GRAPHITE OCCURRENCES IN NE-HUNGARY

LÍVIA LESKÓNÉ MAJOROS[1]*, MÁTÉ ZSIGMOND LESKÓ[1], KRISZTIÁN FINTOR[2], SÁNDOR SZAKÁLL[1], FERENC KRISTÁLY[1]
[1]*Institute of Mineralogy and Geology, University of Miskolc*
[2]*Department of Mineralogy, Geochemistry and Petrology, University of Szeged*
**asklivia@uni-miskolc.hu*

Abstract: Graphite is a versatile, basic industrial mineral, which is also included on the list of Critical Raw Materials for the European Union. In our study, three NE-Hungarian graphite-bearing occurrences are in focus: Dédestapolcsány (Uppony Mts.), Szendrőlád and Meszes (Szendrő Mts.). The collected samples are investigated with polarizing petrographic and ore microscopy, scanning electron microscopy, X-ray powder diffraction, inductively coupled plasma mass spectrometry, inductively coupled plasma atomic emission spectroscopy and Raman spectroscopy. According to our results, the graphite flakes are located in the deformed zones in all cases. Based on the geology of the areas and the obtained results, the graphite has organic material origin formed by regional metamorphism in the shear zones.

Keywords: *graphite, critical raw material, graphitization, shear zone, regional metamorphism*

1. INTRODUCTION

Graphite, a critical raw material for the European Union since 2011 [1-4], plays an ever-growing role nowadays. It is mainly used in metal extractive industry, automobile industry, in fireproof materials, lithium-ion batteries and in the high-tech industry [5]. In our study, we focus on three potentially graphite-bearing occurrences in NE-Hungary. Previously, several detailed investigations were carried out in Dédestapolcsány [6], in Meszes [7] and in Szendrőlád [8]. Our aim is to review the results and to supplement them by further measurements (for instance with Raman spectroscopy results).

2. MATERIALS AND METHODS

The first occurrence is Dédestapolcsány (Rágyincs Valley, Uppony Mts.), exposing the Tapolcsány Formation (Silurian, deep sea facies) [9]. The collected samples are black colored, intensely deformed and schistose fine-grained siliceous black schists (Fig. 1). The second occurrence is Szendrőlád (Szendrő Mts.), exposing the Szendrőlád Limestone Formation (middle-late Devonian, basin facies) [9]. The examined samples are intensely deformed black schists from the Szendrőlád-6 drill hole (from 278-295 m depth) and from surface outcrops along the valley of Helle Creek (Fig. 1). The third occurrence is Meszes (Szendrő Mts.), exposing the Szendrő

Phyllite Formation (Carboniferous, gradually deepening basin facies) [9]. The collected samples are intensely deformed, schistose black phyllites (Fig. 1).

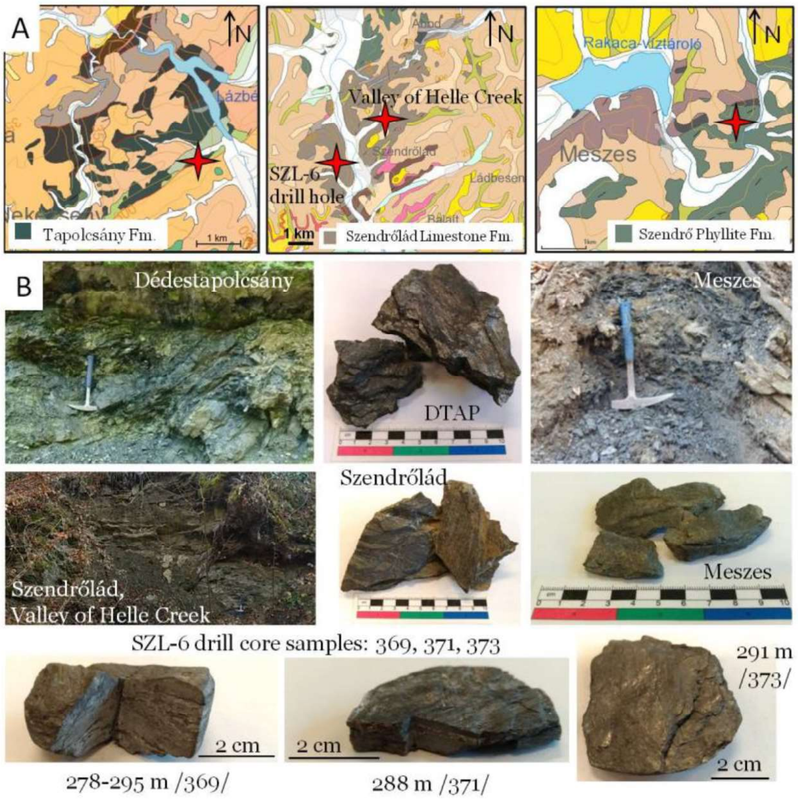

Figure 1

(a) Schematic geological maps [10] of the investigated areas marked with stars the sampling points. (b) The surface outcrops and the collected samples

