Journal of Geological Society of Sri Lanka Vol. 17 (2015), 65-73
J.W. Herath Felicitation Volume

USE OF CRYSTAL MORPHOLOGIES TO UNRAVEL THE ORIGIN OF VEIN GRAPHITE IN SRI LANKA

H.P.T.S. HEWATHILAKE[1,*], N.W.B. BALASOORIYA[2], H.M.T.G.A. PITAWALA[3] AND H.W.M.A.C. WIJAYASINGHE[1]

[1]*National Institute of Fundamental Studies, Kandy, Sri Lanka*
[2]*Faculty of Applied Sciences, South Eastern University, Sammanthurai, Sri Lanka*
[3]*Department of Geology, University of Peradeniya, Peradeniya, Sri Lanka*
[*]*Corresponding Author: e-mail: tharindu.tsh@gmail.com*

ABSTRACT

Sri Lanka is well known for its high quality vein graphite with extensive mineralization and large reserves. Sri Lankan vein graphite has distinctly different structural variations, which can be used to elucidate the formation of vein graphite. Therefore, this study focuses on the origin of Sri Lankan vein graphite by interpretation of its chemical characteristics, crystal morphologies and structural variation. Two major veins exposed at the deep and shallow levels at the Kahatagaha - Kolongaha mine were selected for the study. Characterization by X-Ray Diffraction, Scanning Electron Microscope and purity analysis (by ASTM - 561) indicate that, the formation of the vein graphite may be attributed to multi stage hydrothermal activity or to different stage of crystallization. At least, two stages of hydrothermal fluid invasion may have caused the crystallization of different morphological layers with different chemistry and crystallinity in single veins.

***Key words:** Vein graphite, Crystal morphology, Hydrothermal activity, Crystallinity*

INTRODUCTION

Graphite is one of the naturally occurring crystalline polymorphs of carbon. A set of loosely stacked one-atom thick graphene layers contribute to the formation of graphite structure. Depending on stacking sequence of layers, crystal structure is classified as two-layer, hexagonal or three-layer rhombohedral.

Naturally occurring graphite is typically classified into three forms; such as (i) flake graphite, (ii) vein graphite and (iii) amorphous graphite (Wyckoff *et al.*, 1963). As the name implies "flake graphite" has a distinctly flaky morphology and is typically found as flat, plate like masses. They occur as disseminated grains in regionally metamorphosed sedimentary rocks such as schists and gneisses, which are very common in many parts of the world. Nevertheless, economically important vein graphite can be found only in few countries such as Montana and USA (Dissanayake *et al.*, 1981, Wijayananda *et al.*, 1983).

Vein graphite deposits of Sri Lanka are occurred within Precambrian high grade metamorphic terrain dominated by granulite-facies rocks (see Figure 1). They have been received more attention due to their high purity (about 95-99 % of pure carbon), extensive mineralization with large reserves, high crystallinity and mode of occurrence (Erdosh *et al.*, 1970; Hapuarachchi *et al.*, 1977). Many studies in the past had discussed the origin of Sri Lankan vein graphite (Katz *et al.*, 1987; Binu-Lal *et al.*, 2003).

Kehelpannala (1995) suggested that the origin of Sri Lankan vein graphite has no direct relationship with the granulite facies metamorphism and major deformations. He further explained that vein graphite mineralization could be related to a magmatic fluid or to a volatile phase emanating from the mantle in a relatively young stage (<550–475 Ma). Even though many studies have been carried out on interpreting the origin of vein graphite (Silva *et al.*, 1987; Dissanayake *et al.*, 1988; Kehelpannala *et al.*, 1993) only very few investigations have been focused on the crystallization process and crystal morphology of the vein graphite. Kehelpannala (1993) identified the six morphological varieties. However, later investigations suggested that

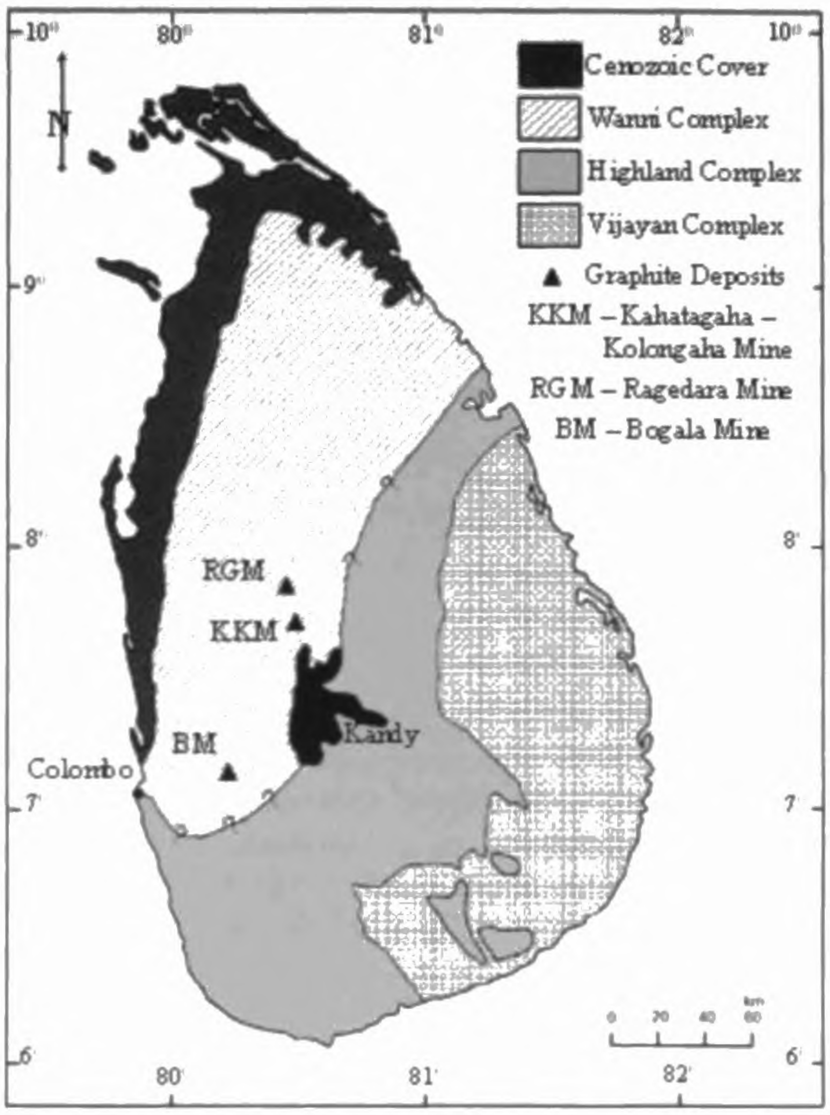

Fig. 1 Map showing major geological subdivisions of Sri Lanka, with the locations of presently mining graphite deposits (after Cooray, 1994).

vein graphite can be categorized into only four morphological varieties (Balasooriya *et al.*, 2002; Touzain *et al.*, 2010).

