Natural Graphite from Neoproterozoic Psammitic Gneiss, Inanalo Mountain, Southern Madagascar

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Abstract We report here, for the first time, powder X-ray diffraction, and laser-Raman spectroscopic data on the graphite samples from Inanalo mountain (S24°24 31 2" E45°23'18 3), 20 km east of the Ampanihy shear zone of the southern Madagascar Our experimental results show that the graphite is highly crystalline, and syngenetic with the degree of graphitisation varying from 148 to 180, yielding the peak metamorphic temperatures of 750 to 850°C Laser Raman spectroscopic studies show only ordered peak at around 1580 cm^{-1} in the frequency range from 1000 to 2000 cm^{-1} The commonly observed disordered peak in natural graphite is found to be absent in the studied sample, indicating high-temperature metamorphism There is no fluid deposited graphite (epigenetic graphite) in the sample The peak metamorphic temperature obtained in the present study is found to be in good agreement with that obtained from the conventional geothermometry studies on the sample from the Beraketa shear zone or the Betroka tectonic belt

Keywords Syngenetic graphite, Laser-Raman studies, XRD, Shear zone, Inanalo Mountain, Southern Madagascar

INTRODUCTION

Natural graphite is known to be formed either by *in-situ* metamorphism of organic matter through the so-called graphitisation (syngenetic graphite) or by precipitation from C-O-H fluids (epigenetic graphite) Graphitisation differs from most mineral transformations occurring during diagenesis and metamorphism in that it is an irreversible process, and hence the short-range parameters of graphite can be used to estimate the peak metamorphic temperature experienced by its host rock (Pasteris and Wopenka 1991, Wopenka and Pasteris, 1993, Pearson et al 1994, Wada et al 1994, Luque et al 1998, Sharma et al 1998, 2000, 2001, Parthasarathy and Sharma, 2001, Parthasarathy et al 2002, 2003) In this paper, an attempt has been made to estimate the peak metamorphic temperature experienced in a part of southern Madagascar region by studying the short-range parameters of graphite from Inanalo Mountain, Bekily province, southern Madagascar

GEOLOGICAL SETTING

Graphite samples are separated from the rock sample M03-22, psammitic gneiss, Inanalo Mountain, southern Madagascar (S24°24'31 2" E45°23'18 3") Figure 1 shows the geological map along with the major shear zones in the studied region This psammitic gneiss is made up of quartz, feldspar, garnet and graphite and lies within the Graphite System of the Androyen, Graphite, and Vohibory Groups of Besairie (1969-1971) and is associated with schists composed almost entirely of graphite Graphite-bearing rocks are common in southern Madagascar and are spatially associated with steeply dipping shear zones that have been interpreted as being rooted in the mantle (Pili et al 1997, 1999) Sample M03-22 was collected approximately 20 km east of one of these shear zones, the Ampanihy shear zone (within the Bekily Belt of Windley et al 1994), which is ~20 km-thick, trends NNE-SSW, and separates the mafic-rich Vohibory series from the rest of southern Madagascar (Fig 1) Thermobarometric determinations on rocks close to where M03-22 was collected have yielded maximum pressures and temperatures of 8±1 kbar and 880± 60°C (Martelat et al 1997, Markl et al 2000) These rocks also preserve evidence for a later medium pressure and temperature event that recorded pressures of 4±1 kbar and temperatures of 690±40°C (Markl et al 2000)

The depositional age of the metasedimentary rocks of southern Madagascar is poorly known, U-Pb age from detrital zircons indicate that they were deposited after

