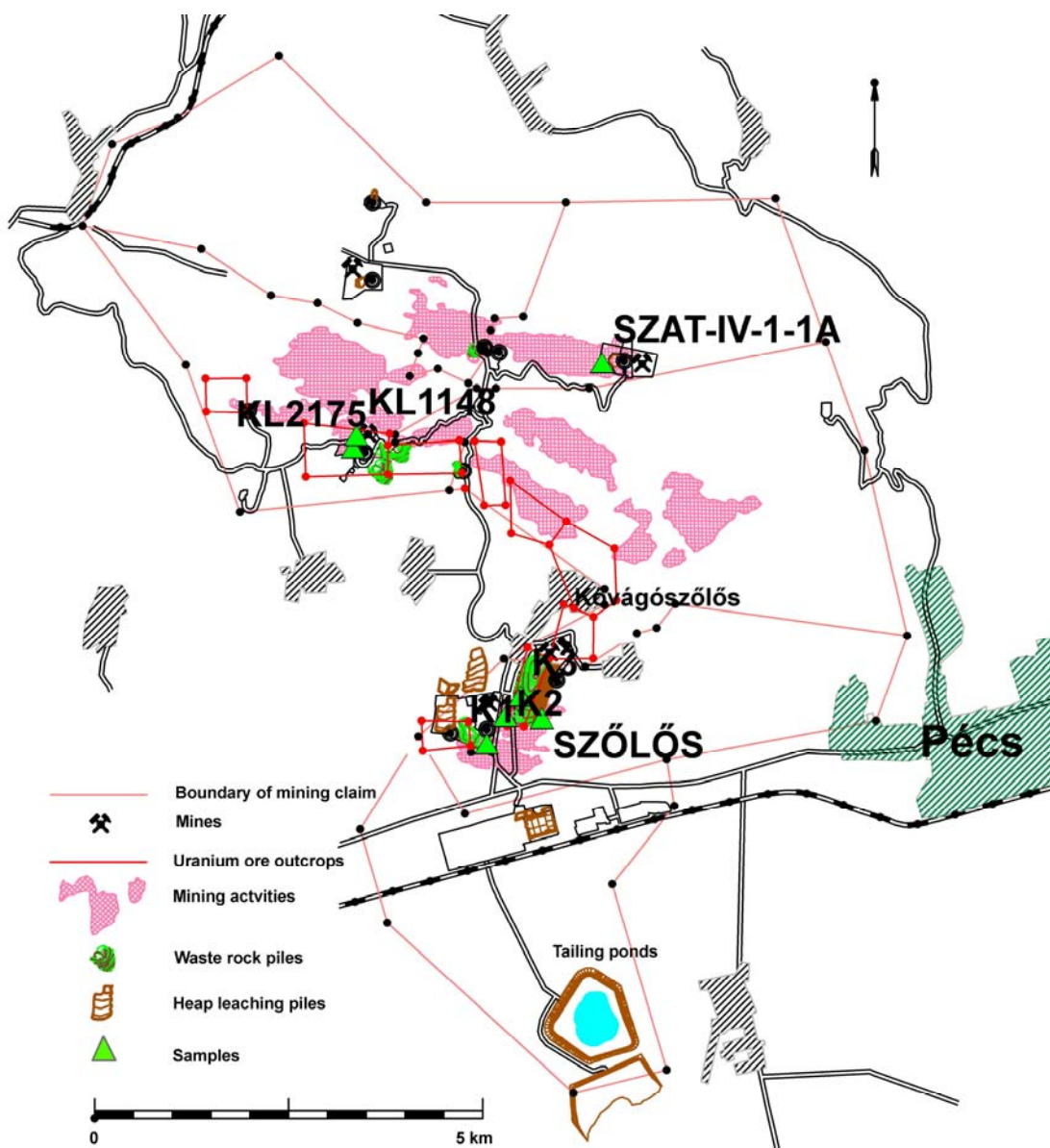


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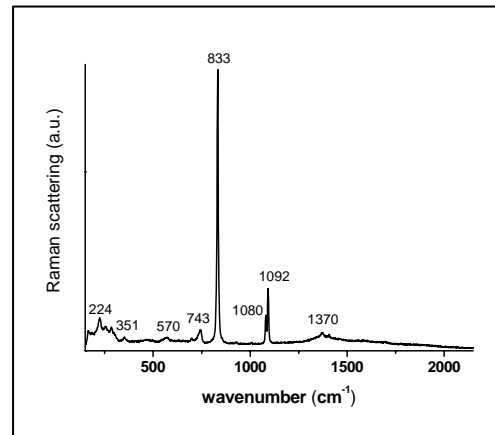


