MINERALOGY OF GRAPHITE FROM THE GRAPHITE-BEARING SCHISTS OF WADI LAWI, SOUTH EASTERN DESERT, EGYPT

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The area of Wadi Lawi in the South Eastern Desert of Egypt is delineated by the Longs. 34°20´ and 34°49´E. and Lats 24°44´ and 24°47´ N. (Fig. 1). The graphite-bearing schists of the studied area are included in the mélange matrix, which constitute a member of Wadi Ghadir ophiolite sequence, previously studied by several authors (El Bayoumi 1980, Shackelton et al. 1980, Ries et al. 1983, Basta 1983 and Bishady et al. 1994).

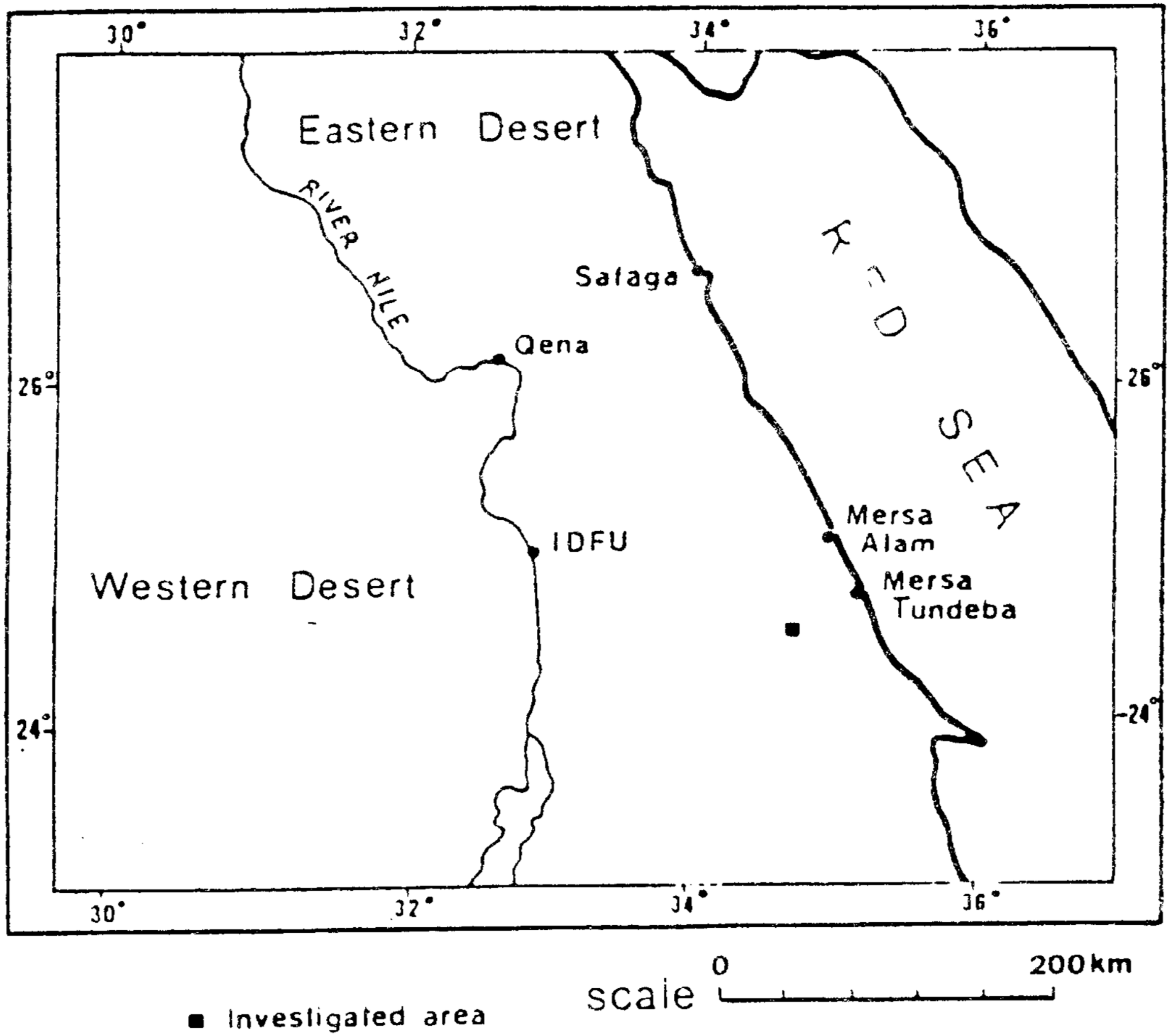


Fig. (1): Location map.

The graphitized schists of Wadi Lawi are associated mainly with the actinolite-bearing schists of the mélange matrix. They are highly friable and occur in a patchy form occasionally enclosing white powdered talc rock, which indicates the effect of metasomatism in the area of graphitization. The graphite-bearing schists exhibit petrographically a well defined schistosity, and can be distinguished into two varieties.