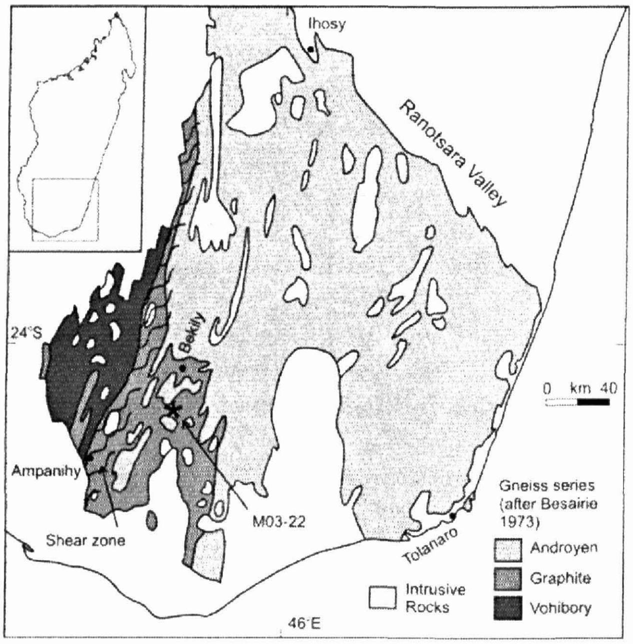

Fig.1. Simplified Geological map of the Southern Madagascar indicating the sample location (*after* Besairie, 1969-1971).

~1.7 Ga (Kröner et al. 1999; Collins et al. 2004), whereas metamorphic monazites and zircons indicate that the metamorphism occurred in the late Neoproterozoic (de Wit et al. 2001). As such, the age constraints are similar to those available for the age of deposition of the extensive metasedimentary rocks in the Southern Granulite Terrain of India (Collins and Santosh, 2004; Ghosh et al. 2004).

EXPERIMENTAL METHODS

The graphite samples were powdered and treated with hydrochloric acid and subsequent HCl-HF mixture to remove any traces of carbonates or silicates present in the samples. The acid-resistant residue was cleaned with double-distilled water and dried at 60° C for 24 hours. Four sets of dried samples were subjected to powder X-ray diffraction (XRD), and Laser–Raman spectroscopic studies. The diffraction patterns were obtained by Philips Diffractometer and also Siemens D-5000 Powder Diffractometer with HOPG graphite monochromator. Cu-Kα1 radiation with a wavelength of 0.15419 nm was used in all the diffraction experiments. 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. Laser Raman spectroscopic studies were carried out at room temperature by using 488 nm line of argon-ion laser with a low power of less than 10 mW in the sample, to avoid any laser–induced heating effect, which could cause a shift in Raman peak (Kagi et al. 1994). Triplicate runs were made in static air atmosphere. The uncertainty in the observed value of the wave number is typically 2 cm^{-1} in the frequency range 2000-3000 cm^{-1}.

RESULTS AND DISCUSSION

Figure 2 shows the representative powder X-ray diffraction patterns of two of the four graphite samples from southern Madagascar (sample M03-22). All the graphite samples exhibit sharp XRD peaks, all of which were indexed to a hexagonal unit cell, with the cell parameters a= 0.24628 and c= 0.6672 nm. The values of the d-spacings of the well-crystallised graphite are found to be in good agreement with the published XRD data on the spectroscopic grade graphite (ICPD card No.23-64). The interplanar spacings d (002) of the Madagascar sample varies from 0.3328 nm to 0.3400 nm. The crystallite size and the degree of graphitisation have been calculated by measuring the full width half maximum of the (002) peak. The size of the crystallites L_C (002) has been calculated using Scherer's equation $L_C = K\lambda / \beta(002) \cos \theta$, where the constant K is 0.9, which is based on experimental parameters (Tagiri and Tsuboi, 1979); β(002), which is the value of full width of Bragg (002) peak at half height (FWHM) in radian; λ, which