Formation of different morphologies of graphite crystals may depend on (i) size and shape of the vein, (ii) prevailing cooling conditions, (iii) nucleation conditions, (iv) composition of the source materials and (v) intensity and frequency of the hydrothermal activities. Therefore, present study is focused to interpret the crystallization process of vein graphite by studying the field relationship, morphological variation and chemical characteristics.

EXPERIMENTAL PROCEDURE

STUDY AREA

Sample collection was done at the Kahatagaha - Kolongaha mine, which is situated in the Wanni Complex, with 32 km north–northwest to Kandy (see Figure 1). Two major veins, which is exposed at the deeper levels and shallow levels in the mine, were selected for this study. One of these selected vein exposes at 345 m and 610 m levels (*vein-A*) while the other vein exposes at 172 m and 585 m levels (*vein-B*).

MATERIALS AND METHODS

The morphological studies were carried out in order to understand the crystallization variation of different veins at different elevations by concerning the four different crystal morphologies of Needle-Platy (NPG), Shiny-Slippery-Fibrous (SSF), Coarse Striated-Flaky (CSF) and Coarse Flakes of Radial (CFR) (Touzain *et al.*, 2010). For the sample collection, the selected two veins were named as *vein-A* (exposed at 345 m and 610 m levels) and *vein-B* (exposed at 172 m and 585 m levels).

Crystallographic nature and its variation have always been considered in the sample collection procedure. Collected samples were size reduced into chips by using a wooden hammer and crushed into powder by using a vibratory disk mill followed by mechanical sieving to obtain powder with a particle size <53 μm.

CHARACTERIZATION

Carbon percentage of each graphite samples was determined according to ASTM-561 method. Scanning Electron Microscope (SEM) studies were carried out using "EEVO/LS 15 ZEISS" to study the morphological and structural features of selected vein graphite. X-Ray Diffraction (XRD) analysis was carried out using a "Rigaku-Ultima IV" X-ray diffractometer, with Cu-Kα1 radiation (λ= 1.54 Å) at the 4 deg/min scanning rate. The crystallinity parameters were calculated and the major and minor impurity phases were analyzed. Coherence length Lc (crystalline size along the c axis) was calculated by using Sherrer's formula, $Lc(Å) = (0.93\times1.5418) / (FWHM_{(002)} \times\cos \theta_{002})$, where, $FWHM_{(002)}$ - Full Width at Half Maximum of the (002) line (FWHM in rad.), λ = 1.5418 Å and θ_{002} = Angle with reference to (002) line. Coherence length La (crystalline size along the a-axis) was calculated by using Warren's formula, $La(Å) = (1.843\times1.5418) / (FWHM_{(100)} \times \cos \theta_{100})$, where $FWHM_{(100)}$ - Full width at half maximum of the (100) line (FWHM in rad.), λ = 1.5418 Å and θ_{100} = Angle with reference to (100) line. The degree of graphitization (D.G.) was calculated according to Maire & Mering (1965), $D.G. \% = ((3.44- d_{002}) / (3.44 - 3.354)) \times 100$, Where d_{002} in Å (Touzain *et al.*, 2010).

RESULTS AND DISCUSSION

MORPHOLOGICAL FEATURES

The vein graphite observed in this study at 345m level of the *vein-A* composed of three different morphologies (see Figure 2 and Figure 3). The thickness of this vein varies from 12 cm to 20 cm. The first layer labeled as A1 (see Figure 2) is a very thin layer (about 1 cm thick) attached to the wall rock, comprises of fine needles of graphite. While the Layer A2, having a thickness of about 3 cm, has coarse particles of graphite and needles, which are oriented towards the center of the vein. Further, the Layer A3, having an average thickness of 14 cm, is composed of comparably large plates of graphite, which can be characterized into NPG and SSF morphologies.

At 610 m level, four distinct crystallographical formations could be observed (see Figure 2 and Figure 3). Here the average vein thickness varies from about 28 to 35 cm. The A4 composed of both the CFR and CSF crystal morphologies with about 2 cm in thickness. The CFR needles are attached to the wall rock. Middle layer A5, with about 13 to 16 cm in thickness, is composed of only with the NPG graphite morphology. Further this NPG layer shows the existing of an admix area at the margin of A4 (the outer layer), but it has a clear separation with A6. The layer A6 is composed of the SSF morphology with a layer thickness of around 5 cm. Finally, the Layer A7, with a thickness of around 3 cm, is attached to the wall rock and consists of both SSF morphology and coarse particles of graphite.

SEM studies show the radial formation of CFR morphology with the pyramidal shapes having sharp edges of graphite (Figure 3B). Figure 3C shows the platy appearance of NPG morphology. SEM image with long fibers with sharp edges shows the characteristic features for SSF morphology (Figure 3D). Amorphous nature of the coarse particles layer attached to the wall rock shown in Figure 3E.