Fine-grained graphite and carbonaceous material are generally dispersed in the groundmass and may fill the cracks and cleavage planes of some other minerals (Fig. 2). Massive dense aggregates of graphitic material may occur as patches, streaks and veinlets exhibiting crumbling and microfolding (Fig. 3).

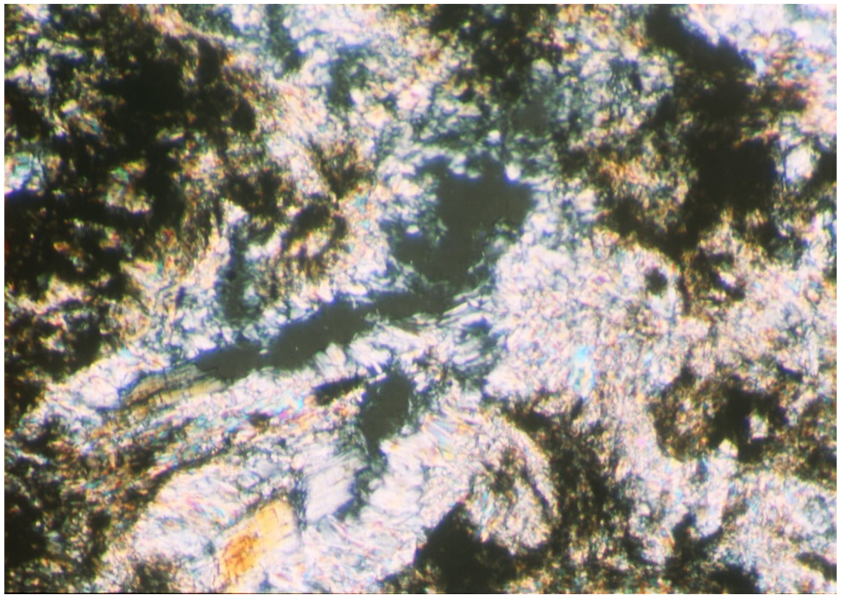


Fig. (2): Photomicrograph of a thin section in graphite-bearing schists, showing graphitic material filling the interstices of the talcose rock. P.P.L. X=34

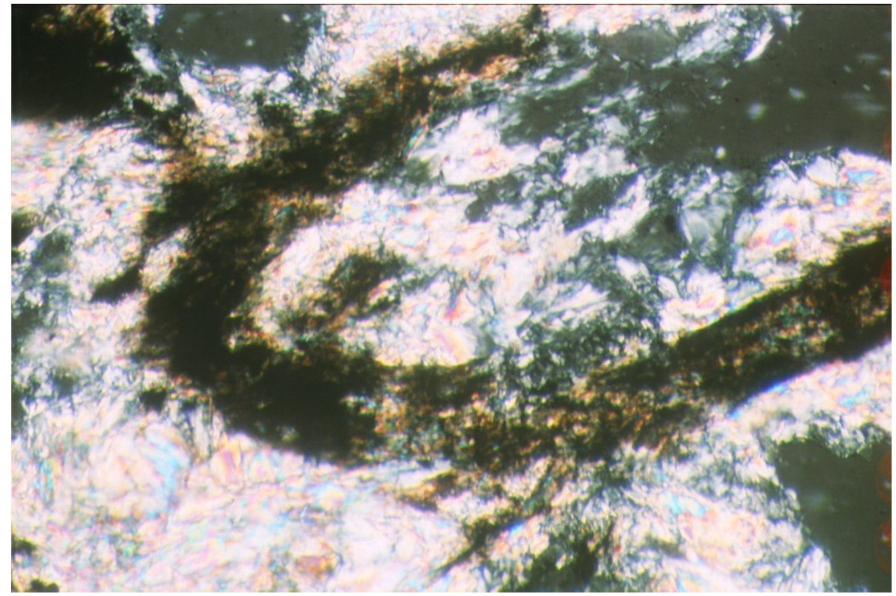


Fig. (3): Photomicrograph of thin section in graphite- bearing schists, showing crumbling of graphite material. C. P. X = 180

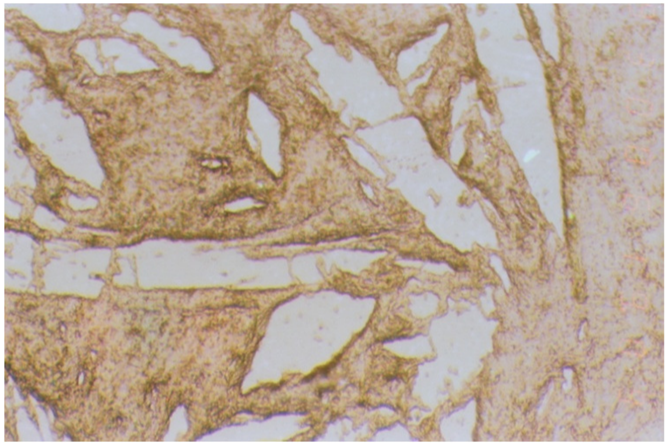


Fig. (4): Photomicrograph of a Polished surface in graphite-bearing schists, showing medium to fine grained graphite blades. P.P.L. X = 100