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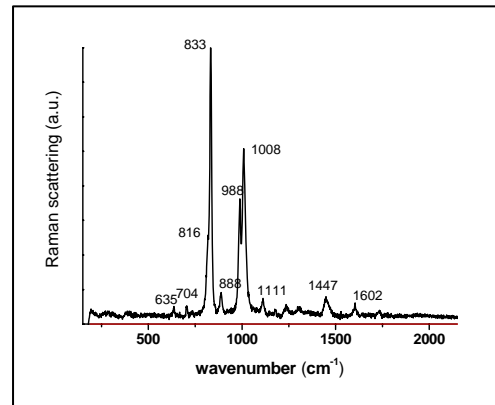
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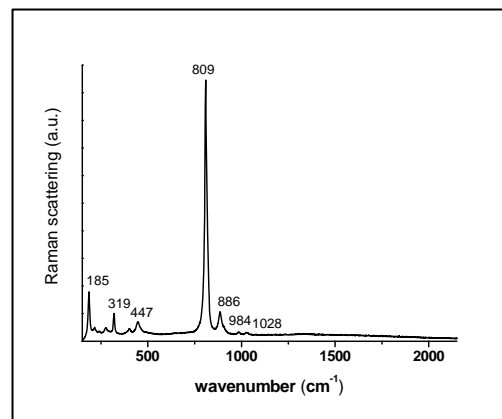
*Fig.1. Map of the former uranium mine in Mecsek Mountains, Hungary with indication of sampling points.*



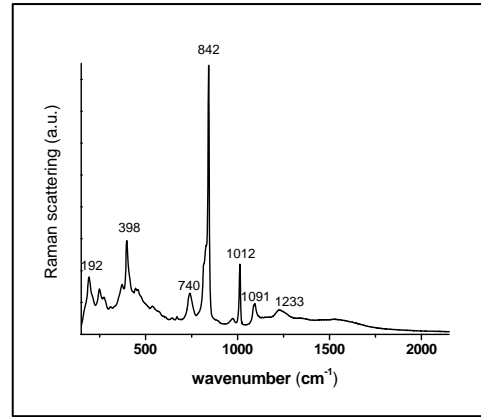
Andersonite  $\text{Na}_2\text{CaUO}_2(\text{CO}_3)_3 \cdot 5\text{H}_2\text{O}$



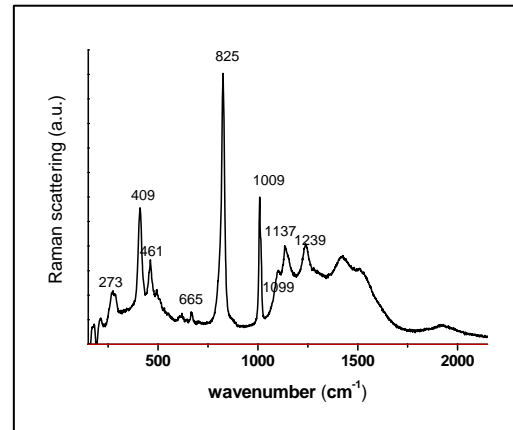
meta-Autunite  $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$



Zeunerite  $\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 12\text{H}_2\text{O}$

