single crystal (well ordered graphite) increasing the crystalline disorder of the carbon material increases the intensity of the disorder-induced broad features near 1360 cm^{-1} and 1620 cm^{-1} in the first order Raman Spectra (Lespade *et al.*, 1982; Pasteris and Wopenka, 1991). The first order Raman Spectra of the carbonaceous matter from the rock sample AM 33 from East Antarctica shows the strong well ordered (O) peak at 1581 cm^{-1} and weak broad peak due to disorder (D) at 1354 cm^{-1} (Fig. 3). There is no edge effect in the Raman spectra of the scaly graphite, as the beam was focussed in the middle of the sample. These results indicate that the studied carbonaceous matter is highly crystallized and the host rock has undergone to high peak metamorphic temperature and pressure conditions. However, it is difficult to estimate the peak metamorphic pressure more accurately by using Raman data alone. Hence we do not make any attempt to estimate the peak metamorphic pressure of the studied sample.

The structural parameter L_a the average length scale of continuity within the sheets are usually determined by the single crystal X-ray diffraction studies on graphite. However, even for single crystal graphite the determination of L_a from XRD (110) lattice reflection is a very difficult task, due to the constraints posed by several corrections involving the instrumental parameter and line broadening effects due to the edge effect (Ergun, 1968). Most of the recent Raman spectroscopic studies on the natural graphite (Pasteris and Wopenka, 1991; Wopenka and Pasteris, 1993; Yui *et al.*, 1996; Sharma *et al.*, 2000) determination of L_a has been done by using the correlation of Tuinstra and Koenig (1970), who have observed in Pyrolitic (synthetic) and natural graphite that the intensity ratio of the disordered to ordered peak varies linearly as a inverse function of

L_a. However, Tuinstra and Koenig (1970) have not mentioned how they evaluated the L_a by XRD analyses. Figure 4 shows the correlation between the intensity ratio $(D/O)_{area}$ and the inverse of the in-plane crystallite size for synthetic pyrolitic (spectroscopic grade) and natural graphite samples (Tuinstra and Koenig, 1970). We have used this linear

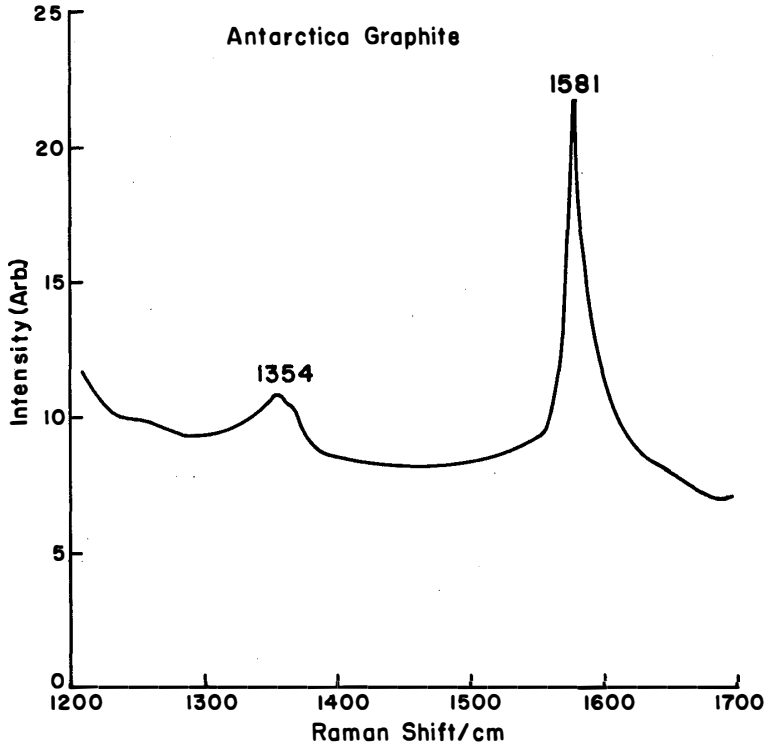

Fig. 3. First order Laser Raman Spectra of the graphite sample from Schirmacher Oasis, East Antarctica. The peaks 1581 cm^{-1} (O), and 1354 cm^{-1} (D) correspond to well-ordered and disordered Raman peak of graphite respectively.

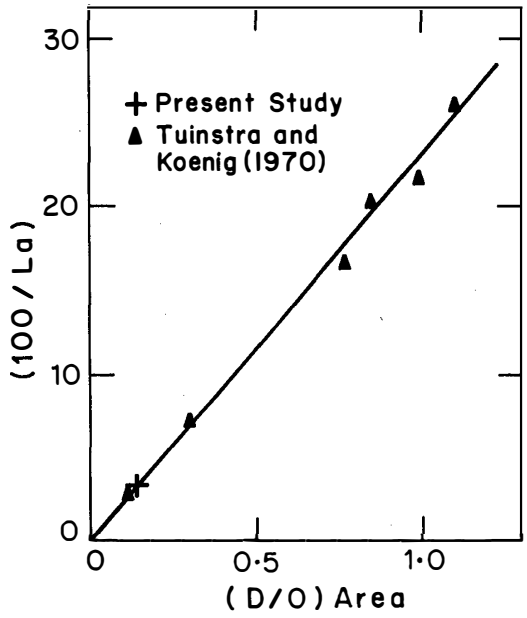

Fig. 4. The correlation of the Raman Intensity with the inverse of the in-plane crystallite size, L_a of the CM from East Antarctica (present study). The triangles are data from Tuinstra and Koenig (1970). The linear line is a least-square fit of the data of Tuinstra and Koenig (1970).