The samples were investigated with polarizing petrographic and ore microscopy (OM) (Zeiss Axio.Imager A2.m microscope with Zeiss AxioCam MRc5 camera), scanning electron microscopy (SEM-EDX) (JEOL JXA-8600 Superprobe in the case of all occurrences, 20 kV, 20 nA, 60 s dwell time for point analysis; ThermoFisher Helios G4 PFIB CXe in the case of Meszes, 20 kV, 3.2 nA, 50 s dwell time for point analysis), X-ray powder diffraction (XRD) (Bruker D8 Advance, Cu K-alfa radiation, 40 kV, 40 mA, parallel beam geometry with Göbel mirror, Vantec-1 PSD detector with 1° opening, 0.007°2θ/24sec counting time), Raman spectroscopy (Thermo Scientific DXR Raman microscope, 532 nm wavelength (green) laser, 2 mW, 3×15 sec exposure time, ~4 cm^{-1} spectral resolution), inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES). ICP-MS and ICP-AES measurements were carried out by ALS Romania SRL.

3. Results

3.1. OM and SEM-EDX analysis

According to our results, all the samples have metamorphic texture. The matrix of the samples consists of quartz (Dédestapolcsány), muscovite, calcite and quartz (Szendrőlád) and phyllosilicates (chlorite, muscovite, phengite) and quartz (Meszes). In the case of Dédestapolcsány, graphite can be found as µm sized flakes scattered in the matrix and as 100-300 µm sized grains (with low S content) arranged in the direction of deformation (Fig. 2). In Szendrőlád samples, the 20-50 µm sized graphite flakes (also with low S content) are arranged in intensely deformed, >300 µm aggregates. From Meszes, the samples contain 50-150 µm sized intensely deformed graphite flakes (without any S content) with kink-band microstructure (Fig. 2). Based on the optical observations, the graphite flakes appear with undulose extinction.

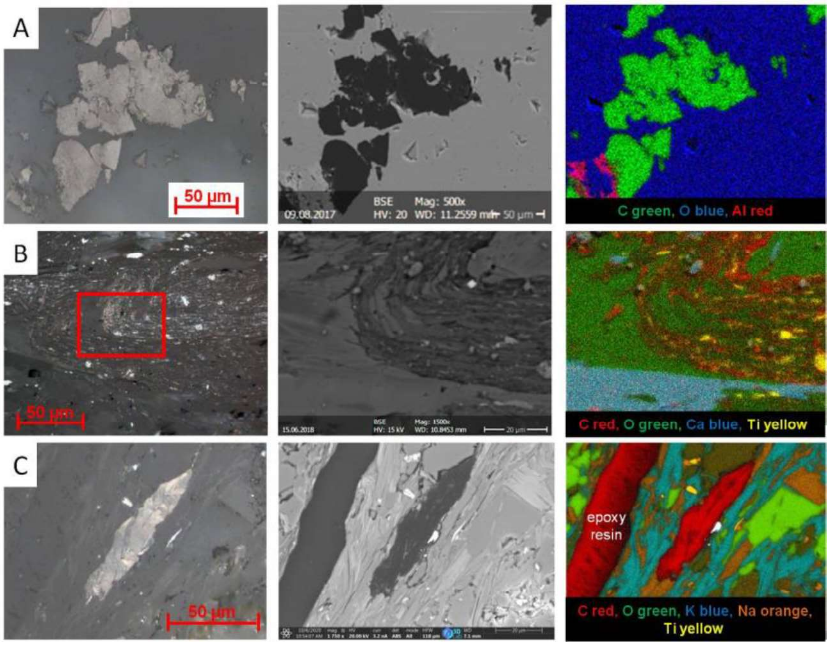

Figure 2

Graphite flakes from Dédestapolcsány (a), Szendrőlád (b) and Meszes (c). Polarizing microscope, reflected light, 1N (left), BSE image (middle), element map (right)

As accessory minerals, ilmenite, TiO_2 (rutile and anatase based on OM) with low Nb and V content, monazite-(Ce), xenotime, zircon and Fe-oxide can be detected in all occurrences. V-bearing muscovite and APS (aluminum-phosphate-sulphate) minerals, for example solid solution series of goyazite-gorceixite appear in Dédestapolcsány samples, while REE-carbonates (solid solution series of bastnäsite-parisite), pyrite, chalcopyrite, fluorapatite, illite, kaolinite and albite can be observed in the samples of Szendrőlád. In Meszes samples, fluorapatite, albite, illite, kaolinite and calcite occur.