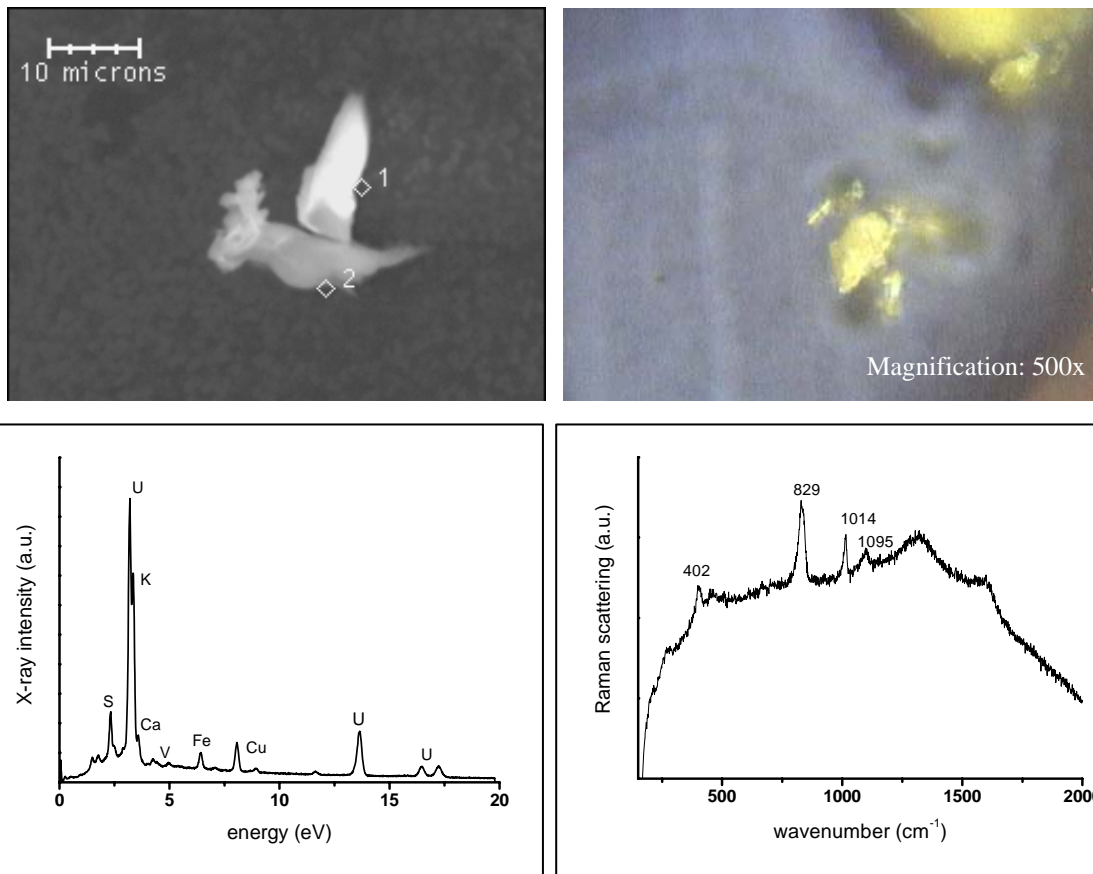


Zippeite  $K_4(UO_2)_6(SO_4)_3(OH)_{10} \cdot 4H_2O$

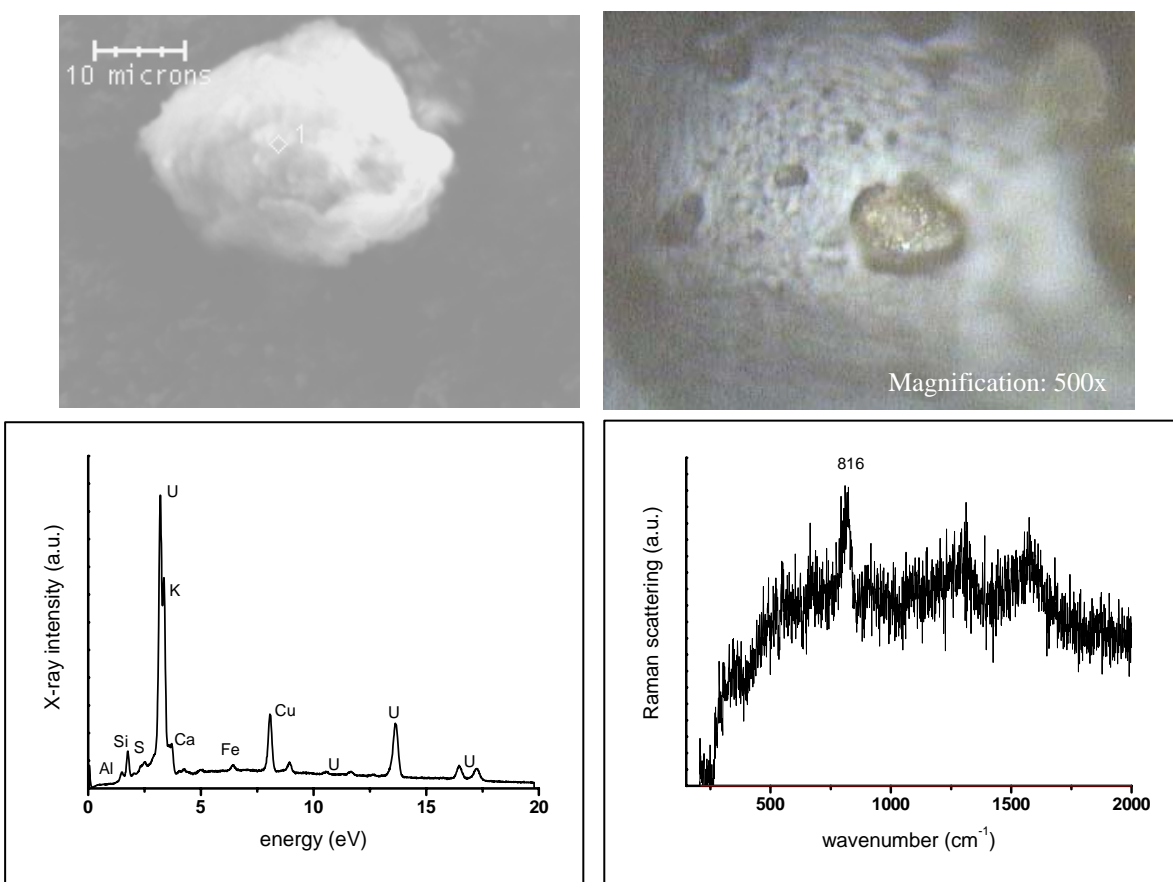


Na-zippeite  $Na(UO_2)_2(SO_4)(OH)_3 \cdot 4H_2O$

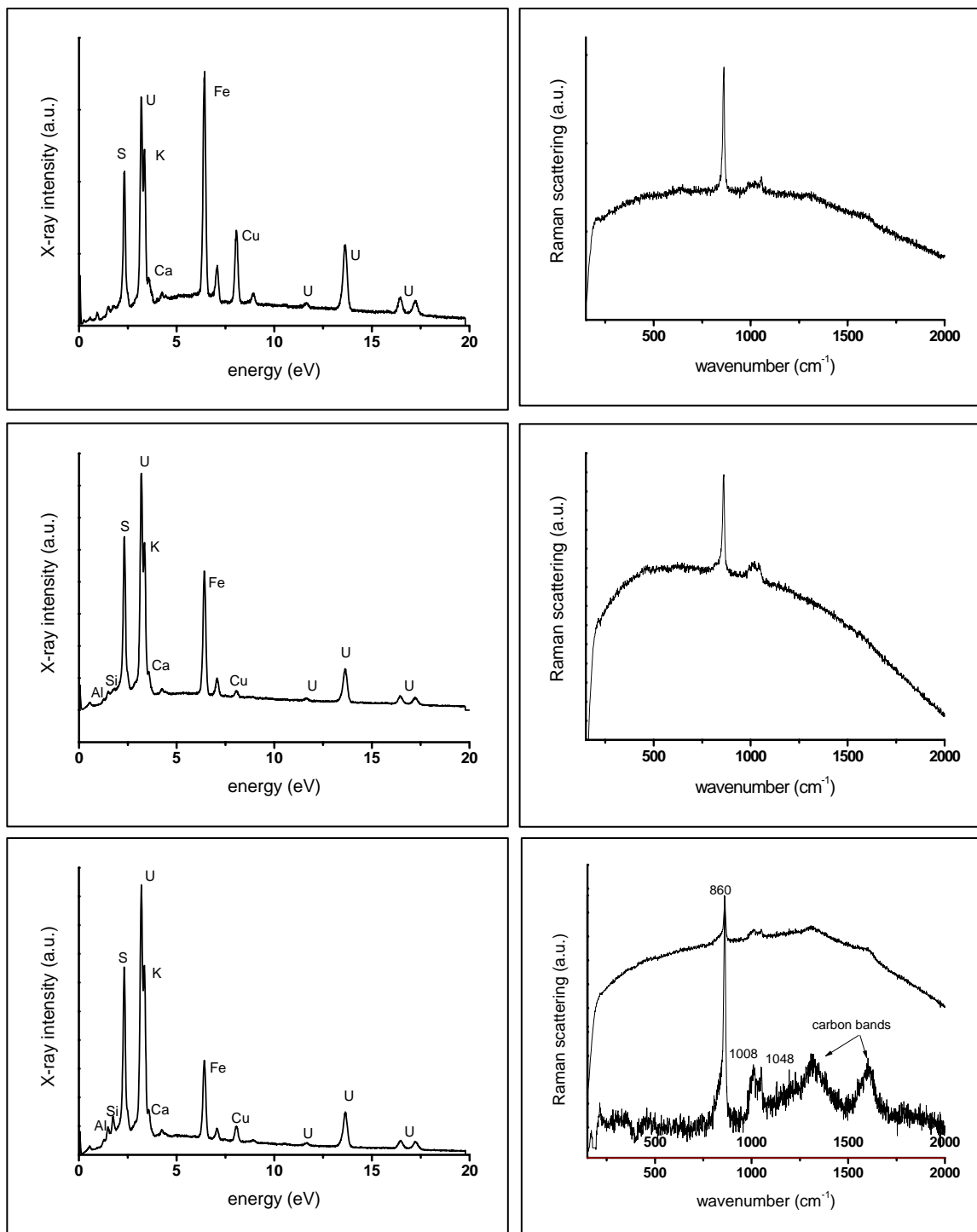
*Fig.2. Secondary uranium minerals collected in Hungary (the details are given in the text).*



*Fig.3. SEM and optical image of Na-zippeite particle measured with two stand-alone instruments. The optical image is rotated upside down. The adequate spectra (SEM/EDX - left and MRS – right) are presented below the images.*



*Fig.4. SEM and optical image of a U-rich particle recorded with two stand-alone instruments. The optical image is rotated upside down. The adequate spectra (SEM/EDX - left and MRS – right) are presented below the images.*



*Fig.5. SEM/EDX spectrum (left) and MRS spectrum (right) of three particles containing U(VI) species, probably UO<sub>3</sub>. The Raman spectra are kept in their original form, except the last plot (background subtracted).*

## **The combined application of SEM/EDX and micro-Raman spectroscopy to analyse uranium minerals from a former uranium mine**

Elżbieta A. Stefaniak<sup>1,2\*</sup>, Anita Alsecz<sup>3</sup>, Ray Frost<sup>4</sup>, István E. Sajó<sup>5</sup>, Zoltán Máthé<sup>6</sup>, Szabina Török<sup>3</sup>, Anna Worobiec<sup>1</sup> and René Van Grieken<sup>1</sup>

<sup>1</sup>Department of Chemistry, University of Antwerp, Universiteitsplein 1, BE-2610 Antwerp, Belgium

