CRITICAL MINERALS IN BLACK SCHISTS FROM SZENDRŐLÁD (SZENDRŐ MTS., NE HUNGARY)

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The EUROPEAN COMMISSION (2020) has recently published the new Study on the EU's list of Critical Raw Materials, in which 30 critical raw materials are included beyond graphite. Natural graphite is associated with several other critical elements, due to their geochemical affinity to organic matter (HOLLAND, 1979; BRUMSACK & LEW, 1982). In our study, we focus on these critical elements and raw materials, namely natural graphite and related elements of graphitization: titanium, niobium, phosphorus, light and heavy rare earth elements (REE).

Rock samples were collected from outcrops along the valley of Helle Creek (NE part of Szendrőlád village, Szendrő Mts., NE Hungary), exposing the Szendrőlád Limestone Formation (Middle to Late Devonian, basin facies) (FÜLÖP, 1994). The collected samples are dark-grey or black coloured, intensely deformed and schistose fine-grained phyllites.

The samples were investigated with polarizing petrographic and ore microscopy (OM), scanning electron microscopy (SEM-EDX), X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and differential thermal analysis (DTA). In addition, experiments on graphite extraction were also performed by froth flotation (CROZIER, 1990) in 5% ethanol solution following the disaggregation by ultrasonic shaking (Hielscher UIP1000hdT).

According to the optical microscopy and scanning electron microscopy (SEM-EDX) results, the samples have metamorphic texture. The matrix consists of oriented and often polysynthetic twinned calcite crystals (usually with low Mg and Fe content). The 50–100 µm sized mica plates (muscovite, Na-bearing muscovite and phengite) and 50–200 µm sized quartz grains can be found mainly in the deformed zones.

Many accessory minerals are also observed by SEM-EDX. As main Ti mineral, 10–50 µm sized TiO_2 minerals (anatase and rutile based on optical observations) are often found in the deformed zones with traces of Nb. As HREE-bearing mineral, 10–30 µm sized xenotime grains occur, while LREE-containing minerals are allanite, 10–20 µm sized bastnäsite-(Ce) needles and 20–80 µm sized monazite-(Ce) grains. Zircon, as Zr-bearing mineral, is also frequent, linked to the deformed zones. Furthermore, as P-bearing mineral, 20–100 µm sized apatite grains are also detected in the samples.

Graphite cannot be detected directly by OM and SEM-EDX, as its thin and µm sized flakes are lost during sample preparation. Only 50–300 µm sized graphitic-illitic mixtures are preserved, which are located in the deformed zones and parallel to the foliation, having high C content, with low S and As content.

Graphite separation experiments were performed to be able to detect graphite directly. The graphitic material recovered by froth flotation was investigated with XRD and TEM. Calcite was removed by acetic acid treatment (5%) and the residue was investigated again with XRD and DTA methods.

According to our results, graphite cannot be detected directly on the XRD curves due to its heavy peak overlapping with quartz peaks. However, its direct quantification is possible by Rietveld refinement. By TEM, 80–200 nm sized, hexagonal-dihexagonal shaped, C-containing grains can be detected with ordered crystal structure. As the thermogravimetric analyzes are performed in air, the thermal reaction of graphite and partially graphitized material can be observed on all simultaneous TG-DTA curves.

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