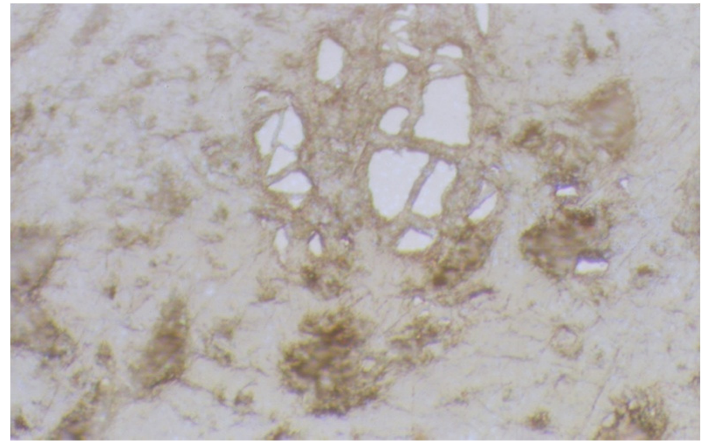


Fig. (5): Photomicrograph of a Polished surface in graphite-bearing schists, showing the skeletal aggregates of magnetite P.P.L X=180

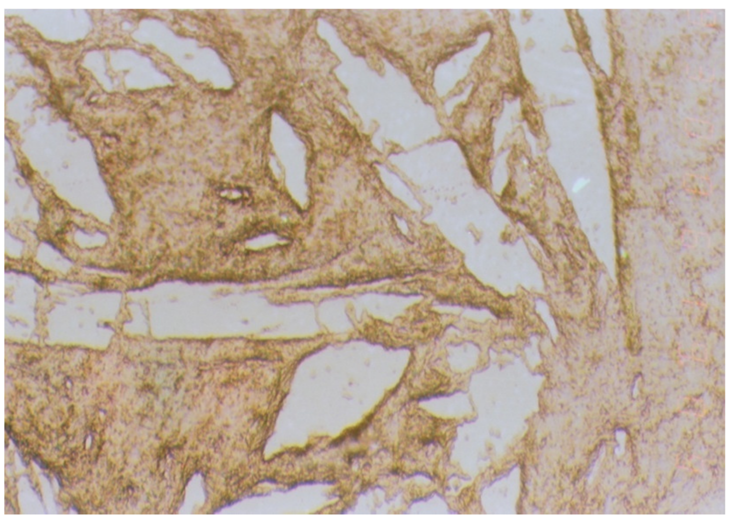


Fig. (6): Photomicrograph of a polished surface in graphite-bearing schists, showing pyrite (P) fine intergrowths in graphite blades.
P.P.L. X = 180

In the polished surfaces of some 15 samples, graphite occurs in both varieties of schists, as fine to medium grained bundles, blades and laths (Fig. 4). It is sometimes bent and crumbled. Graphite exhibits grayish white color, with strong anisotropism and wavy extinction. Bireflectance in graphite is clear, where Rmax in oil ranges from 10 to 14, for Wadi Lawi graphitic material, which can be compared with that of the semi-graphite to full-ordered graphite mentioned by Diessel and Offler (1975) and Kwieciňska (1980).

The most commonly associated opaque mineral is magnetite, which occurs as subhedral medium to fine grains, forming skeletal aggregates (Fig. 5). Fine grained pyrite is enclosed in graphite (Fig. 6), whereas it is also commonly seen scattered in the gangue. Scarce specks of chalcopyrite are noticed.

Carbonaceous material was separated from other, acid dissolved materials in three samples of the graphite-bearing Wadi Lawi schists, by the treatment with hot HF and HCl, following a procedure that does not affect the chemistry and crystal structure of graphite (French 1964, Landis 1971, Grew 1974 and Itaya 1981).

X-ray diffraction (XRD)

Landis (1971) mentioned that the term graphite is used for the fully ordered variety. All sub-graphic carbon can be designated as graphite-d, and increase in degree of disorder can be expressed in terms of subscript values (d_1, d_2 and d_3) . Fully ordered graphite is characterized by a diffraction pattern with an intense, sharp and symmetrical (002) (hexagonal index with I index omitted) reflection at 3.35 – 3.36 Ả, as well as other considerably weaker reflections (e.g. 100, 101, 004) at higher angels . The decrease of ordering from graphite to graphite-d is accompanied by; A- The absence of reflections other than (002), B- Broadening and markedly skewing of the (002) peak, and C- The increase of d002 values up to 3.5-3.75 Ả for d_2 and d_3.