<sup>2</sup>Permanent employment: Department of Chemistry, Catholic University of Lublin, Al. Kraśnicka 102, 20-718 Lublin, Poland

<sup>3</sup>Hungarian Academy of Science, KFKI Atomic Energy Research Institute, P.O. Box 49, H-1525 Budapest, Hungary

<sup>4</sup>Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia

<sup>5</sup>Chemical Research Centre of the Hungarian Academy of Sciences, Pusztaszeri út 59-67, H-1025, Hungary

<sup>6</sup>Mecsek Ore Environment, Pécs, P.O. Box: 121, H-7614, Hungary

### ABSTRACT

Samples of the secondary uranium minerals collected in the abandoned uranium mine at Pecs (Hungary) were investigated by two micro-techniques: scanning electron microscopy (SEM/EDX) and micro-Raman spectroscopy (MRS). They were applied to locate U-rich particles and identify the chemical form and oxidation state of the uranium compounds. The most abundant mineral was a K and/or Na uranyl sulphate (zippeite group). U(VI) was also present in the form of a trioxide; evidently in much lower content than sulphate. Few particles with U<sub>3</sub>O<sub>8</sub> and uraninite (primary mineral exploited formerly in this mine) were also detected. This research has shown the successful application of micro-Raman spectroscopy for the identification of uranyl mineral species on the level of individual particles.

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\* Corresponding author; email: [elzbieta.stefaniak@ua.ac.be](mailto:elzbieta.stefaniak@ua.ac.be); tel. +3238202381; fax +3238202376.



