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Uranium-bearing phosphatized limestones of NW Greece

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ABSTRACT

Sedimentary Mesozoic rocks from NW Greece (Epirus region), and particularly laminated phosphatized limestones, bedded chert-rich limestones and brecciated phosphatized limestones, were examined for their actinide content. Gamma-ray measurements using a HPGe detector showed that the above geological materials exhibit high radioactivity, mainly attributed to the ^{238}U-series. The ^{238}U content (up to 7700 Bq/kg) was determined by the 1001 keV photopeak of ^{234m}Pa, the ^{238}U daughter. Bulk geochemical analyses using ICP-OES/MS showed variable U concentrations with a notable value of 648 ppm in the case of dark organic-rich material hosted into the brecciated phosphatized limestones. 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 "average phosphorite". Powder-XRD combined with optical microscopy, SEM–EDS and FTIR confirmed abundant apatite, besides calcite, as well as organic compounds (organic matter/O.M.) which should be associated to the high U content. According to Th/Sc vs. Zr/Sc discrimination diagrams the organic-rich part of the U-bearing phosphatised limestones exhibits a mafic trend, in contrast to the rest of the studied rocks lying close to typical pelagic sediments. However, Eu/Eu* vs. Ce/Ce* diagrams, in combination with SEM–EDS, indicated that the organic-rich part is a typical sedimentary material whereas the organic-poor (and also U-poor) part of the rock is secondary calcite related to surface waters. As far as we know, the studied rocks from NW Greece are classified as among the richest U-bearing phosphatized limestones and/or sedimentary phosphorites in the world.

Introduction

The Epirus region (NW Greece) is generally composed of Mesozoic (250–65 Ma old) sedimentary rocks of the Ionian geotectonic zone of External Hellenides (Fig. 1), derived from the Tethys Paleo-Ocean. As these rocks are mostly limestones and shales, which are fundamentally poor in U (2.2 and 3.7 ppm respectively, Krauskopf and Bird, 1994; Mason and Moore, 1982), no elevated U concentrations would be expected in the Epirus area. However, it is known, from unpublished internal reports by the Greek Atomic Energy Commission (GAEC) and Institute of Geology and Mineral Exploration (IGME), that in some areas the natural radioactivity is high due to the presence of phosphate-rich sedimentary rocks, i.e. phosphorites (Koukouzas et al., 1978). In addition, Skounakis (1979), in an unpublished work, reported U-bearing phosphorites and phosphatized limestones.

Phosphorites are marine sediments of biogenic origin, containing 15–20 wt.% P_2O_5 (Boggs, 2009) and also an average of 120 ppm U (Li and Schoonmaker, 2003). When phosphorites are present in sedimentary formations they may significantly contribute in radiometric irregularities and actinide (likely U) geochemical anomalies. Additionally, they are rich in light rare-earth elements/LREE, but not in Th (6.5 ppm) and other heavy rare-earth elements/HRRE. Moreover, phosphatized limestones contain less P_2O_5 than phosphorites, but higher than limestones possessing an average of about 0.03–0.7 wt.% (Boggs, 2009) and less U. In general, the concentration of U in phosphorites and P-rich sedimentary formations of various geological ages worldwide, is referred in the range of ca. 3–600 ppm (e.g. Baturin and Kochenov 2001, and references therein; Soudry et al., 2002; Bech et al. 2010).

In this work we present, for the first time, mineralogical and spectroscopic data about Mesozoic sedimentary rocks from Epirus, derived from Tethys Paleo-Ocean, hosting unique U-bearing (up to 648 ppm)

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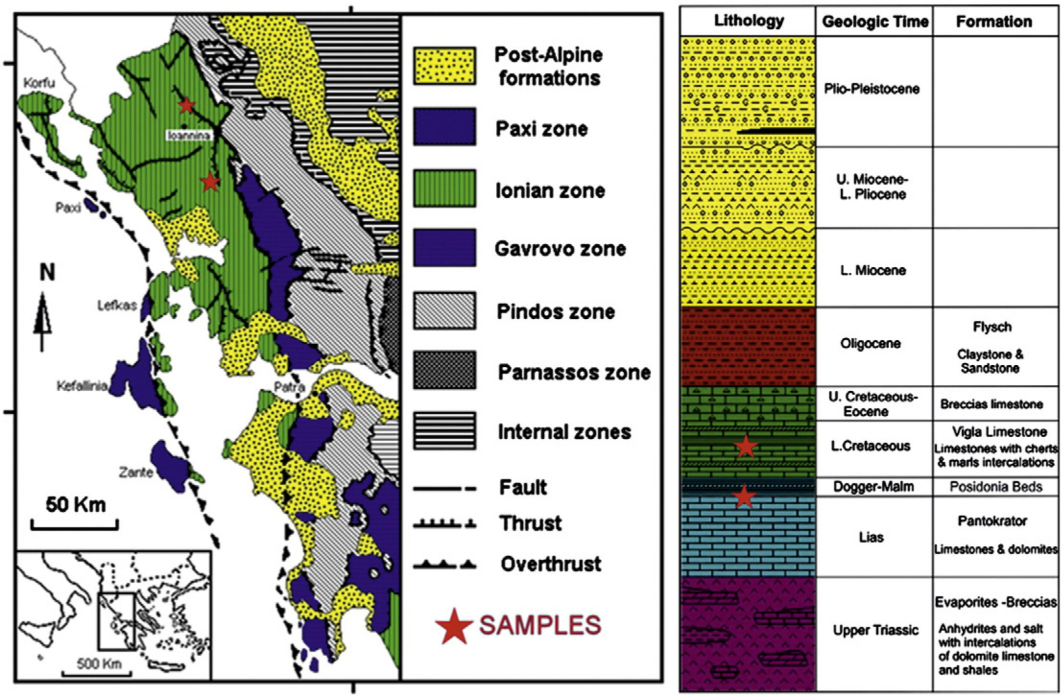