3.2. XRD analysis

By XRD, graphite cannot be detected directly on the diffractogram of any sample due to its low quantity, nanocrystalline size, preferred orientation and heavy peak overlapping of peak (hkl = 002) between 26°-27°(2θ) with quartz peaks (hkl = 101) and (hkl = 110). Figure 3 shows an XRD pattern of Dédestapolcsány sample where the asymmetric peak between 26°-27°(2θ) is well illustrated.

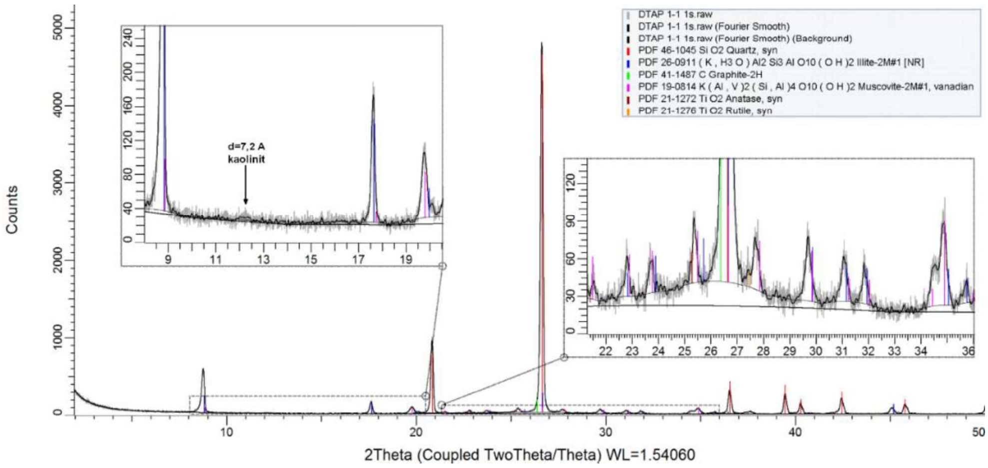

Figure 3

Diffractogram of sample from Dédestapolcsány showing the asymmetric peak between 26°-27°(2θ)

3.3. ICP-MS and ICP-AES analysis

By ICP-MS and ICP-AES measurements, bulk rock and trace element analysis are possible to get detailed information of the samples (Fig. 4).