XRD patterns for Wadi Lawi graphitic material, and the data concerning the 002 peak extracted from these patterns, compared with those of Landis (1971) (Table 1), show that the graphitic material in sample (39) is compared with the fully ordered graphite. The other two samples (42 and 34) are related to the graphite-d1 of Landis (op.cit.), on the basis of skewing of the (002) peak, in addition to the disappearance of any other reflections. other than the (002) on the reflectometer traces of these samples.

Table 1- XRD data concerning the 002 peak.

Reference	I/I$_o$	Correct d_{002} at max.	Height / Width At ½ height	d_{002} Å at (½ width at ½ height)
Wadi Lawi				
S. No. 39	**98**	**3.35**	**57***	**3.3**
S. No. 23	**4**	**3.35**	**6**	**3.35**
S. No. 42	**4**	**3.35**	**10**	**3.35**
Graphite(Landis1971)	**-**	**3.35-3.36**	**30**	**3.35-3.36**
Fully ordered	**-**	**3.35-3.36**	**3-15**	**3.38-3.41**
Graphite d_1	**-**	**3.37-3.44**	**3-15**	**ca. 3.40**
Graphite d_{1A}				

The skewed (002) peak presented in the diffractograms of the sample (42 & 23), may be attributed to a mixture of slightly ordered graphitic materials (e.g. fully ordered graphite and graphite-d1), Grain size, shape and crystallinity of the separated graphite material, from Wadi Lawi samples, were investigated using the transmission electron microscope (TEM). Nevertheless the coarser flakes are common, reaching up to 8 microns, the particle size of the graphitic material was widely varied (Fig. 7). They exhibit irregular particles with ragged, platy, angular to subrounded outlines, and frequently aggregated.