The *vein-B* shows and average thickness of 15 cm at 172 m level and this vein is composed with all the four different morphological layers (see Figure 2 and Figure 4). The layer B1 attached to the wall rock has 1 to 2 cm thickness variation with the graphite coarse particle formation. B2 layer, with an average thickness of 3 cm, is composed of fibrous formation of

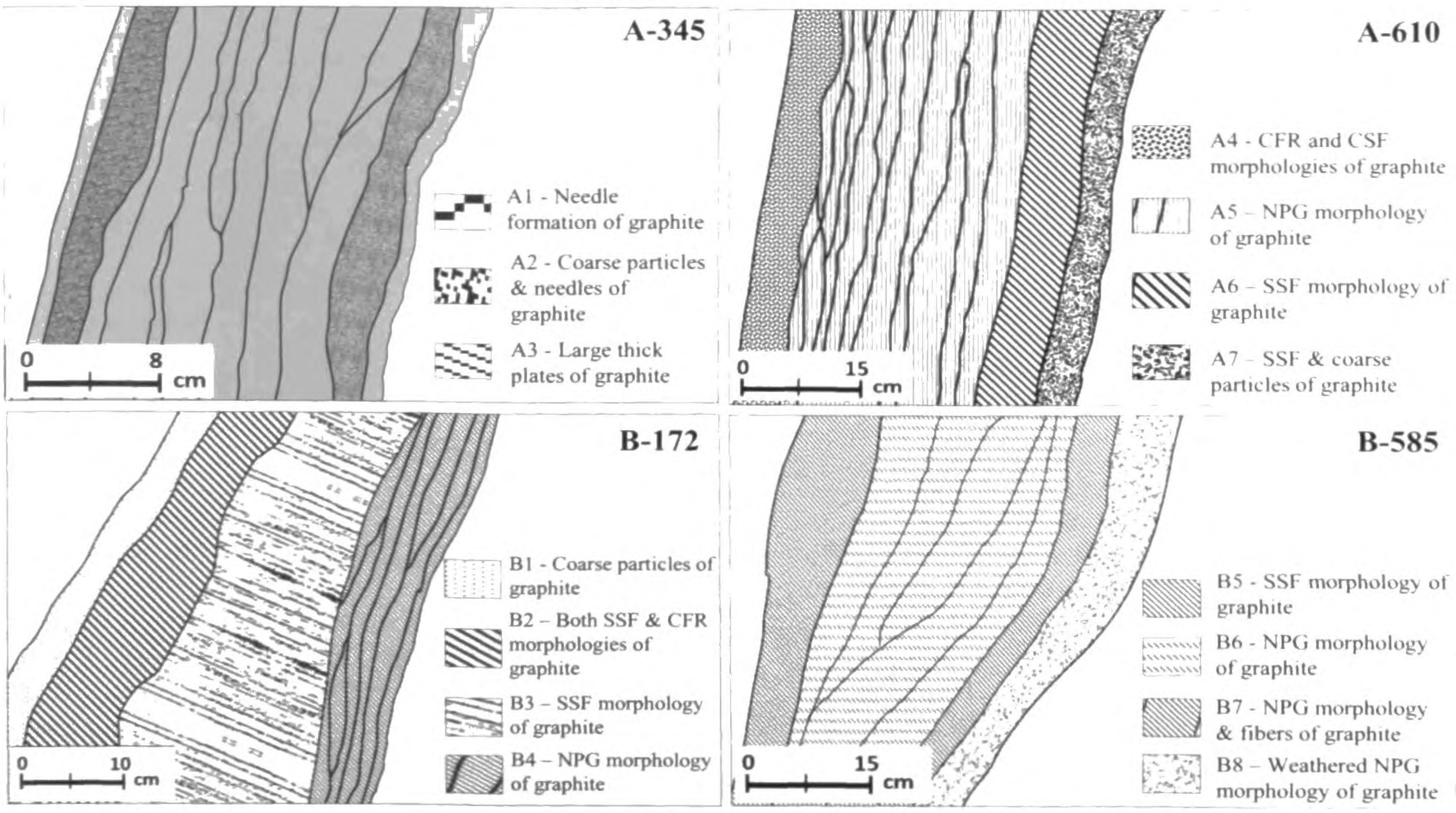

Fig. 2 Schematic diagram of vein-A exposed at 345 m level (upper left) and 610 m level (upper right) and vein-B exposed at 172 m level (lower left) and 585 m level (lower right). A-345 and A-610 represent the different sampling locations in the vein-A at 345 m and 610 m levels, respectively and B-172 and B-585 represent the sampling locations of vein-B at 172 m and 585 m level, respectively.