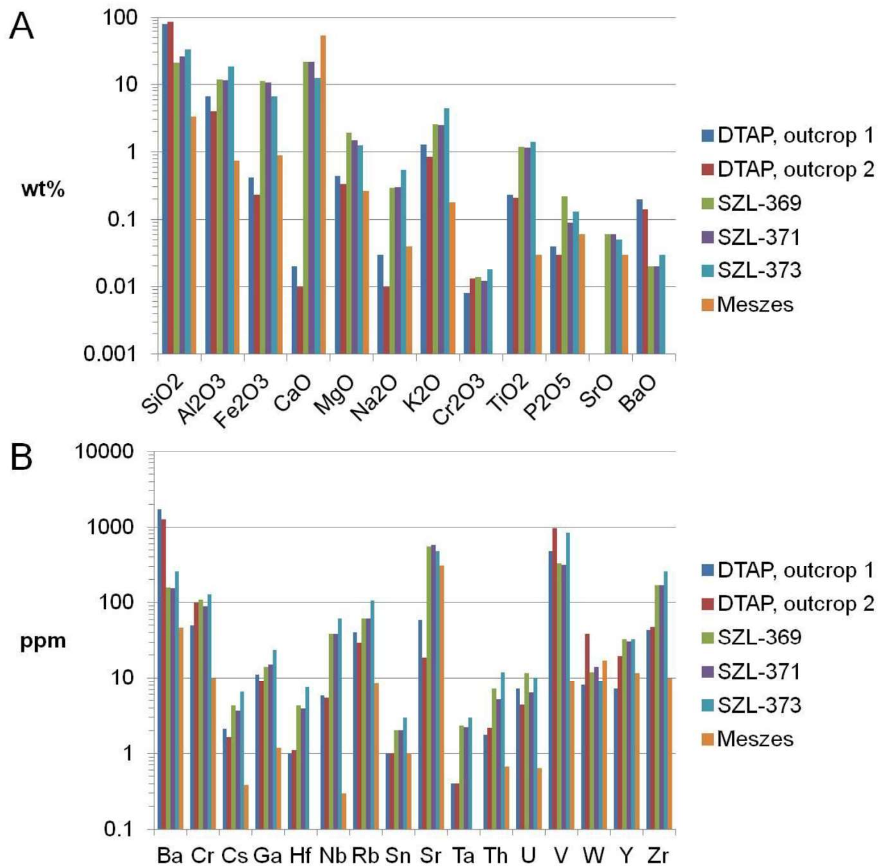

Figure 4

Bar charts of the results of bulk rock (a) and trace element (b) analysis by ICP-MS and ICP-AES

3.4. Raman spectroscopy

Raman spectroscopy is a useful method to identify the degree of graphitization of carbonaceous material [11]. Regarding the first order bands, the appearance of G band, D1 band and D2 band in all occurrences (Fig. 5) refers to a joint presence of well-crystallized graphite and graphitised material (which does not reach the cristallinity grade of well-ordered graphite). Differences between the studied samples can be seen by the different intensity ratios of G band (well-crystallized graphite) and D1 band (graphitised material). In the case of Meszes, the total splitting of the S2 band in the second order Raman spectrum (Fig. 5) indicates a total maturation of carbonaceous material into a highly crystalline graphite.

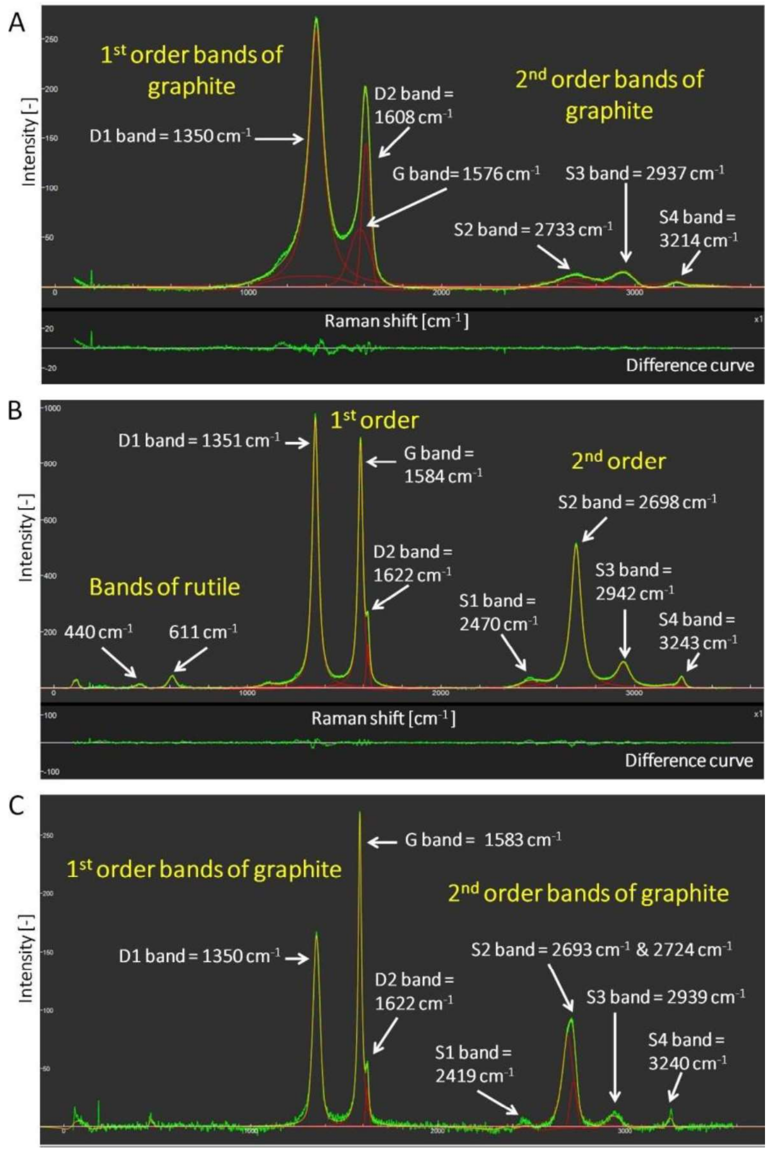

Figure 5

Decomposed Raman spectrum of one measurement point of sample: (a) Dédestapolcsány, (b) Szendrőlád, (c) Meszes