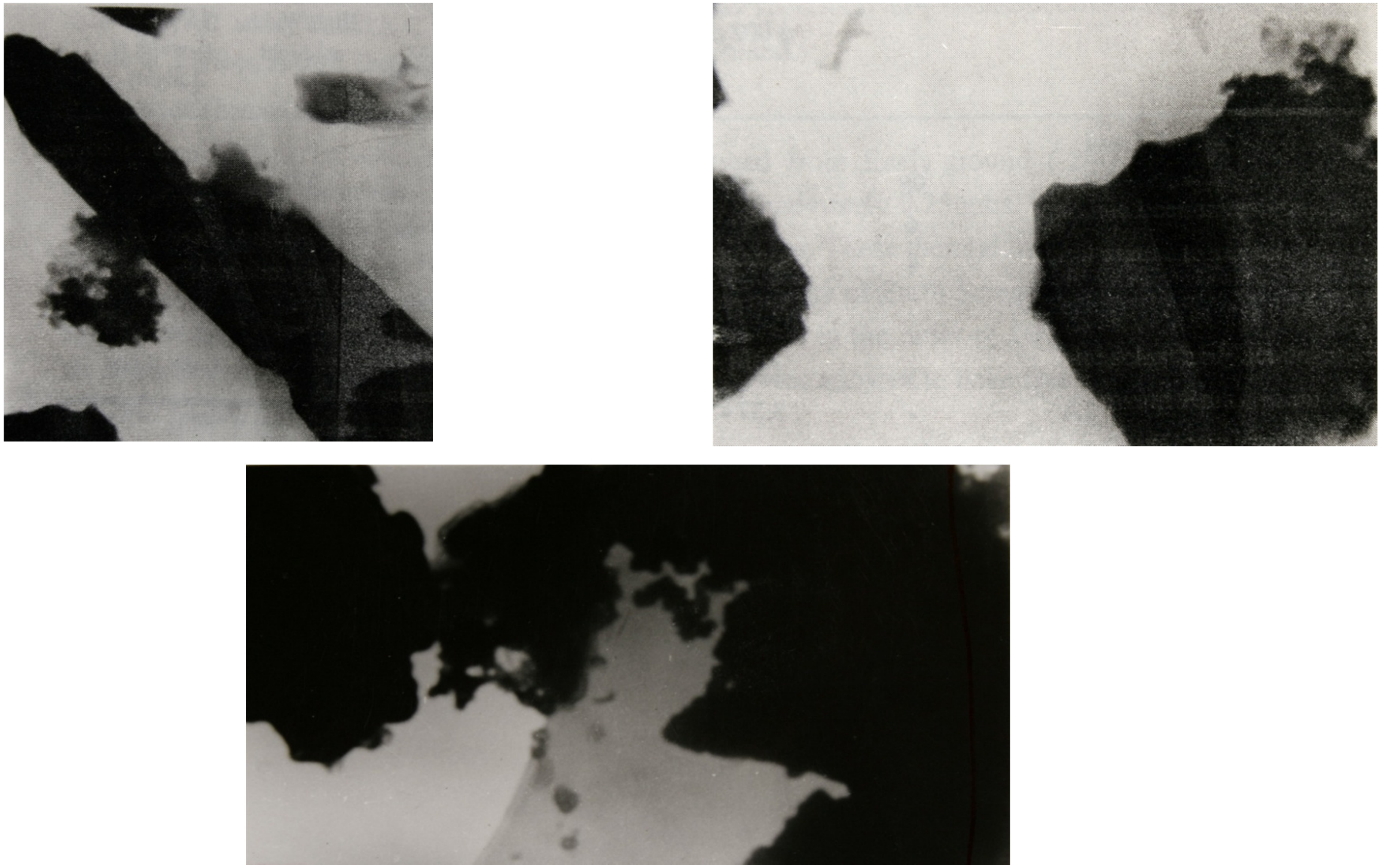


Fig (7): Transmission Electron micrograph of the separated graphitic material from wadi Lawi samples

Note : the variation in size and shape of particles. Well formed , subhedral hexagonal crystallites are evident in the samples.

A & B from sample (39) , and C from sample (42).

A & B : X = 2800 and C : X = 7000.

Electron diffraction patterns were obtained from numerous particles in each sample. Aggregated concentrations may give polycrystalline electron diffraction patterns. Wadi Lawi graphitic samples exhibit two main pattern varieties (Fig. 8);

A-Distinct spot pattern of the diffractional reflexes of the graphite lattice, representing the fully-ordered structure of graphite, and

B- Ring patterns, which may be with weak superimposed spots corresponding to (100) and (110) reflections, exhibiting lower ordering in graphite.

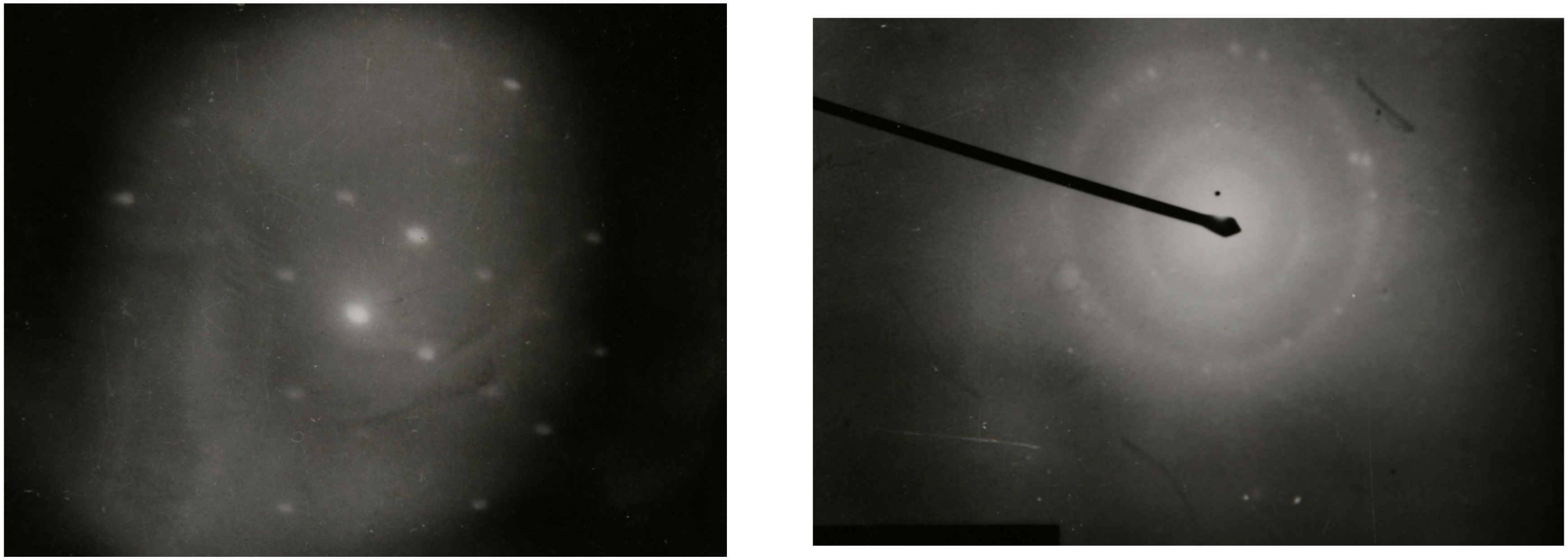


Fig. (8): Electron diffraction patterns obtained from different graphite crystallites.
A : Spot pattern in bright field from well-ordered graphite plate.
B : Ring patterns with weak superimposed spots corresponding to (100) and (110) reflexes , obtained in dark field , from less – ordered graphite plates.

