



Distribution of uranium in sedimentary and synthetic carbonate apatites using radiochemical and atomic analytical techniques

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Organic-rich phosphatized limestones (phosphorous content: 9.4 – 27%) from Epirus region (NW Greece) were found to present enhanced uranium concentration (155-647 mg/kg). On the other hand, their total rare-earth element content (ΣREE) was low (56-180 mg/kg) compared to other phosphate rock formations around the world. The mineralogical and chemical investigation of the phosphatized limestones by a number of techniques (scanning electron microscopy (SEM-EDS), X-ray diffraction (XRD), electron microprobe, Raman spectroscopy and Fourier-transform infra-red spectroscopy (FT-IR)) revealed the presence, along with organic matter, of apatites (carbonate- and fluoroapatite), and calcite. Synchrotron radiation micro-X-ray fluorescence (SR μ -XRF) measurements, performed using as targets rock samples and selected carbonate apatite crystals, indicated uranium accumulation in rock areas containing carbonate apatite, zircons, and organic matter. The same technique also revealed uranium presence in the carbonate apatite crystals. Micro-X-ray Absorption Near-Edge Structure (μ -XANES) measurements, using the UL3- and UM4- edges, demonstrated the presence of uranium in the tetravalent oxidation state (U(IV)) in the samples. The U-presence in the carbonate apatite crystals was also visualized, after neutron irradiation and etching, by observation of the fission tracks. Ce, Nd, and Y were also detected in the rock samples by SR μ -XRF. Carbonate apatites, synthesized in the laboratory, showed considerable uranium sorption capacity. Sorption experiments performed in solutions of pHinit 4 to 10 showed a partial dissolution of the carbonate apatite crystals surface and precipitation of meta-autunite ($\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$). The XRD examination of the solids indicated that the formation of meta-autunite gradually decreased with increasing solution pH. The further increase of the solution pH (pHinit 13) led to the complete disappearance of meta-autunite and increase to a maximum of the uranium uptake.

References

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