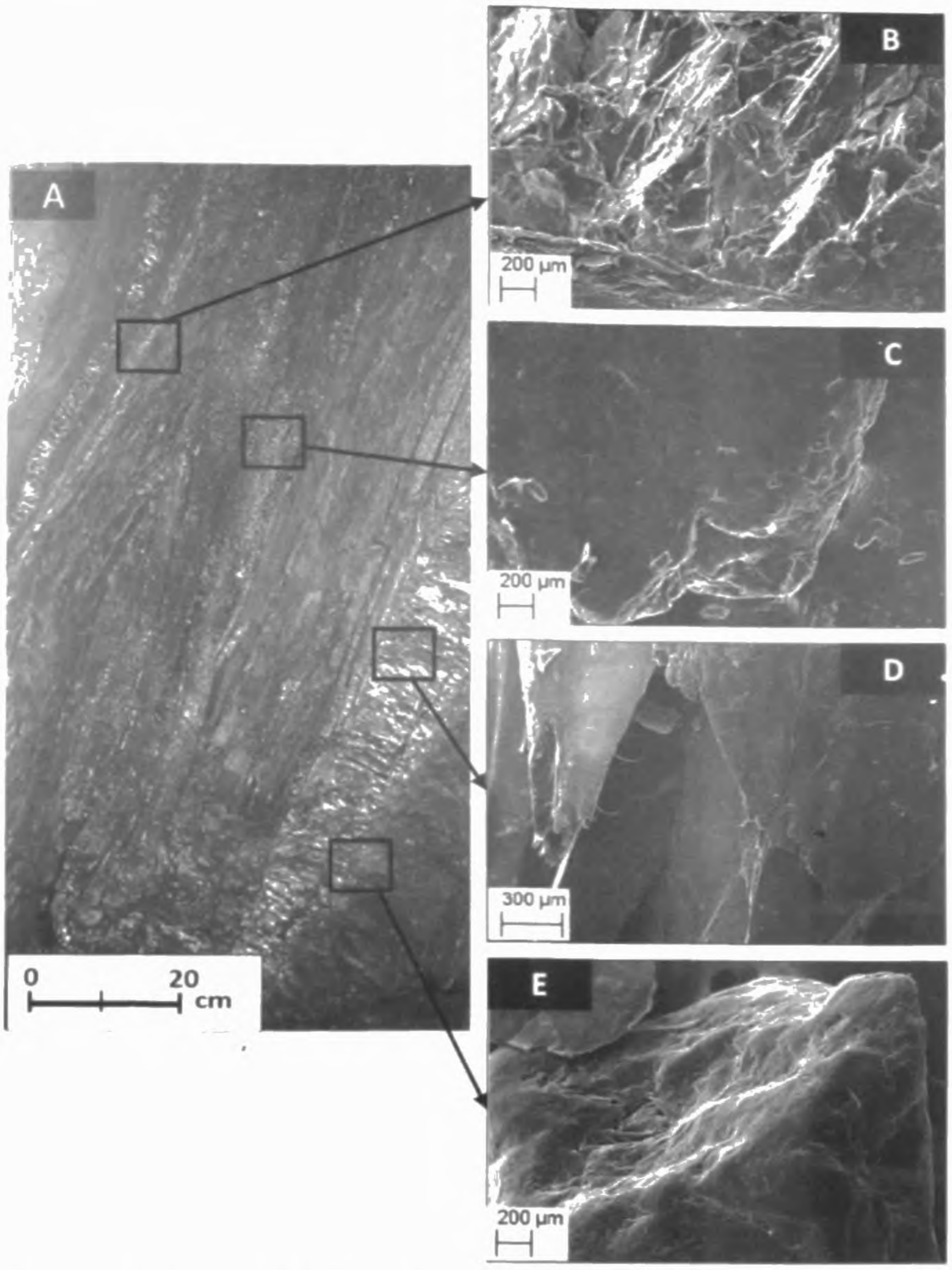

Fig. 3 Mode of occurrences of Vein-A exposed at 610 m level. B, C, D and E are the Scaning Electron Microscopy images of the samples obtained from different morphological layers

graphite that exhibits the characteristics of both SSF and CFR morphologies. Layer B3 is prominently composed with the SSF morphology that exhibit a fibrous formation of graphite oriented towards the middle of the vein and its thickness varies from 4 to 7 cm. The B4 layer, having an average thickness of around 4 cm, is composed with thick plates of graphite that characteristically belongs to the NPG morphology.

The deeper expose of the *vein-B* found at 585 m level, has the average vein thickness around 30 cm. B5 layer has SSF morphology with very fine fibers of graphite and layer thickness varies from 3 to 5 cm. The neighboring layer, B6 composed with thick plates of NPG morphology, is incorporated with graphite coarse particles. This layer has 7 to 15 cm thickness variation. Further, the Layer B7 is dominant with NPG morphology of graphite, however it shows a mingle behavior of both NPG and fibrous formation. The average layer thickness of this layer is around 5 cm. Finally, the Layer B8 consists of weathered NPG plates and its thickness varies around 10 cm.

SEM images obtained on the vein graphite samples of *vein-B* is shown in Figure 4. Characteristic fibrous formation appearing as tightly strict, continuous column with very sharp edges is shown in Figure 4B. Figure 4C and 4D show the distinct platy nature of the NPG morphology. Nevertheless, Figure 4C is composed of NPG morphology with discontinuous short steps, and Figure 4D has straight thin plates of NPG morphology.

CARBON CONTENT

Carbon contents of the selected samples are given in Table 1. The results show that purity increases significantly towards the middle of the veins at all localities. The carbon content varies with the crystal morphology and it is shown that NPG variety has the highest carbon content. In contrast, the CFR variety has the lowest carbon content. This finding is comparable with the previous studies of Amaraweera and Hewathilake, where carbon content decreases in the order of NPG > SSF > CSF > CFR (Amaraweera *et al.*, 2013; Hewathilake *et al.*, 2015).

However, some of the layers that have coarse graphite crystals, CSF and CRF formation together with NPG or SSF morphologies tend to reduce the carbon content compared to pure NPG and SSF morphologies.