The occurrence of the two structural states – confirmed by XRD previously mentioned – are comparable with those of Landis (1971), Itaya (1981) and Buseck and Bo-Jun (1985). While Landis (op.cit.) suggest that this is due to the intermixing (inter-layering) of the fully-ordered graphite, with a less ordered variety, Itaya (op. cit.) mentioned that it may be due to the presence of both fully-ordered detrital graphite and metamorphosed carbonaceous material in the same sample, where the sharp reciprocal lattice points observed by Landis could be due to the detrital graphite. Buseck and Bo-June (1985), considered that the variability of the structures revealed by HRTEM images appear to be the continuous process of graphitization of the carbonaceous material through the progressive metamorphism. They (op. cit.) on another hand attributed that structural heterogeneity to that the precursor materials may have consisted of both graphitized and non-graphitized carbon.

C-Carbon Isotopic composition

$\delta = R_{sample} - R_{standard} / R_{standard} * 1000$

as: $R = C^{13} / C^{12}$ for carbon, and $R = O^{18} / O^{16}$ for oxygen.

δ^{13} C values of Wadi Lawi graphite range from -22.85‰ to -23.39‰ with an average -23.06‰, refer to an organic protolith for that graphite, whereas graphite δ^{13} values around -22‰ (PDB) exhibit the isotopic characteristics in silicate rocks and confirm their organogenic origin (Oehler and Smith 1977; Hoefs 1987and Schrauder et al. 1993).Schrauder et al. (op.cit.) mentioned also that the small variations of carbon isotopic composition from various localities (which are also included in table 2) imply that the protoliths were homogeneous in terms of carbon isotopic composition.

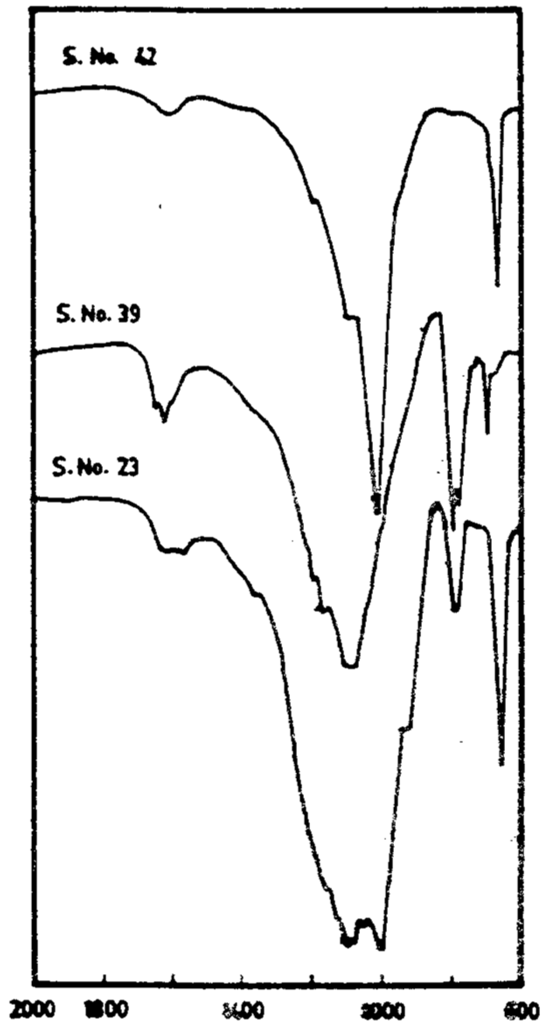
In spite of the igneous origin of Wadi Lawi graphite schists (Bishady et al.1994), graphite organogenic origin is suggested, whereas the juvenile carbon is believed to have $\delta^{13}C$ value of about -7‰, and if it was derived from magmatic carbon monoxide the δ^{13} C of the source gas should have been approximately -5 to -7‰ (Vinogradov and Kropotova 1968 and Dengens 1969, Deines and Gold 1969 and Weiss et al. 1981). The addition of any filtration CO2-rich fluids during metamorphism seems unlikely in view of the presence of low δ^{13} C values of graphite (Schrauder et al. 1993). Accordingly, the possibility cannot be eliminated that this graphitic carbon in Wadi Lawi schists is related to post depositional contaminations, which is in agreement with the suggestions of Oehler and Smith (1977), through their investigations of reduced carbon in the early Archean rocks from Isua, Greenland.

Table 2- Carbon and oxygen isotopic composition of graphite from Wadi Lawi and some world averages.