KEYWORDS: uranium minerals, uranyl ion, uranium mine, micro-Raman spectroscopy, SEM/EDX

## 1. INTRODUCTION

Uranium minerals have drawn the attention of scientists due to their hazardous nature and their commercial importance. Among the different analytical techniques involved in the study of uranium containing minerals, micro-Raman spectroscopy has been intensively applied due to the ease of operation and fast assessment of their molecular characteristics. Among the uranium oxides, thermodynamically the most stable forms are  $\text{UO}_2$ ,  $\text{U}_3\text{O}_8$  and  $\text{UO}_3$ , although  $\text{UO}_2$  may go through alteration process with the increase of U oxidation state [1]. In an aqueous environment exposed to air, the most stable species of U is uranyl ion  $\text{UO}_2^{2+}$  [2]. Its structure is nearly linear and while exposed to a laser beam, it gives a strong and sharp vibrational band due to the symmetric O-U-O stretch, which is usually present in the range  $700\text{-}900\text{ cm}^{-1}$  of the Raman spectrum. The exact wavenumber depends on the ligands attached [3]. Among the uranyl minerals, a vast majority include carbonates, silicates, phosphates/arsenates and sulphates. Beside the uranyl ion and an oxy-acidic residue, the molecular structure involves also a simple one- or two-valence cation.

There are over 200 uranium minerals discovered and classified to date [4]. They are divided mainly into “primary” and “secondary” minerals referring to their origin and occurrence. Primary uranium minerals (pitchblende or uraninite) are found most commonly in veins or pegmatites and also in flat-lying deposits in sedimentary rocks [5]. When exposed to weathering at or near the surface, the primary uranium minerals alter to form the bright-colored secondary uranium minerals. These are mainly uranyl phosphates, carbonates, sulfates, hydrous-oxides and silicates, produced as a result of complete oxidation of the primary minerals. They may be formed by ground-water solutions that have dissolved uranium from a broad area of slightly mineralized rocks and concentrated by precipitation in veins and fracture zones [5]. Most likely these minerals can be collected in the area of uranium mines, particularly where enrichment procedure is undertaken.

Uranium mining has always been a strategic issue of each country's economy, quite often prioritized over the environment protection. Unfortunately, most uranium ores are low-grade (0.1-0.2%), leaving behind a huge burden of dump rocks and tailing wastes [6]. Enrichment procedure is usually drastic and involves e.g. the heap leaching or milling of the ore – both procedures involve leaching out of uranium by sulphuric acid or ammonium carbonate solution. Both also result in producing of tailing wastes in amount of 99.9% of the mined ore. The volume of sludge and its hazardous properties (radioactivity, acidity) remains a real threat to the environment, even a long time after mine closure. One of the examples is the former uranium mine at the foot of the Mecsek Mountains, close to the town of Pécs, in southern Hungary. Exploration of the ore and enrichment processing lasted for almost 40 years (1953-1997) and resulted in 19 million ton of waste rock and 28.5 million ton of uranium ore chemically treated, of which over 20 million ton was turned into tailings [7]. For more than 10 years since the mine shutdown, the whole area has been under the strict control and subjected to remediation [8].

Primary minerals exploited in this Hungarian mine were uraninite  $\text{UO}_2$  and coffinite  $(\text{U,Th})(\text{OH})_{4x}(\text{SiO}_4)_{1-x}$ . These minerals contain U(IV) and are not very mobile. Thus it remained attached to soil particles, so the hazard might be caused by soil dust re-suspension. As a result of mine activity, especially chemical treatment, the area became a source of secondary minerals containing uranyl ions  $\text{UO}_2^{2+}$ , more soluble and less immobilized by soils.

The task of our work was the determination of secondary U-minerals formed in the abandoned roads in the area of abandoned uranium mine in the Mecsek Mountains in Hungary. Because of their marginal significance in uranium ore mineralization their investigations were de-emphasized (there is a lack of information in the record of former investigation). These phases have been formed in the outcrops of the uranium ore mineralization and in the structure zone crossing ore bodies by oxidation of the primary mineral (uraninite). The precise knowledge of the secondary uranium minerals occurring in the closed down mine is important for remediation program following the mine closure (migration of U and stability of secondary minerals forming in the dump piles).

To achieve this, a combination of two micro-analytical techniques: SEM/EDX and MRS was applied. A detection and recognition of U minerals in the shape of fine particles was facilitated by first recognizing U-rich particles with a help of BSE image

of SEM, followed by recording of X-ray spectra, and afterwards re-locating the same particles with a Raman microscope followed by measurement of molecular spectra. Both methods provide complementary results and mutual conformation of stand alone analyses; hence altogether it is a fast and easy tool for the recognition of U minerals at the single particles level [9].

## 2. MATERIALS AND METHODS

### 2.1. Samples

Majority of uranium ore samples were collected in the former area of ore mine, Mines I.-V. (K1, K2, K3, KL-1275, KL-1148, SZAT-IV-1-1A and SZŐLŐS samples). Fig.1. presents a map of the ore location and the surrounding. The geological characterization of the western part of the mountains is described elsewhere [10]. One sample derives from Balaton Highlands (its provenance Badacsonyörs) (Fig. 2), The Upper Permian age Balaton Highlands Sandstone Formation contains the uranium ore mineralization, according to studies it is unworkable ore mineralization,

Two types of samples were collected: 1) yellow to green minerals assumed to be secondary uranium minerals; 2) samples in order to analyze single particle composition and detect the uranium minerals. Soil particulate matter was sampled in seven independent places: K1, K2, K3, KL-2175, KL-1148, SZŐLŐS, SZAT-IV-1-1A. The sampled material was crushed to reach the size below 2 mm.