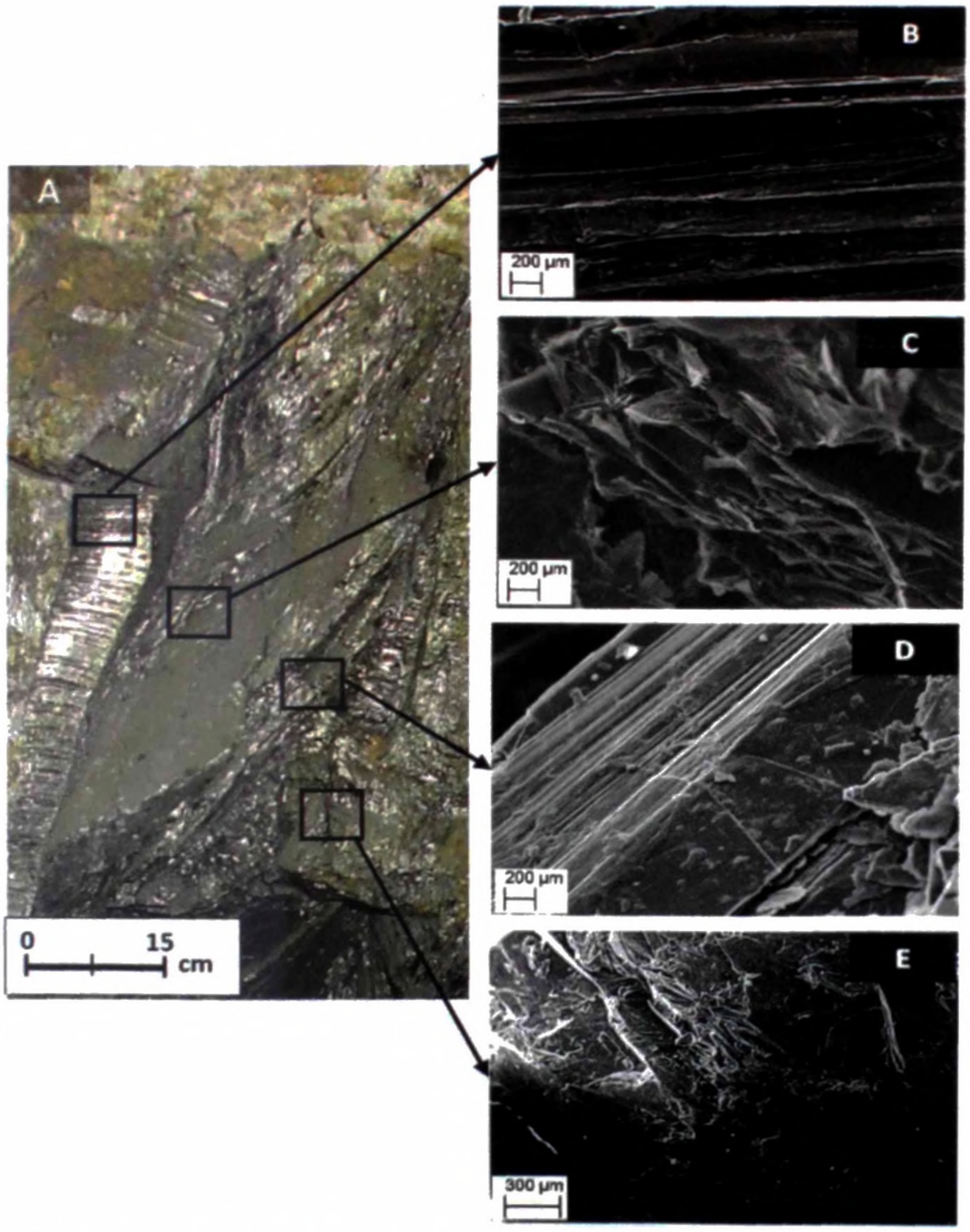

Fig. 4 Mode of occurrences of Vein-B exposed at 545 m level. B, C, D and E are the SEM images of different morphological layers

Table 1 Carbon content of the each graphite layer at different depths of vein-A and vein-B

Vein – A			*Vein – B*		
Depth from the surface (m)	Layer ID	C%	Depth from the surface (m)	Layer ID	C%
345	A1	99.67	172	B1	99.44
	A2	99.83		B2	99.71
	A3	99.18		B3	99.87
				B4	99.60
610	A4	98.84	585	B5	99.46
	A5	99.34		B6	99.76
	A6	99.16		B7	99.58
	A7	98.42		B8	98.49

CRYSTALLINITY AND IMPURITIES

The XRD phase analysis further explains the purity of the different layers of *vein-A* determined by the carbon content analysis. The intensity of the peaks related to impurity phases present in the each of the X-ray diffraction patterns obtained on *vein-A* (see Figure 5) is comparable with the results of purity analysis. At 610 m level, each layer has calcite and silicate minerals as impurities. However, the layers attached to the wall rock are dominated