Fig. 1. Geological map and stratigraphic column of the U-bearing sedimentary rocks (modified after Marnelis et al., 2007).

organic-rich phosphorite into phosphatized limestones. In addition, accurate measurements of actinides, and namely U, in Epirus rocks showing elevated radioactivity, using high-resolution analytical and spectroscopic techniques, are given.

Materials and methods

Sampling was based on previous unpublished internal reports by the Greek Atomic Energy Commission (GAEC) and Institute of Geology and Mineral Exploration (IGME) concerning radiometric irregularities in the Mesozoic sedimentary rocks of western and north-western Greece and particularly in the mountainous Epirus region (Koukouzas et al., 1978). However, the final samples (Fig. 1) were selected by surveying the suspected sedimentary formations by means of a portable radiation detector (NaI Canberra-MCB2). Thus, the radioactive specimens concerned laminated phosphatized limestones (sample DRYM1) and brecciated phosphatized limestones partially rich in organic matter (sample PER2A and PER2B). Besides, a non-radioactive sedimentary rock typical for the area, namely a bedded chert-rich limestone (sample PER1), was also used for comparison reasons ("background" radioactivity towards U – and actinide – content). The sample DRYM1 (Fig. 2a) was collected in the Drymonas region from Cretaceous horizons which consist mainly of carbonate rocks (limestones rich in phosphorus) alternating with cherts (Vigla Formation). This region geotectonically belongs to the eastern limit of the middle Ionian Zone of External Hellenides (Fig. 1). The samples PER1 and PER2 (Figs. 1 and 2b & c) were collected from Mt. Mitsikeli near Ioannina lake and city, and particularly from the villages of Perivleptos and Stoupena. The highly-radioactive rock (PER2) is located approximately 10 km N–NW of Ioannina within a brecciated phosphatized limestone of the uppermost layers of Jurassic Sinion–Pantokrator formation.

Gamma-ray spectrometry was applied for the determination of natural and artificial radionuclides activity concentrations in the studied samples. The measurements were performed by means of a HPGe n-type detector (GC5021 Canberra) with 50% nominal relative efficiency and 2.3 keV energy resolution at 1.33 MeV, along with a computerized MCA system (8715 Model and Gamma Vision® software by Canberra) for the data acquisition. A cylindrical lead shield surrounded the detector in order to reduce the ambient gamma-ray background. The energy-dependent detection efficiency was determined using a ^{152}Eu reference source. Four samples where properly prepared and measured for 24 h each, whereas a phantom sample was also used in order to extract the background contribution from the experimental spectra. The measured data were analyzed using the SPECTRW spectrometry software package (Kalfas and Tsoulou, 2003) and the quantitative analyses were subsequently performed as described elsewhere (Tsabaris et al., 2007). The ^{238}U activity was measured from spectrum photopeaks corresponding to radionuclides ^{234m}Pa at 1001 keV, ^{234}Th at 63.3 keV and ^{214}Bi at 934 keV (Karangelos et al., 2004). Radionuclides ^{137}Cs and ^{40}K were measured from 661.67 keV and 1461 keV photopeaks, respectively. The activity concentration (Bq/kg) of ^{235}U was determined from the 143.76 keV, 163.15 keV and 205 keV photopeaks where possible (sample PER2B, see Fig. 3), whereas elsewhere from the double photopeak at 186 keV assuming secular equilibrium between ^{238}U and ^{226}Ra (Tsabaris et al., 2007).

The natural actinide content of the studied rocks (also derived from gamma-ray spectrometry) was determined by ICP-MS (PerkinElmer Sciex Elan 9000) after $LiBO_2/LiB_4O_7$ fusion and HNO_3-digestion of 0.2 g of sample. The major and trace element content of the samples was also determined by ICP-OES and MS; loss on ignition (LOI), total C and S were also measured using standard methods. The mineralogical study and phase characterization was performed by optical microscopy, powder X-ray diffraction/XRD (Siemens D5005 – now Bruker AXS – diffractometer), scanning electron microscopy/SEM–EDS (Jeol JSM-5600 equipped with Oxford EDS) and Fourier-transform infrared spectroscopy/FT-IR (PerkinElmer GX-1 FT-IR).

Results and discussion

Among the sedimentary rocks studied by HR gamma-ray spectrometry, the lowest U activity (taken into account as natural radioactivity "background" in the area) corresponds to bedded chert-rich limestones (PER1) and the highest to the organic-rich part of the brecciated phosphatized limestones (PER2B). The activity concentration results for the characteristic radionuclides of each natural radioactivity series, ^{40}K and the anthropogenic ^{137}Cs are shown in Table 1. The U "background"