### 2.2. XRD analysis

All samples were analysed by means of X-ray powder diffraction XRPD (Philips model PW 3710 based PW 1050 Bragg-Brentano parafocusing goniometer using  $\text{CuK}\alpha$  radiation ( $\lambda = 0.15418$  nm), graphite monochromator and proportional counter). The XRD scans were digitally recorded with a step size of  $0.04^\circ$  and evaluated for phase composition with full profile fitting method. XRD results were applied mainly to recognize secondary uranium minerals and to estimate the concentration of pure mineral phase and its contaminants. They were afterwards applied for MRS as reference materials. These were andersonite, meta-autunite, zeunerite, zippeite and Na-zippeite.

### 2.3. SEM/EDX measurements

This technique was applied in order to locate U-rich particles with a help of BSE image. It was performed on a JEOL JSM 6300 Scanning Electron Microscope (JEOL, Tokyo, Japan) equipped with both a backscattered electron detector (BSE) and a secondary electron detector (SE). The grains of samples were attached to the carbon disks and directly placed in the chamber (without any other processing). Additionally, a Si (Li) X-ray detector PGT (Princeton Gamma Tech, Princeton, NJ, USA) was employed for acquiring the X-ray spectra from each U-containing particle (accelerating voltage: 30kV, beam current: 2nA). SEM/EDX measurements were followed by MRS therefore no coating was applied to avoid a contamination of the samples. To enable a further relocation of the same particle within the image of the two stand alone instruments, TEM grids were applied, as described elsewhere [9].

### 2.4. MRS measurements

The proper recognition of U-rich species in particulate matter must have been preceded with building up the spectral library. Each sample of pure uranium mineral was analysed first and their spectra were used as reference spectra. Afterwards, the single particle analysis of ore particulate matter was performed. Raman spectra were recorder with a Renishaw InVia micro-Raman spectrometer coupled with a Peltier cooled CCD detector. Excitation was provided by 785 nm laser. Samples were scanned using a synchroscan mode from 100 to 2000  $\text{cm}^{-1}$  at a nominal spectral resolution of about 2  $\text{cm}^{-1}$ . The acquisition time for each scan as well as the number of accumulations varied in order to provide a better signal-to-noise ratio. Spectra were obtained using 100x, 50x or 20x magnification objectives. Calibration was done using the 520.5  $\text{cm}^{-1}$  line of silicon. Data acquisition was carried out with the Spectracalc software package GRAMS (Galactic Industries, Salem, NH, USA). Spectral analyses were performed by comparison with spectra from an in-house library as well as a commercially available spectral library.

## **3. RESULTS AND DISCUSSION**

### 3.1. Collection of secondary uranium minerals

Bulk analysis performed by XRD proved the presence of mainly uranyl minerals, occurring as large “blooming” agglomerates, shown in Fig.2. Single grains were selected from the bulk and measured by means of MRS, so the images in Fig.2 are accompanied by the appropriate Raman spectra. Each of the secondary uranium minerals exhibits a Raman activity from vibrations of uranyl group and oxyacidic anion; the relevant bands of symmetric stretching appear in the certain range of a Raman spectrum: 700-900  $\text{cm}^{-1}$  for  $\text{UO}_2^{2+}$  and 900-1100  $\text{cm}^{-1}$  for the anion component. The spectrum is also composed of symmetric bending vibrations of groups, as well as antisymmetric stretching or bending. Recognition of uranyl minerals by MRS should then be quite conclusive; in some cases, however, the Raman shifts might overlap, therefore exact spectral frequencies of vibrations attributed to reference samples are very helpful, if not essential.

Andersonite, a green mineral of a formula  $\text{Na}_2\text{CaUO}_2(\text{CO}_3)_3 \cdot 5\text{H}_2\text{O}$ , is an uncommon secondary mineral, formed in the oxidized zone of uranium-bearing deposits. It may appear also as post-mining form, coating walls of mine caves and shafts. It is known for its greenish fluorescence under ambient office light and UV lamps [11]. Soluble in water, it occurs everywhere in uranium mines under dry conditions. Andersonite is sometimes found in sandstones hosted in uranium deposits, or formed by human interventions [12]. In the andersonite structure two symmetric stretching modes of  $\text{CO}_3^{2-}$  are active (Fig. 2): 1080 and 1092  $\text{cm}^{-1}$  [13]. In the region of higher shift values there are antisymmetric stretching bands of this group (1370  $\text{cm}^{-1}$ ). 833  $\text{cm}^{-1}$  band is a result of symmetric stretching mode of  $\text{UO}_2^{2+}$ ; however it is likely to overlap with symmetric bending mode of a carbonate group. In case of uranyl carbonates there is always a potential overlap between these two, because a region of the symmetric bending modes of carbonates is 800-940  $\text{cm}^{-1}$  [13]. The range 100-500  $\text{cm}^{-1}$  shows the symmetric bending modes of  $\text{UO}_2^{2+}$ , of which 224, 570 and 743 bands belong to andersonite. The shift at 351  $\text{cm}^{-1}$  is unidentified.