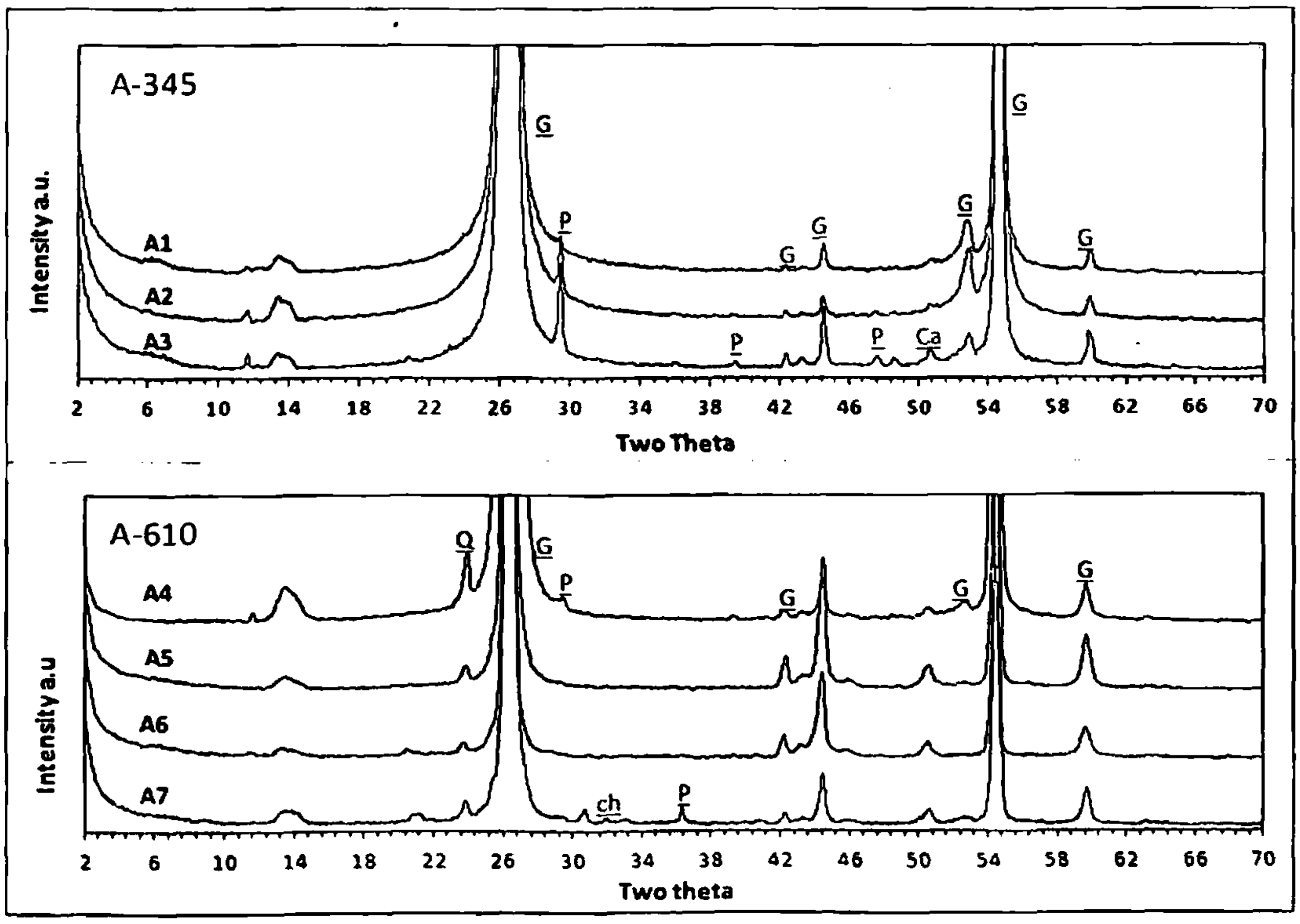

Fig. 5 XRD patterns obtained on the layers at different elevations (345 m - A1, A2 and A3 and 610 m - A4, A5, A6 and A7) of the vein-A. The prefixes denote: G - graphite, Q - quartz, P - pyrite, Ca - calcite and Ch – Chlorite

Table 2 Crystallographic parameters of each layer at two different depth of vein-A

Depth from the surface (m)	Layer ID	L_c (nm)	L_a (nm)	Degree of Graphitization
	A1	30.01	66.48	91.98
345	A2	25.64	65.06	94.77
	A3	28.26	79.10	91.98
	A4	21.64	34.83	86.13
	A5	22.91	35.56	77.40
610	A6	23.41	41.48	64.23
	A7	23.06	35.56	77.40

by pyrite, chlorite and chalcopyrite as impurities with minor amount of calcite and silicate minerals.

The coherence length Lc and La have only minor differences with respect to the crystal morphology of the graphite in each exposing level. At the 610 m level, Lc and La vary in the range of 21 - 23 nm and 34 - 41 nm, respectively. However, the vein propagate towards the surface, both the Lc and La values of each layer increases considerably (Lc and La values increases to the range of 25 - 30 nm and 65 - 79 nm, respectively). The degree of graphitization also follows the similar trend as the coherence length parameters when the vein propagates towards the surface.

Two exposing levels of *vein- B* (Figure 6) have the same trend of impurity distribution as observed with the vein-A. The layers, which are readily attached to the wall rock, are rich with quartz, calcite, chlorite, pyrite and chalcopyrite minerals. While the layers in the middle of the vein, are composed of quartz and calcite only. At the deeper expose of vein-B at 585 m, the coherence length values Lc and La vary between 19.0 - 23.5 nm and 27.5 - 39.0 nm, respectively.

For the layers in 172 m level, Lc and La lengths are varying between 28.5 -31.0 nm and 48.0 - 69.0 nm, respectively. The vein propagates from deeper level (585 m) to shallow level (172 m), and the corresponding Lc and La show a significant increment with that. Also the degree of graphitization follows a similar increment

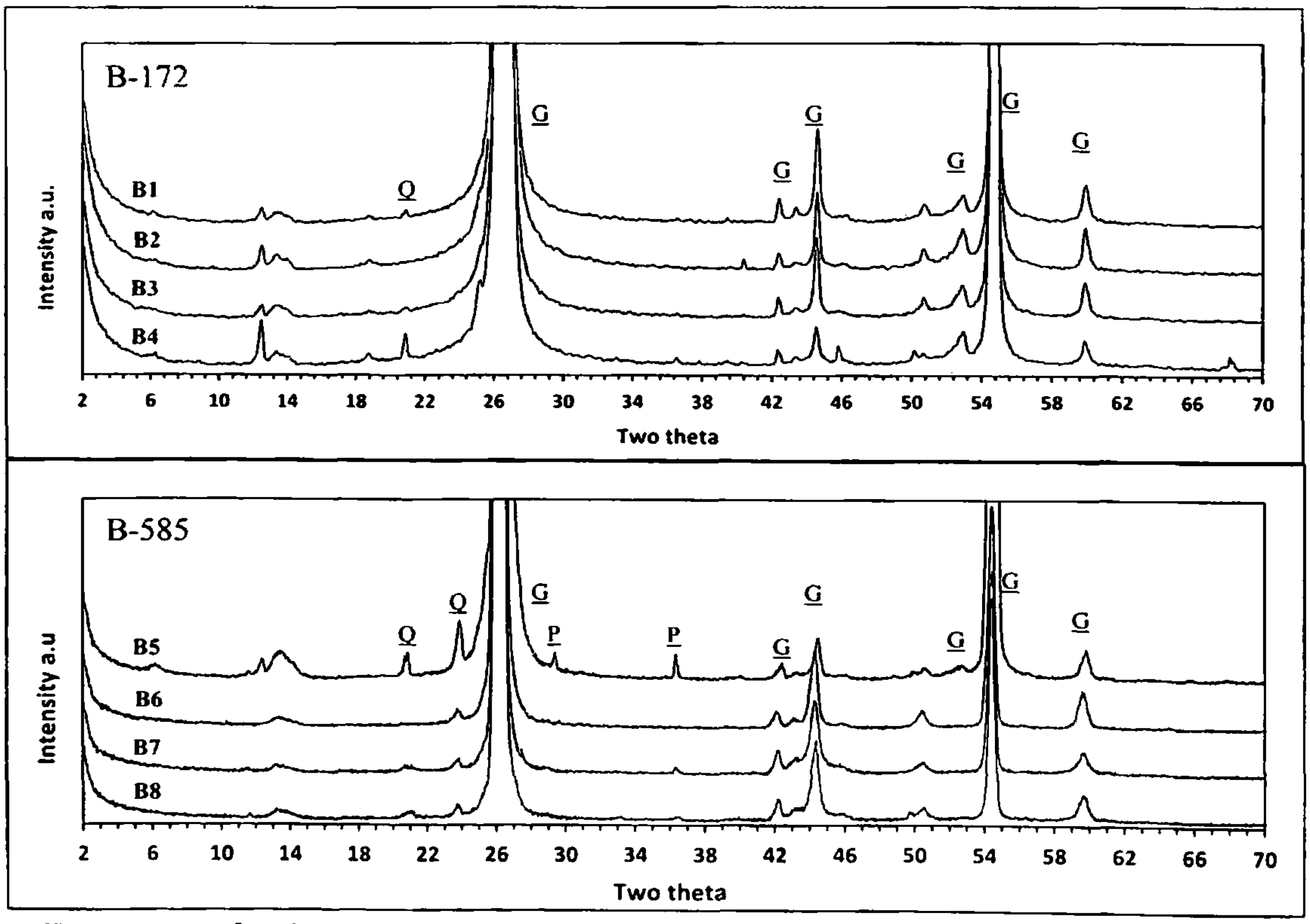

Fig. 6 XRD patterns for the each layer at different elevations (172 m - B1, B2, B3 and B4 and 585 m - B5, B6, B7 and B8) of the vein-B. The prefixes dnotes: G - graphite, Q - quartz, P – pyrite

