

Analysis of unknown uranium ore samples with micro-XANES and micro-XRD methods

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Uranium as a necessary raw material for the nuclear fuel cycle is usually extracted from uranium ore. There exists only one uranium ore deposit in Hungary that is located in the south of the country at the foot of the Mecsek Mountains at the western border of the city of Pécs. The geological cross section in the western Mecsek from 2500 m depth to the surface consists of the following minerals: sandstone, rhyolite, clay stone, Kővágószőlős sandstone formation with uranium ore-bearing layers and covered by sandstone and limestone. A wide variety of uranium minerals exist in the Mecsek Mountains: uraninite, pitchblende, soddyite, autunite, liebigite, zippeite, uranopilite and clarkeite [1]. Recognition of uranium species in U-rich particles from unknown uranium ore samples was the aim of the investigations described in this work. The particles came from the ore of the closed uranium mine.

Ground uranium ore samples were prepared on double sided carbon tape. Uranium particles were pre-selected with laboratory micro-XRF technique at KFKI AEKI. Two-dimensional elemental maps were recorded of the ore samples and uranium-rich particles were localized in the samples. The mineral composition of the ore particles and the oxidation state of uranium in the particles was investigated at the micro-fluorescence beamline L at HASYLAB using μ -XRD and μ -XANES. For simultaneous μ -XRF and μ -XRD, the energy of the synchrotron radiation was tuned to 21.0 keV using the NiC multilayer monochromator. A single-bounce capillary was employed to form a beam spot size of 15 μ m diameter. The diffraction images were recorded using a MarCCD camera. Corundum and silicon samples were measured for calibration. For μ -XANES, the measurement set-up was slightly modified using a Si(111) double monochromator and a polycapillary half-lens. The absorption spectra were recorded in fluorescent mode, tuning the excitation energy near the L_3 absorption edge of U by stepping the Si(111) monochromator, while recording the U- $L\alpha$ fluorescent yield using an energy-dispersive Radiant silicon drift detector. The used energy step size varied between 0.5 (edge region) to 2 eV (more than 50 eV above edge). UO_2 , UO_3 and U_3O_8 particles were used as standards. The measuring time for each energy point varied from 5 s to 30 s depending on the concentration of the element of interest.

Three unknown uranium ore samples from the Mecsek mountain were characterized (Figure 1, Table 1). In particles from sample K2 uranium was found 73-100 % in the U(VI) form. Uranium minerals zippeite $K_4(UO_2)_6(SO_4)_3(OH)_{10}\cdot 4(H_2O)$ and Na-zippeite $Na_4(UO_2)_6(SO_4)_3(OH)_{10}\cdot 4(H_2O)$ were identified by μ -XRD in these particles. In sample K3 the oxidation state of uranium was different in every particle, but with μ -XRD uraninite (UO_2) and zippeite was identified (Figure 2). In sample K1, 43-44% of U was found to be present as U_3O_8 , 35-36% as U(IV) and 19-21% as U(VI). In this sample only UO_2 was identified as uranium mineral.

Many uranium minerals contain uranium in the U(VI) form. For the investigation of the oxidation state of uranium μ -XANES is a very efficient method but the information is often not sufficient. Micro-XRD was used as a complementary method for deriving the mineral composition of the particles. Oxidation state measurements of one element in the sample are not sufficient for solving an environmental problem, the mineral composition is also important to estimate the environmental damages.