Autunite is a representative of a group of minerals called “autunite minerals” with a general formula  $\text{M}(\text{UO}_2)_2 (\text{XO}_4)_2 \cdot 8\text{-}12\text{H}_2\text{O}$ , where M is a common bivalent cation and X is P or As [5,14]. The main mineral, of which the group name is derived, autunite, is calcium uranyl orthophosphate  $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12\text{H}_2\text{O}$ . The difference between meta-autunite and autunite is a number of water molecules attached; meta-mineral contains only 8 water molecules. Further dehydration of meta-autunite leads to

the loss of more water molecules but no other mineral species is formed (just partially dehydrated meta-autunite). The species collected in the sampling territory appeared to be meta-autunite. The features of their Raman spectra are very similar to each other and are well represented (Fig.2). Uranyl stretching vibration is active at  $833\text{ cm}^{-1}$  (strong band) and  $816\text{ cm}^{-1}$  (weak band).  $988$ ,  $1008$  and  $1111\text{ cm}^{-1}$  are likely to be assigned to  $(\text{PO}_4)^{3-}$  stretching vibrations. The shift at  $635\text{ cm}^{-1}$  is probably due to water librational modes, while origin of  $704$  and  $888\text{ cm}^{-1}$  bands remain unknown.

Zeunerite has a structure typical for uranyl micas [14], with an arsenate equivalent of  $\text{XO}_4$  anion and a copper divalent cation attached; its formula is  $\text{Cu}(\text{UO}_2)_2(\text{AsO}_4) \cdot 12\text{H}_2\text{O}$ . Unlike other uranyl minerals, there are practically no Raman activity in the spectral range  $900\text{-}1100\text{ cm}^{-1}$ , we observe a strong band at  $809\text{ cm}^{-1}$ . It is a result of overlapping the symmetric stretching vibrations of both the uranyl and arsenate units.  $886\text{ cm}^{-1}$  vibration is probably a result of antisymmetric stretching of  $\text{AsO}_4$ .  $319$  and  $447$  bands belong also to the spectrum of zeunerite, and intense band at  $185\text{ cm}^{-1}$  is assigned to the  $\text{OUO}$  bending modes.

From the rich group of uranyl sulphates, two representatives were collected in the former uranium mine in Hungary: zippeite and sodium zippeite. Like autunite, the mineral zippeite gave the name to the whole group of minerals, where the cation bound to the uranyl group can be substituted by any of the monovalent or divalent metals. A precursor of the system, zippeite of a formula  $\text{K}_4(\text{UO}_2)_6(\text{SO}_4)_3(\text{OH})_{10} \cdot 4\text{H}_2\text{O}$  is *de facto* K-zippeite, and the other species might be: Na-zippeite  $\text{Na}_4(\text{UO}_2)_6(\text{SO}_4)_3(\text{OH})_{10} \cdot 4\text{H}_2\text{O}$ , Ni-zippeite  $\text{Ni}_2(\text{UO}_2)_6(\text{SO}_4)_3(\text{OH})_{10} \cdot 16\text{H}_2\text{O}$ , Co-zippeite, Zn-zippeite etc. The Raman spectrum of zippeite presented in Fig.2 exhibits typical features for zippeite [15-17] such as  $1012\text{ cm}^{-1}$  shift attributed to a symmetric stretching vibration of  $(\text{SO}_4)^{2-}$  group and  $1091\text{ cm}^{-1}$  of anti-symmetric one. An intense band of  $842\text{ cm}^{-1}$ , with two others overlapping from the shorter wavelength side, are caused by symmetric stretching of the  $(\text{UO}_2)^{2+}$  group. The spectral region from  $400$  to  $700\text{ cm}^{-1}$  is usually attributed to bending activity of sulphate anions; however these bands are not very distinct except one at  $398\text{ cm}^{-1}$ . There is also one more shift of unknown origin, which presence in the zippeite spectrum was not confirmed in the literature [15-17].

Raman spectrum of sodium zippeite, shown in Fig.2, does not resemble the spectrum of the same mineral described elsewhere [16]. A typical  $(\text{SO}_4)^{2-}$  stretching band is assigned to  $1009\text{ cm}^{-1}$ , but the position of  $(\text{UO}_2)^{2+}$  symmetric stretching vibration is located at  $825\text{ cm}^{-1}$  which is shifted to the lower wave number region in the Raman spectrum. This is rather not typical for uranyl sulphate because in most cases (K-zippeite, uranopilite) uranyl stretching band is visible around  $840\text{ cm}^{-1}$  [18-20], however sometimes  $(\text{UO}_2)^{2+}$  stretching vibrations appear at  $812\text{ cm}^{-1}$  (the strongest shift in the spectrum of johannite) [20]. Our investigated sample can also be contaminated by other minerals fairly abundant in this area, such as quartz and pyrite. This may be reflected in the spectral range around  $400\text{ cm}^{-1}$ . On the other hand, this part of the spectrum is also assigned to the bending modes of a sulphate ion, which is consistent with the literature data [16]. The spectral region above  $1000\text{ cm}^{-1}$  is attributed to antisymmetric sulphate stretching, particularly the bands  $1099$  and  $1137\text{ cm}^{-1}$ . It should be however emphasized that this Raman spectrum may be compromised by fluorescence, especially in the range between  $1000$  and  $1700\text{ cm}^{-1}$ .

