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High uranium concentrations in sedimentary rocks of Epirus (NW Greece)

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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 (<0.1, 2.2 and 3.5 ppm respectively) and therefore no elevated actinide concentrations would be expected in Epirus region. However, it is known (internal reports from Greek Atomic Energy Commission and IGME) that in some areas the natural radioactivity is high due to the presence of phosphate-bearing sedimentary rocks (phosphorites). 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. Uranium in the ocean waters (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 U6+ to U4+ related to sulfate bio-reduction. Samples from Epirus region concerning laminated phosphatized limestones (sample: DRYM1), bedded chert-rich limestone (sample: PER1) and tectonized/re-processed phosphatized limestone (sample: PER2), were scanned in the field using a portable radiation detector. 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 sample PER2. Gamma-ray measurements using HPGe showed that the above geological material exhibits high radioactivity mainly due to 238U-series (234mPa: 8182 Bq/Kg, 226Ra: 6852 Bq/Kg, 214Pb: 7260 Bq/Kg, 214Bi: 6232.18 Bq/Kg). Powder-XRD, SEM-EDS and further chemical analyses indicated abundant apatite and organic matter, besides calcite, which should be associated to the high U content. Relatively high concentrations of Cd, probably related to apatite, were also revealed. 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. The sample is going to be subjected to further microscopic (TEM) and Synchrotron-based investigation (EXAFS) in order to elucidate the nature of U in the matrix.