Table 3 Crystallographic parameters of each layer at two different elevations of vein - B

Depth from the surface (m)	Layer ID	L_c (nm)	L_a (nm)	Degree of Graphitization
172	B1	30.67	53.37	91.98
	B2	29.21	48.35	91.98
	B3	28.15	54.35	97.67
	B4	28.95	68.98	91.98
585	B5	23.21	27.25	99.15
	B6	19.03	38.71	81.77
	B7	22.02	35.56	81.77
	B8	23.15	34.85	73.02

pattern when come to the shallow levels (see Table 3).

CRYSTALLIZATION SEQUENCE

Based on the analysis of the results, it can be suggested that the crystallization of graphite may have taken place either from multistage hydrothermal fluids or multistage crystallization process from single hydrothermal activity. In a multistage crystallization, arrived hydrothermal fluid into the vein initiate the crystallization towards the middle of the vein from the wall rock. The temperature gradient and impurity element inclusions from the wall rock, may lead to higher degree of crystallization of graphite near to the wall rock. Then initially formed layers may apply a pressure towards the middle of the vein that could formed a thick platy morphological layers of vein graphite.

If the vein crystallization follows a multi stage hydrothermal inclusion, the first insertion of hydrothermal fluid into the fractured zone tend to cool down and most prominently formed the radiating crystals of graphite (CFR morphology,) which directly attached to the wall rock (see Figures 7, S-01 and S-02). This layer attributes to the higher degree of crystallization with minimum disturbance with available free space. Simultaneously, the optimum rate of nucleation was provided by wall rock contaminations and impurities present in the hydrothermal fluid. Middle layers in the vein were formed by the second phase hydrothermal fluid insertion.

The next layer readily attached to the CFR morphological layer mostly composed of fine and thick fibers with the SSF morphology of graphite. Characteristically, these fibers are loosely stacked on each other and mostly, formed perpendicular to the direction of vein propagation. However, some cross sections of the vein have coarse particles or small flakes

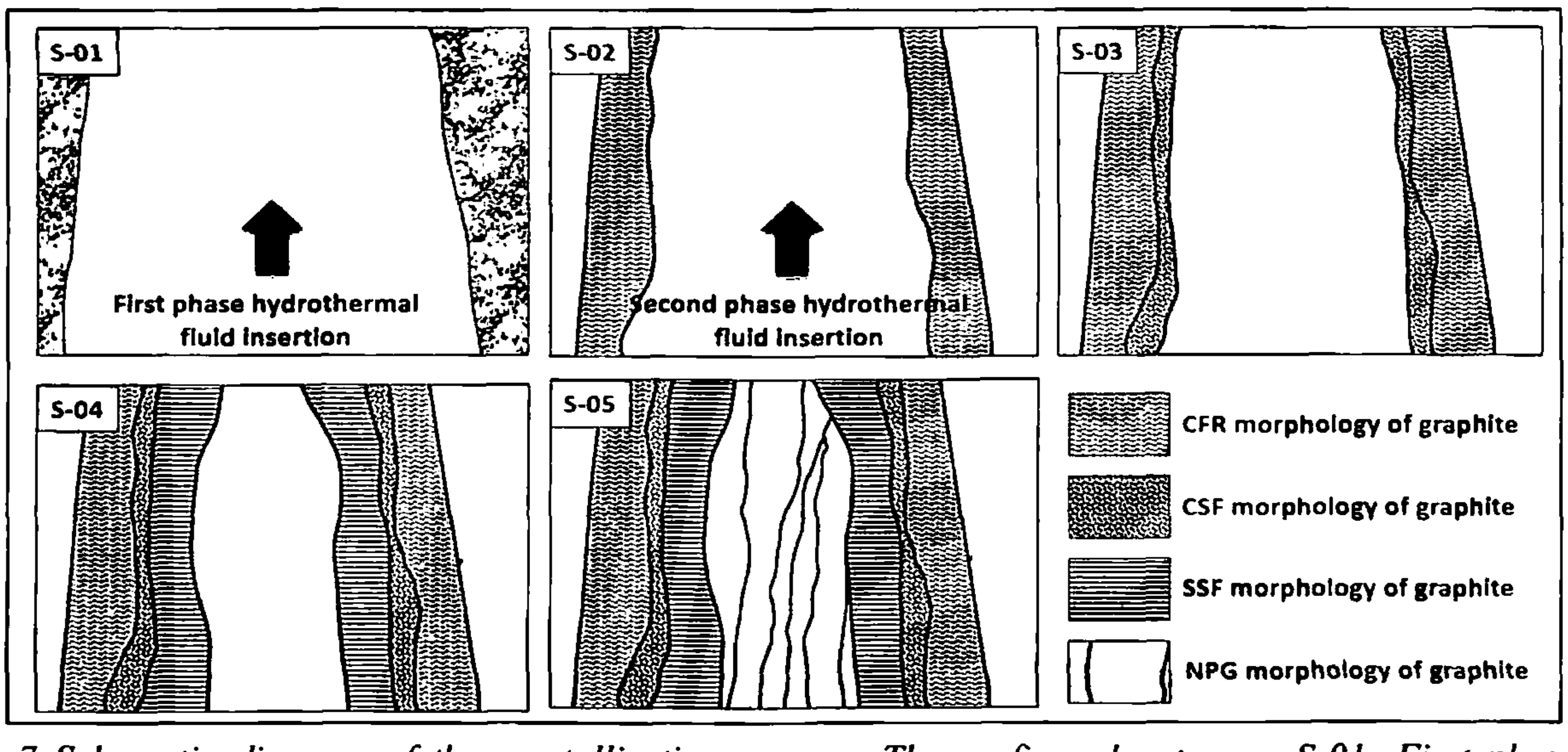

Fig. 7 Schematic diagram of the crystallization process. The prefixes denotes: S-01- First phase hydrothermal fluid insertion, S-02 - Crystallization of CFR morphology & Second phase hydrothermal fluid insertion, S-03 - Crystallization of CSF morphological layer, S-04 - Crystallization of SSF morphological layer, S-05 - Crystallization of NPG morphological layer