4. DISCUSSION AND CONCLUSIONS

According to our results, graphite can be found in flaky form in each sample located in the direction of deformation. Commonly, the flakes are intensely deformed as well. In the case of Dédestapolcsány and Szendrőlád, low sulphur content is also measured in the flakes by EDX. Beside the low sulphur content, many geochemically related elements of graphitization occur in the accessory minerals based on SEM-

EDX, ICP-MS and ICP-AES measurements. For example, the maximum V content is 957 ppm for Dédestapolcsány and 843 ppm for Szendrőlád, or the elevated REE-content in Dédestapolcsány samples (~100 ppm) and in Szendrőlád samples (~300 ppm). These evidences refer to organic material origin of graphite. Based on the geology of the investigated areas [9], the Uppony and Szendrő Mts. went through on low – lower middle grade regional metamorphism affected by the Darnó shear zone. In the case of all occurrences, the collected samples are located in the shear zone. Due to the metamorphic texture of the samples, the observed marks of shearing deformations and the appearance of graphite and critical element-bearing minerals in the deformed zones detected by OM and SEM-EDX, the formation of graphite is connected to shear zones and regional metamorphism. The elevated Sr content in Szendrőlád and Meszes samples suggests a depositional environment related to active rifting basin, while the APS minerals from Dédestapolcsány may have low temperature hydrothermal origin. As a conclusion, the joint usage of the applied methods is a good tool to investigate graphite-bearing rocks: their texture, the mineral assemblage, chemical composition, crystallized phases and the degree of graphitization.

ACKNOWLEDGEMENTS

The research was funded by the Hungarian Ministry of Innovation and Technology from the National Research, Development and Innovation Fund, under the grant contract No. TKP-17-1/PALY-2020 issued by the National Research, Development and Innovation Office.

REFERENCES

[1] European Commission (2011). Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions – Tackling the challenges in commodity markets and on raw materials. Brussels, *COM(2011) 25 final*.

[2] European Commission (2014). Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions – On the review of the list of critical raw materials for the EU and the implementation of the Raw Materials Initiative. Brussels, *COM(2014) 297 final*.

[3] European Commission (2017). Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions – on the 2017 list of Critical Raw Materials for the EU. Brussels, *COM(2017) 490 final*.

[4] European Commission (2020). *Study on the EU's list of Critical Raw Materials – Final Report*. DOI: 10.2873/11619

[5] Mitchell, C. J. (1993). *Industrial Minerals Laboratory Manual: Flake Graphite.* BGS Technical Report, Keyworth, Nottingham, WG/92/30.

[6] Majoros, L. (2019). *Mineralogical and petrographical examinations of graphitic materials in black schists from Uppony Mts and Szendrő Mts and their Carpathian connections.* (In Hungarian). University of Miskolc, Institute of Mineralogy and Geology, MSc diploma thesis, 102 p.

[7] Leskóné Majoros, L., Leskó, M. Zs., Szakáll, S., Kristály, F. (2021). Critical minerals and elements in the Szendrő Phyllite Formation (Szendrő Mts., NE-Hungary). (In Hungarian). *Multidisciplinary Sciences*, 11, 1, pp. 90-97. https://doi.org/10.35925/j.multi.2021.1.9

[8] Majoros, L., Fintor, K., Koós, T., Szakáll, S., Kristály, F. (2022). Metamorphic graphite from Szendrőlád (Szendrő Mts., NE-Hungary) detected by simultaneous DTA-TG. *Journal of Thermal Analysis and Calorimetry*, 147, pp. 3417-3425. https://doi.org/10.1007/s10973-021-10713-6

[9] Fülöp J. (1994). *Geology of Hungary, Paleozoic II.* (In Hungarian). Budapest, Akadémiai Kiadó.

[10] Gyalog, L., Síkhegyi, F. (series editor) (2005). *Geological Map of Hungary, 1:100 000.* Published by the Hungarian National Geological Institute, Budapest. Available online: https://map.mbfsz.gov.hu/fdt100/ (accessed on 12 October 2022).

[11] Beny-Bassez, C., Rouzaud, J. N. (1985). Characterization of carbonaceous materials by correlated electron and optical microscopy and Raman microspectroscopy. *Scan. Electron Microsc.*, 1, pp. 119-132.