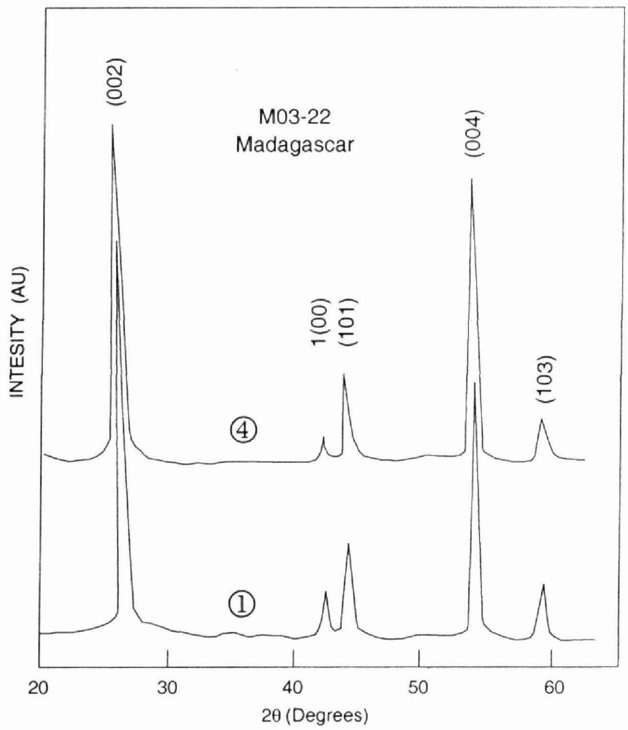

Fig.2. Powder X-ray diffraction pattern of graphite samples M03-22-1 and M03-22-4 from Southern Madagascar.

is the wave length in angstrom (1 angstrom= 0.1 nm), and θ, which is the angle of diffraction in radian. The graphitisation degree (GD) has been calculated by using the relation suggested by Wada et al. (1994)

$$GD= [\{d\ (002)-3.7\}/ \text{Log}\ \{L_C/1000\}]\ X\ 100.$$

This relation has been successfully applied in determining the structural parameters of natural graphite from different geological settings throughout the world (Tagiri, 1981, Pearson et al. 1994; Yui et al. 1996; Sharma et al. 1998, 2000, 2001; Parthasarathy and Sharma, 2001; Baiju et al. 2005). Wada et al. (1994) have observed a linear relationship between the DG and peak metamorphic temperature. The measured parameters of interplanar spacing d(002), full width at half maximum b(002), size of the crystallites along the c-axis L_C (002), and the graphitisation degree (GD) of the Madagascar samples are listed in Table 1. In southern Madagascar, one might expect the presence of the fluid-deposited (epigenetic) graphite due to the presence of mantle-derived fluid infiltration along the crust-cutting ductile shear zones (Pili et al. 1999; de Wit et al. 2001). However, it is clear from Fig.2 and Table 1 that samples do not show any rhombohedral graphite, which is characteristic of fluid deposited or epigenetic graphite. Such fluid deposited graphite has been observed in samples obtained from the core samples KTB borehole (German continental deep drilling; Pasteris and Chou, 1998) and in samples collected from shear zones of the Eastern Ghat Mobile Belt of India and the Achankovil shear zone (Parthasarathy et al. 2006; Chetty and Parthasarathy, 2005). Epigenetic graphite is deposited from C-O-H fluids when saturation is attained. Luque et al. (1998) have discussed the characteristics and mechanism of formation of the epigenetic graphite in great detail.

Table 1. Short-range order parameters, crystallinity, degree of graphitisation and peak metamorphic temperature obtained from the Madagascar samples.

Sample No	d(002) in Å	β (002) in Å	L_C(002) in Å	GD	T in °C
M03-22-1	3.340	0.139	572	148	755
M03-22-2	3.336	0.140	568	148	754
M03-22-3	3.330	0.140	568	151	762
M03-22-4	3.328	0.136	585	180	857