References	$\delta^{13}C$ (PDB)	$\delta^{18}O$ (VSMOW)
Wadi Lawi graphite		
S. No. 39	-22.93	-10.16
S.No. 23	-22.85	-14.49
S. No. 42	-23.39	-16.49
Kwiecińska (1980)		
Graphite in gneisses, phyllites and mica schists (Pninerdo, Italy)	-23.60	-22.20
Quartz-graphite schist	-27.80	-17.70
Graphite ore (Witoslowice, Poland)	-21.10	-20.00
Graphite disseminated in gneisses (Black Donald Mine, Ontario, Canada).	-21.20	-19.10
Weiss et al. (1993)		
Graphitized coal	-21.90	nd
Graphite from schists	-21.70	nd
Flake graphite marble	-3.65	nd
Schrauder et al. (1993)		
Graphite in gneisses of Elsenreich	-21.50	nd
Graphite in gneisses of Amstal	-23.15	nd

nd= not determined

$\delta^{18}O$ (VSMOW) for Wadi Lawi graphite ranges from -10.16 to -16.49‰ with an average of -13.17‰. These values are hardly comparable with the $\delta^{18}O$ values estimated for graphite separated from metamorphic siliceous rocks. Wadi Lawi graphite $\delta^{18}O$ values played a good role with those of graphite separated from carbonate bearing rocks (Table 2). Kwieciňska (1980) mentioned that the isotopic composition of oxygen does not show any regularities in the graphites she studied. The present author think that the main reason of that argument, is due to the lack of correct data on the oxygen isotopic composition in graphite separated from siliceous rocks to be compared with.



Wave number (cm-1)

Fig. (9): DTA patterns for graphitic material separated from Wadi Lawi schists

Notice ; the endothermic peak of the remnant quartz at 570° C in sample 39.

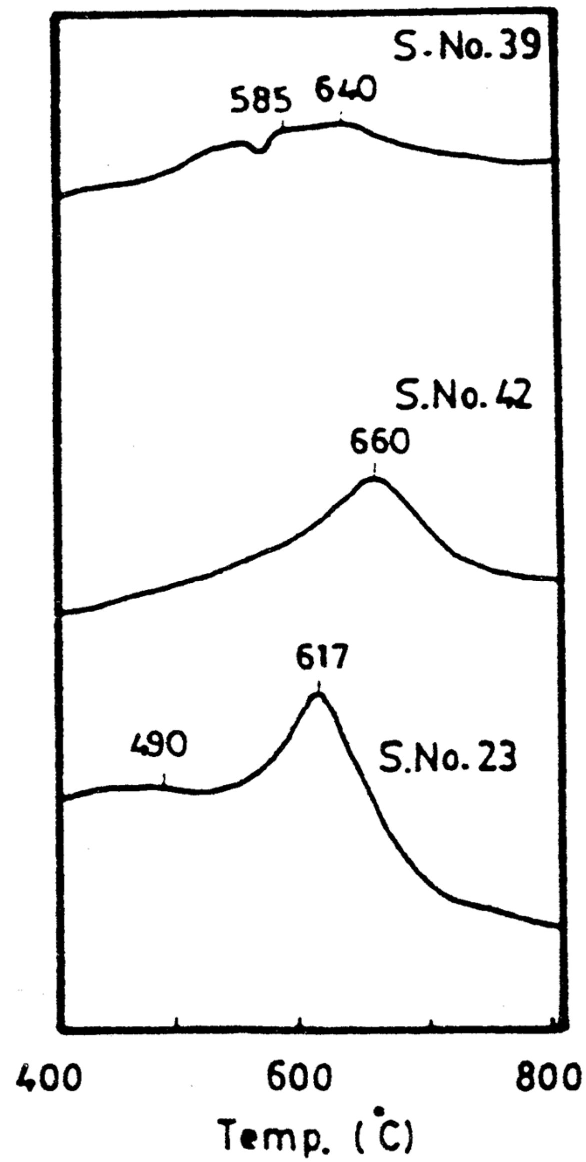
D – Differential thermal analysis (DTA)

DTA was applied on Wadi Lawi graphite samples to determine their nature and also to define their metamorphic conditions.

In agreement with that previously mentioned by Diessel and Offler (1975), Kwieciňska and Parachoňiak (1976) and Kwieciňska (1980), the DTA curves of Wadi Lawi graphite (Fig. 9). Show distinct exothermal effects in the range of 585° to 640℃, and generally followed by small endothermic reactions. Skewing of these DTA peaks and their relatively low intensity can be interpreted according to Kwieciňska (1980) suggestions that the DTA peaks may show variations in shape and breadth depending on the amount of graphitic substances, whereas Diessel and Offler (1975) noted also that there is an increase in both peak width and temperature with increasing metamorphic grade.

E- Infra Red Spectra (IR)

The chemical structure of the separated graphic material from Wadi Lawi samples investigated by IR spectroscopy, where figure (10) shows several bands appearing in all of the detected samples, ranging from 580 to 990 cm-1. These bands are characteristic for the out of plane bending for the aromatic hydrocarbons (Pavia et al. 1979), which confirm the organogenic origin of these graphitic materials.