correalation to estimate the L_a of natural graphite samples from Dharwar and found this method is very reliable in estimating the intraplane-crystallite size (Sharma *et al.*, 2000). This method of estimating the L_a was also validated in other CM (Wopenka and Pasteris, 1993). Typical error involved in estimating the L_a values by using the Raman spectroscopic method few per cent (1 to 2%) compared to the single crystal data (Wopenka and Pasteris, 1993). $(D/O)_{area}$ ratio of the studied sample has been estimated as 0.143 and shown in Fig. 4. This linear correlation yields the value of L_a as 298 Å. The pyrolitic (spectroscopic grade pure) graphite has maximum L_a=320 Å. The crystallite size, L_a of the studied sample shows very clearly that the graphite from the East Antarctica rocks is highly crystallized. This indicates that the host rock of the CM was subjected to high grade metamorphism.

The first order Raman Spectrum is sensitive to the degree of crystallinity of CM ranging from kerogen and coal to granulite-grade graphite (Wopenka and Pasteris, 1993). Beny-Bassez and Rauzaud (1985) measured the in-plane crystallite size, L_a directly from the fringes and using high resolution transmission electron microscope (HRTEM). They correlated the L_a with the Ist order Raman spectroscopic parameters S_{1350}, the ratio between surfaces of 1350 cm^{-1} band and whole spectrum of the region (1300 to 1700 cm^{-1}). Later S_{1350} is defined as the peak area ratio $(D/D+O)\times100$ by Wopenka and Pasteris (1993).

Graphitization is an irreversible and in many cases, disequilibrium process. The irreversibility that the highest degree of crystallinity will be retained during retrograde metamorphism (Grew, 1974; Pasteris and Wokpenka, 1991). Only Raman spectral analysis could indicate the metamorphic grades higher than the those inferred from accompanying silicate mineralogy. It is quite possible that the samples undergo to the high grades of metamorphism before their final equilibrium (Pasteris and Wopenka, 1991).

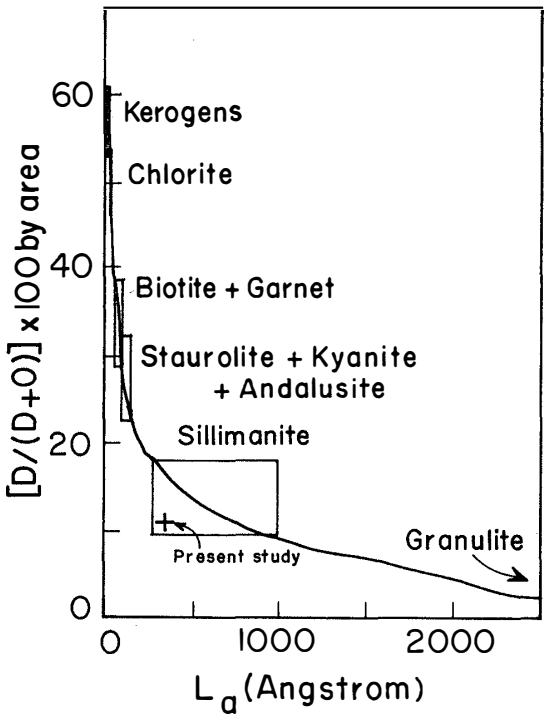

Fig. 5. Plot of the Raman spectroscopic parameter, $(D/D+O)_{area}$ vs. the in-plane crystallite size, (L_a) of the CMs. The boxes represent the Raman data of different CMs from different metamorphic grades (after Wopenka and Pasteris, 1993). The data on graphite from Schirmacher Oasis, East Antarctica (present study) is indicated as + sign.

Figure 5 Shows the correlation curve between $(D/D+O)\times100$ and in plane crystallite size L_a. The rectangles representing different metamorphic zones are obtained from the work of Wopenka and Pasteris (1993). Comparison of our results with those of Wopenka and Pasteris (1993), shows that the host rock of the graphite sample from East Antarctica falls in the sillimanite zone. However, the coexisting mineral assemblages indicate the host rock of CM lies in the upper-sillimanite zone. For determining the peak metamorphic temperature, *P-T* diagrams for different metamorphic rocks (Spear, 1993) and the correlation between L_a and $(D/D+O)\times100$ (Fig. 5), have been used . The peak metamorphic temperature of the graphite bearing rocks of East Antarctica has been estimated to be about 700°C .

Fluid inclusion studies on the entrapped monophasic CO_2 in the Leucogneisses from the same area, show pressures of 0.55 GPa and temperatures of 675±25°C (Rameshwar Rao *et al.*, 1998). The peak metamorphic temperatures obtained using Laser Raman Spectroscopic technique in the present study are consistent with those observed from the geothermobarometry based upon mineral assemblages (Hussain unpublished) and fluid inclusion studies. However, in other area of East Antarctica Satish and Wada (2000) have obtained peak metamorphic temperature ~850°C using carbon isotope thermometry between calcite and graphite of granulite facies marble in the Skallen region of Lützow-Holm Bay region, which is far away from the studied area.

5. Conclusions

The present studies reveal that (i) carbonaceous matter of Schrimacher Oasis rocks is highly reflective and crystallized sample viz., well ordered hexagonal graphite; (ii) the host rock of graphite samples has witnessed high grade metamorphism; and (iii) the peak metamorphic temperature of the host rock falls in sillimanite zone, ~700°C. The peak metamorphic temperature obtained by spectroscopic methods are in consistent with those observed from the conventional geothermobarometry method, based upon mineral assemblages.

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