Tagiri and Oba (1986) have demonstrated the use of the crystallinity parameters L_C and d_{002} in classification of carbonaceous matter into coaly material, disordered graphite and highly crystalline graphite. This method has been used very successfully for the characterization of carbonaceous matter throughout the world (Wada et al. 1994; Sharma et al. 1998; Baiju et al. 2005). Wada et al. (1994) have analysed several samples of carbonaceous matter extracted from limestone and pelitic rocks of Ryoke metamorphic terrain, and derived a simple linear correlation between degree of graphitisation (GD) and peak metamorphic temperature. The relation is T (in °C) = 3.2 X GD (in Å) + 280. By substituting the values of GD obtained from the Madagascar samples, we obtain an estimate of the peak metamorphic temperature of 754 to 856 °C. Laser-Raman spectra are very sensitive to changes that disrupt the translational symmetry of the solid materials studied, as in small dimensional crystals. It is well known that carbonaceous matter can occur in a wide range of crystallite sizes. The usefulness of Laser-Raman spectroscopic studies of graphite in estimating degree of metamorphism has first been suggested by Pasteris and Wopenka (1991). The Raman spectrum of carbonaceous matter is generally composed of first order (110-1800 cm^{-1}) and second order (2500-3100 cm^{-1}) regions. Laser-Raman spectra of the most of the naturally occurring graphite samples with small graphite crystallites (basal plane ≤ 25 nm), exhibit disordered peak at about 1350 cm^{-1}. Figure 3 shows the Laser-Raman spectra of the

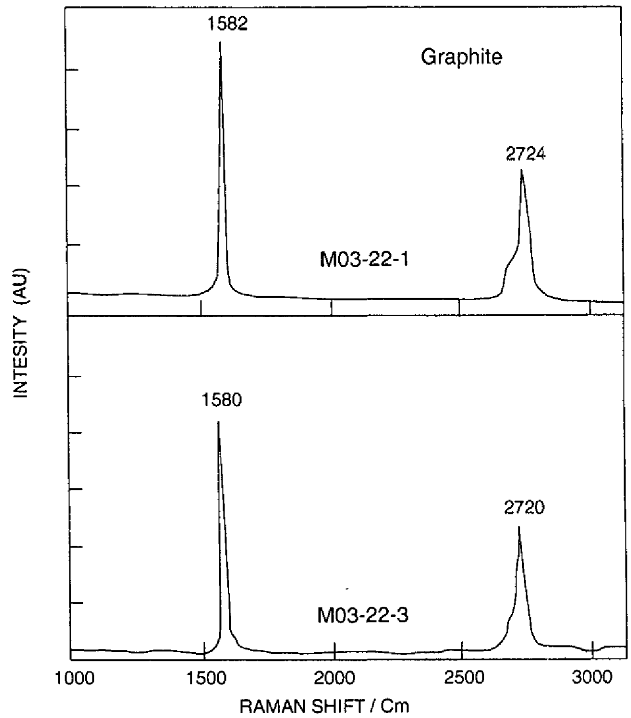

Fig.3. Laser–Raman spectra of the graphite samples from the southern Madagascar showing the first order Raman peak near 1582 and the second order Raman peak near 2720 cm^{-1}.

graphite from Southern Madagascar (samples M03-22-1 and M03-22-3) at room temperature The strong peaks at 1582 cm^{-1} the Raman (O) peak corresponds to the E_{2g} vibration mode of a crystal with D_{6h}^{4} symmetry, i e to in-plane vibration of aromatic carbons in the graphitic structure In the second order region graphite shows peak at about 2720 cm^{-1}, which splits into two components at 2686 and 2724 cm^{-1} during the final stage of the graphitisation process This splitting was then interpreted as a result of the transition between the two-dimensional structures towards the tridimensional one (Beyssac et al 2002) It is worth mentioning here that the Madagascar samples do not show the disordered Raman peak near 1350 cm^{-1} and the peak near 2496 cm^{-1} due to presence of any C-H fluids, thereby independently confirming the ultra high-temperature crystalline syngenetic origin of graphite in Madagascar samples

CONCLUSIONS

The present study of powder-x-ray diffraction and Laser–Raman spectroscopic studies on the graphite from the psammitic gneiss of southern Madagascar suggests a syngenetic origin of the graphite The peak metamorphic conditions obtained for the Madagascar samples lies in the range of 750-850^{0}C, consistent with published mineral equilibria determinations (Martelat et al 1997, Markl et al 2002) Rock-fluid interactions in the region (if any) could be later episodes, as the studied samples do not show any evidence for the presence of mantle derived fluids in the graphite mineralization

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