### 3.2 Single particle analysis

The results of the bulk analysis were used to enhance the spectral library in order to facilitate recognition of uranium species on a single particle level. The particles containing uranium were first selected with SEM/EDX based on BSE features; afterwards, based on their shape, morphology and marked location, they were relocated under Raman microscope and their Raman spectra were recorded. The two analogous images, accompanied by the adequate spectra, are shown in Fig.3. They show a grain of Na-zippeite, the most abundant U-compound detected in the ore samples. Together with K-zippeite, this mineral comprised almost 50% of all recognized particles. Table 1 contains the summary of the successful and less successful measurements. The second column contains the number of particles located in each sample with a help of BSE. In the third column there is a number of particles recognized by MRS, although it refers not only to their chemical composition but also to a successful relocation of the same particles analyzed first by SEM/EDX. The combination of these two micro-techniques is still challenging, especially when two stand alone instruments are used. The ultimate goal is to achieve ideal correlation of the two beams exposing the same spot [9].

In many cases, both relocation and recognition of U-species according to MRS was quite feasible, especially when the particles had a distinct bright color and were relatively isolated. Unfortunately, MRS spectrum was quite often affected by other components (aluminosilicates, pyrites, organic matter). Moreover, due to intense fluorescence, the Raman activity of uranium compounds was not recordable. One of the numerous examples is given in Fig.4. The Raman spectrum was compromised by fluorescence and the signal was weak and noisy, however the shift at  $816\text{ cm}^{-1}$  should indicate the presence of U(VI) form. It is very likely to be attributed to zeunerite, since many particles in this sample (KL2175) contains arsenopyrite, which upon oxidation leads to formation of arsenates. Unfortunately the spectrum is too ambiguous to make any justifiable statement.

An intriguing species of uranium was detected in one sample among all the examined particles. Both SEM/EDX and Raman spectra of three selected particles are presented in Fig.5. Although Raman spectra are evidently influenced by fluorescence, the distinct Raman shift at  $860\text{ cm}^{-1}$  clearly indicates  $(\text{UO}_2)^{2+}$  presence. Moreover, this band is accompanied by two other weak ones:  $1008$  and  $1048\text{ cm}^{-1}$ , both probably resulting from vibration of  $\text{SO}_4$  group. However, the value of  $860\text{ cm}^{-1}$  is rather too high for symmetric stretching vibration of uranyl group bound to a sulphate ion, as it was usually visible at lower wave numbers [15-20]. It is more likely to ascribe this band to  $\text{UO}_3$  Raman activity, although two neighbouring shifts should be expected, according to the literature data [21]. Such a high wave number shift of uranyl symmetric stretching vibrations is also noticeable in the complex of uranyl ion with organic ligands [22]; however this would be unlikely for uranyl ion to be preserved in this form in oxidized ore samples.  $\text{UO}_3$  is one of the most thermodynamically stable compounds in U-O system, which makes it resistant to chemical change in the environment and, on the other hand, quite immobilized. On the contrary to zippeites, this species was found only in one of seven examined spots. Moreover, the EDX spectra showed in Fig 5 point quite elevated amount of iron and sulphur. It is very likely that ubiquitous pyrites got oxidized into sulphates which would explain the presence of sulphate bands in the spectra. Unfortunately, due to high fluorescence, full recognition of chemical forms present in this rather doubtful.

#### 4. CONCLUSIONS



After more than ten years after closing down of the uranium mine in Hungary, this area is a rich source of secondary uranium minerals, mainly in the form of colorful agglomerates, among which andersonite, autunites and zippeites are most abundant. The risk of pollution is however related to their solubility and mobility under the natural conditions. Investigations of individual ore particles proved that uranyl sulphates (K- or Na-zippeites) were most abundant, occurring in various spots in the mine. Occasionally, other uranium forms were detected such as  $UO_3$  or  $U_3O_8$ ; rarely some residual uraninite particles.

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**Figure captions:**

Fig.1. Map of the former uranium mine in Mecsek Mountains, Hungary.

Fig.2. Secondary uranium minerals collected in the area of the former uranium mine by the city of Pécs, Hungary.

Fig.3. SEM and optical image of Na-zippeite particle measured with two stand-alone instruments. The optical image is rotated upside down. The adequate spectra are also presented below.

Fig.4. SEM and optical image of a U-rich particle recorded with two stand-alone instruments. The optical image is rotated upside down. The adequate spectra are presented below.

Fig.5. SEM/EDX spectrum (left) and MRS spectrum (right) of three particles containing U(VI) species, probably  $\text{UO}_3$ . The Raman spectra are kept in their original form, except the last image (background subtracted).

Table 1. Statistics of the measurements of U-rich ore particles collected in the abandoned uranium mine in Hungary.

SAMPLE	FOUND BY SEM/EDX	RECOGNIZED BY MRS	SPECIES
K1	1	0	unknown (1)
K2	5	5	Na-zippeite (1), zippeite (4)
K3	9	5	Na-zippeite (3), zippeite (1), uraninite (1), unknown (4)
KL2175	4	0	arsenopyrite(1), fluorescence (2), unknown (1)
KL1148	10	10	zippeite (1), U <sub>3</sub> O <sub>8</sub> (1), UO <sub>3</sub> ??? (8)
SZŐLŐS	14	0	unknown(3), fluorescence (10), burnt (1)
SZAT-IV-1-1A	4	0	arsenopyrite (1), fluorescence (3)