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The nature of uranium in sedimentary rocks of Epirus region (NW Greece)

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Uranium in the ocean waters (typical concentration: 3.2 ppb) follows anoxic pathways and it is mainly removed from the solution by chemical processes taking place at the interface of organic-rich sediments. It is therefore correlated to organic carbon whereas the diagenetic cycle of the element may include reduction of U\textsuperscript{6+} to U\textsuperscript{4+} related to sulphate bio-reduction. However, further tectonic and weathering processes may modify the primary distribution and speciation of U in marine sediments. The average abundance of U in carbonate sedimentary rocks is 2.2 ppm while the concentration of U in relevant Tethyan rocks from SE Europe and the Middle East is reported to be in the range 1–10 ppm. There are also limestones and dolomitic limestones from Mt. Kithaeron (central Greece), containing unusually elevated U concentrations up to ca. 56 ppm. [e.g. 1-3].

Epirus region (NW Greece) is generally composed of Mesozoic (250 - 65 million years old) sedimentary and ophiolitic rocks derived from the Tethys paleo-Ocean. The sedimentary rocks are mostly limestones and shales while the ophiolitic rocks represent old oceanic crust (a sequence of ultrabasic and basic rocks originating in Earth’s mantle). Ophiolites, limestones and shales are fundamentally poor in actinide elements (typical concentrations: \(<0.1, 2.2\) and 3.5 ppm respectively) and therefore no elevated actinide concentrations would be expected in Epirus region. However, in some areas the natural radioactivity is high due to the presence of phosphate-bearing sedimentary rocks, i.e. phosphorites [4].

Phosphorites are marine sediments containing an average of 120 ppm U, and may significantly contribute in U geochemical anomalies. Additionally, they are rich in light rare-earth elements/LREE, but not in Th (6.5 ppm) and other HFSE. However, the studied samples from Epirus region concerned tectonized/re-processed phosphatized limestone. Detailed gamma-ray measurements using HPGe showed that the geological material exhibits significant radioactivity mainly due to \textsuperscript{238}U-series (\textsuperscript{234m}Pa: 8182 Bq/Kg, \textsuperscript{226}Ra: 6852 Bq/Kg, \textsuperscript{214}Pb: 7260 Bq/Kg, \textsuperscript{214}Bi: 6232.18 Bq/Kg). Bulk geochemical analyses using ICP-OES/MS showed variable U concentrations with a notable value of 648 ppm in the case of the dark organic-rich part of the rock (Fig. 1). Relatively high concentrations of Cd, probably related to apatite, were also revealed [4]. On the other hand, the rock is geochemically depleted in LILE (e.g. Cs, Rb, K), as well as in As, Sb and Se in contrast to red soils (“Terra Rossa”) of the region [5].

The SR \(\mu\)-XRF study (Fig. 2) revealed that U is accumulated (together with P, Sr, Y, and most likely S) in certain areas of the dark organic-rich part of the rock which includes, according to supplementary XRD, SEM-EDS and FT-IR data, abundant apatite and organic matter. The areas with very low U and high Ca concentrations consist of calcite, whereas V and La are related to metallic Fe-oxide phases. The corresponding UL\textsubscript{3}-edge \(\mu\)-XANES spectra indicated the presence of U\textsuperscript{4+} which could be associated to apatite-group minerals and/or organic matter. The occurrence of U\textsuperscript{4+} in calcite [3, 6], formed in low-T, is considered to be less possible.
Fig. 1: U-bearing phosphatised limestone sample from Epirus region (NW Greece) and Upper Continental Crust-normalized multielement spidergrams indicating an exceptional U geochemical anomaly [4].

Fig. 2: SR μ-XRF elemental maps and representative preliminary UL3-edge μ-XANES spectra of Epirus U-bearing phosphatised limestone together with U⁴⁺ and U⁶⁺ reference materials.

References

[5] A. Godelitsas et al., to be submitted.