with the CSF morphology of graphite in between the CFR and SSF morphological layer (see Figure 7, S-03 and S-04).

The middle layer is composed of thick plates of NPG morphology (Figure 7, S-05). This layer has the highest carbon content and a lower degree of crystallization. Moreover, these thick plates of graphite have sharp contact with outer layers and mostly they are arranged parallel to the direction of vein propagation. This characteristic formation exhibits that second phase crystallization occurred towards the middle of the vein and SSF layer crystallization took higher degree of freedom compared to the middle NPG layer.

CONCLUSIONS

The studied graphite veins at different elevation levels have different formation in terms of chemical composition, morphological features and crystallographic parameters. However, within a single vein such properties are varying with the depth. Consequently, in a vein, the degree of graphitization and purity of the graphite are increasing towards the shallow depth. But they are decreasing towards the wall rock. The crystallographic sequence suggests that the formation of the vein graphite in Kahatagaha-Kolongaha mines may be resulted from multi stage hydrothermal invasion or due to different stages of crystallization. However, the finding of the present study should be confirmed by detailed studies on different vein graphite deposits in the country.

ACKNOWLEDGEMENTS

The Kahatagaha- Kolongaha mines of Sri Lanka and the financial assistance from Innovative Research Grant-2013 of University Grant Commission of Sri Lanka are acknowledged.

REFERENCES

Amaraweera, T.H.N.G., Balasooriya, N.W.B., Wijayasinghe, H.W.M.A.C., Attanayake, A.N.B. and Dissanayake, M.A.K.L. (2013) Purity Enhancement of Sri Lankan Vein Graphite for Lithium-ion Rechargeable Battery Anode, Proceedings, 29th Technical Sessions of Geological Society of Sri Lanka, pp 101-104.

Balasooriya, N.W.B., Dahanayake, K., Touzain, P. and Bandaranayake, P.W.S.K. (2002) Structure characteristics of Sri Lanka graphite. Ceylon J. of Sci. Physical Sciences, 9:41-48.

Binu-Lal, S.S., Kehelpannala, K.V.W., Satish-Kumar, M. and Wada, H. (2003) Multistage graphite precipitation through protracted fluid flow in sheared metagranitoid, Digana, Sri Lanka: evidence from stable isotopes. Chemical Geology, 197: 253-270.

Cooray, P.G. (1994) The Precambrian of Sri Lanka, A historic review. Precambrian Research, 66:3-18.

Dissanayake, C.B. (1981) The origin of graphite of Sri Lanka. Organic Geochemistry, 3:1-7.

Dissanayake, C.B., Gunawardena, R.P. and Dinalankara, D.M.S.K. (1988) Trace Elements in Vein Graphite of Sri Lanka. Chemical Geology, 68:121-128.

Erdosh, D. (1970) Geology of Bogala mine, Ceylon and the origin of vein type graphite. Mineral Deposita, 5:375-382.

Hapuarachchi, D.J.A.C. (1977) Decarbonation Reactions and the origin of vein graphite in Sri Lanka. J. Nat. Sci Council of Sri Lanka, 5:29-32.

Hewathilake, H.P.T.S., Wijayasinghe, H. W. M. A. C., Balasooriya, N.W.B. and Pitawala, H.M.T.G.A. (2015) Proceedings, 31st Technical Sessions of Geological Society of Sri Lanka, pp 28.

Katz, M.B. (1987) Graphite deposits of Sri Lanka: a consequence of granulite facies metamorphism. Mineral Deposita, 22:18-25.

Kehelpannala, K.V.W. (1993) Structural Evolution in the Area Surrounding the Kahatagaha–Kolongaha Graphite Mines, N–NW of Kandy, and the Origin of Vein Graphite in Sri Lanka. Ph.D. Thesis, University of Mainz, Mainz-Germany.

Kehelpannala, K.V.W. (1995) Origin of Vein Graphite in Sri Lanka - Another View. In handbook on Geology and Mineral Resources of Sri Lanka, K. Dahanayake, (ed.) GEOSAS-II, Colombo, Sri Lanka pp 95-103.

Kehelpannala, K.V.W. (1999) Epigenetic Vein Graphite Mineralization in the Granulite Terrain of Sri Lanka. Gondwana Research, 2: 654-657.

Silva, K.K.M.W. (1987) Mineralization and wall-rock alteration at the Bogala graphite deposit, Bulathkohupitiya, Sri Lanka. Economical Geology, 82:1710-1722.

Touzain,Ph., Balasooriya, N.W.B., Bandaranayake, P.W.S.K. and Descolas, G. (2010) Vein Graphite from the Bogala and Kahatagaha–Kolongaha Mines, Sri Lanka: A Possible Origin. The Canadian Mineralogist, 48:1373-1384.

Wijayananda, N.P. (1987) The Graphite Industry in Sri Lanka, Science education series 24, Natural Resources energy and science authority, pp 23-25.

Wijayananda, N.P. and Jayawardana, D.E. De S. (1983) Some aspects of the geology of graphite mineralization in Sri Lanka, with particular reference to the Kahatagaha-Kolongaha Area. Trans. Inst. Mining Metall., Applied Earth Science, 92:93-98.

Wyckoff, R.W.G. (1963) Crystal Structures. Inter-science,1:24.