Discussion and conclusions

The mineralogy of the graphitic materials in the graphite-bearing schists of Wadi Lawi shows that they range from semi-graphite (graphite-d1) to graphite (full-ordered graphite). the isotopic composition, the DTA and IR of the present work graphite, refer to organic protoliths for Wadi Lawi graphitic materials.

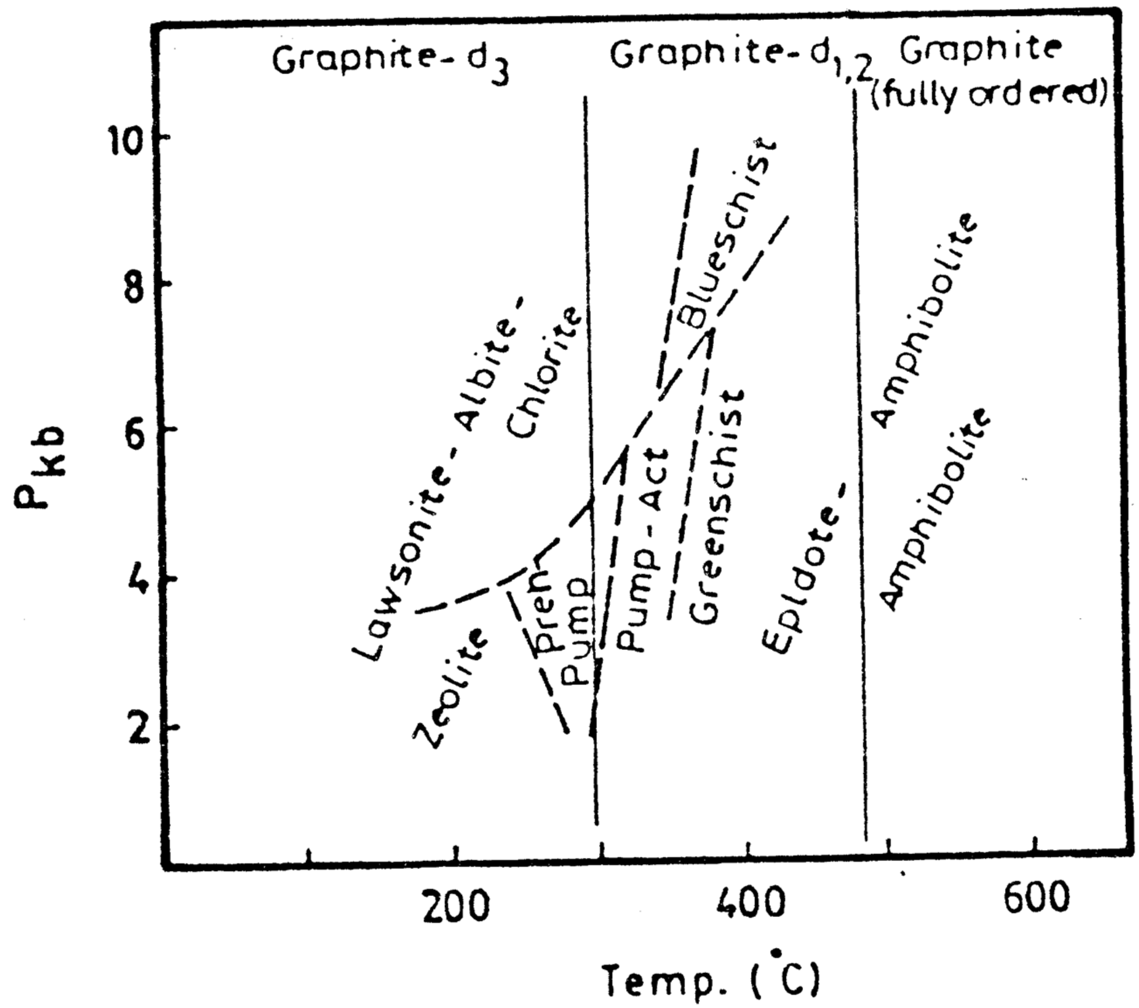


Fig. (11): P - T facies metamorphic grid , showing estimated conditions at which fully-ordered graphite occur in nature . The curve after Landis (1971).

XRD and DTA investigations can reveal that the graphitic material is formed under conditions of the greenschist facies

It is also suggested - according to Landis (1971) as in figure (11), in addition to Grew (1974), estimations for the temperature of the first appearance of layered ordering in graphite (300 to 500℃ at a pressure of 3 Kb or more) - that the temperature of graphite formation in Wadi Lawi ranges from 400 to 600℃ in a pressure range of 4 to 6 Kb.