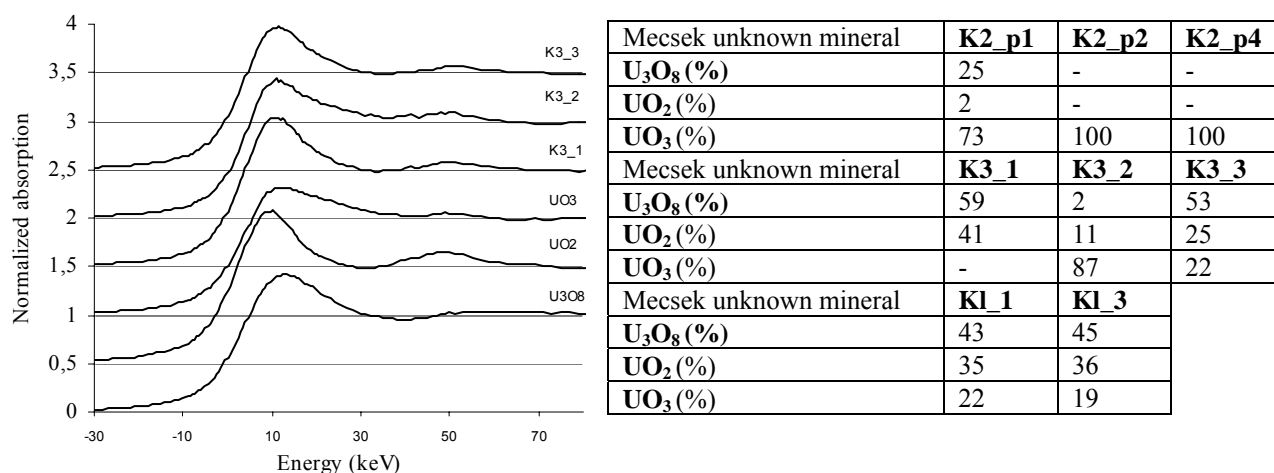


Figure 1. Some of the micro-XANES results at the U-L₃ collected from K3 uranium ore particles and table 1. Uranium oxidation state of some particles in the unknown uranium ore samples

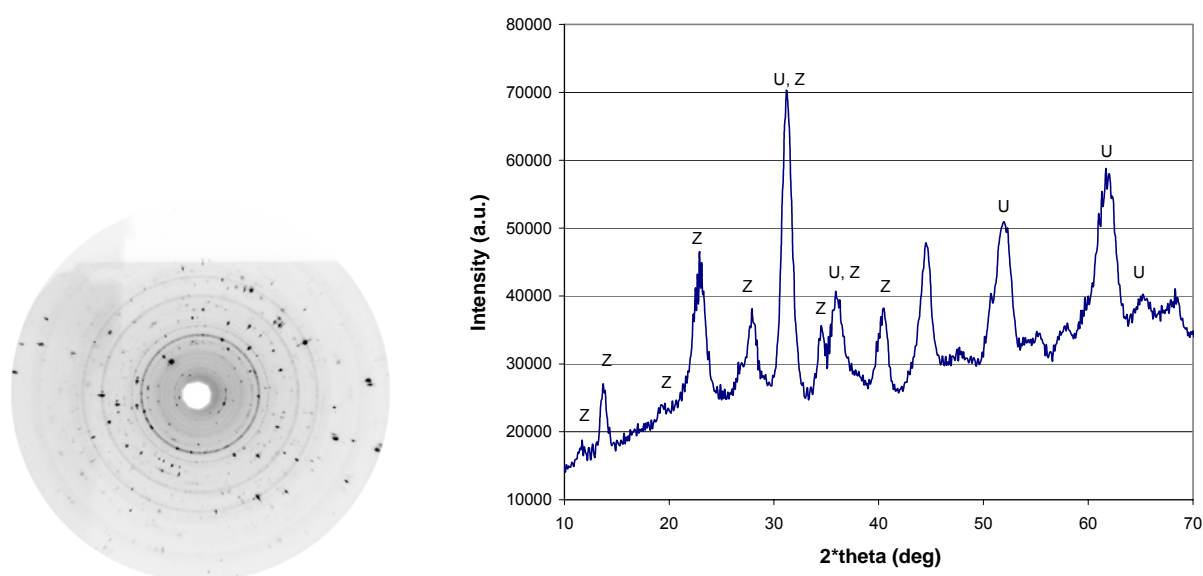


Figure 2: μ -XRD collected from particle K3_3, diffraction image (left) and integrated diffraction pattern indicating the peaks of the identified uranium minerals (Z) zippeite and (U) uraninite (right)

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References

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