Uranium-bearing phosphatized limestones of NW Greece

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A B S T R A C T

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 238U-series. The 238U content (up to 7700 Bq/kg) was determined by the 1001 keV photopeak of 234mPa, the 238U 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 phosphoritite”. 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 phosphatized 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.

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Introduction

The Epirus region (NW Greece) is generally composed of Mesozoic 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 However, it is known, from unpublished internal reports by the Greek Atomic Energy Commission (GAEC) and Institute of Geology and Mineral Exploration (IGME), that in some areas the natural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.% P2O5 (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/HREE. Moreover, phosphatized limestones contain less P2O5 than phosphorites, but higher than limestones possessing an average of about 0.03–0.7 wt.% P2O5 (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)
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 $^{152}\text{Eu}$ 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 $^{238}\text{U}$ activity was measured from spectrum photopeaks corresponding to radionuclides $^{234}\text{Pa}$ at 1001 keV, $^{234}\text{Th}$ at 63.3 keV and $^{214}\text{Bi}$ at 934 keV (Karangelos et al., 2004). Radionuclides $^{137}\text{Cs}$ and $^{40}\text{K}$ were measured from 661.67 keV and 1461 keV photopeaks, respectively. The activity concentration (Bq/kg) of $^{235}\text{U}$ 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 $^{238}\text{U}$ and $^{226}\text{Ra}$ (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$_4$O$_7$ 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, $^{40}\text{K}$ and the anthropogenic $^{137}\text{Cs}$ are shown in Table 1. The U “background”
sample exhibited $44 \pm 2$ Bq/Kg concerning $^{238}$U and significant $^{40}$K ($23 \pm 1$ Bq/Kg). On the other hand, exceptionally high activities of $^{238}$U and $^{235}$U were observed for the sample PER2B ($7700 \pm 425$ Bq/kg for $^{238}$U and $322 \pm 24$ Bq/kg for $^{235}$U). Besides, the organic-poor part of the same rock (PER2A) exhibited decreased values (approximately two orders of magnitude) for the aforementioned natural series. The laminated phosphatized limestone (sample DRYM1) also showed increased activity concentrations compared to the background values. Activity values were found to be $10.5 \pm 0.5$ Bq/kg for $^{235}$U, $269 \pm 13$ Bq/kg $^{238}$U and $3.9 \pm 0.2$ Bq/kg $^{40}$K (Table 1). It should be emphasized that the activities of $^{232}$Th series, for all studied rocks, were measured below the limit of Minimum Detectable Activity (MDA) 3 Bq/kg.

The U concentrations (in ppm), as calculated from the HR gamma-ray spectra (IAEA, 1989), are shown in Fig. 4. The values are consistent with the ICP-MS measurements presented in Table 2, revealing 2.9 ppm of U.

Table 1

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<tr>
<th>Natural decay series</th>
<th>Activity (Bq/kg)</th>
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<tr>
<td></td>
<td>DRYM1</td>
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<tr>
<td>$^{238}$U</td>
<td></td>
</tr>
<tr>
<td>$^{234}$Pa</td>
<td>269 ± 13</td>
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<tr>
<td>$^{226}$Ra</td>
<td>215 ± 11</td>
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<tr>
<td>$^{214}$Pb</td>
<td>208 ± 10</td>
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<tr>
<td>$^{214}$Bi</td>
<td>191 ± 10</td>
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<tr>
<td>$^{208}$Tl ($&lt;3$ MDA$^a$)</td>
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<tr>
<td>$^{232}$Th</td>
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<tr>
<td>$^{238}$U</td>
<td>10.5 ± 0.5</td>
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<tr>
<td>$^{227}$Th</td>
<td>9.9 ± 0.5</td>
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<tr>
<td>$^{223}$Ra</td>
<td>4.3 ± 0.2</td>
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<tr>
<td>$^{219}$Rn</td>
<td>3.9 ± 0.2</td>
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<tr>
<td>Natural $^{40}$K</td>
<td>3.9 ± 0.2</td>
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<tr>
<td>Anthropogenic $^{137}$Cs</td>
<td>2.9 ± 0.2</td>
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$^a$ Minimum detectable activity.
in the case of the “background” sample (PER1) and values in the range 7.2 ppm to 648 ppm in the case of phosphatized limestones. It is worth noting that the value of 648 ppm, recorded in the organic-rich part of the and tectonized/re-processed phosphatized limestones (PER2B), represents one of the richest U-bearing phosphatized limestones and/or sedimentary phosphorites in the world (e.g. Baturin and Kokenov 2001, and references therein; Soudry et al., 2002; Bech et al. 2010). The positive U geochemical anomaly, in comparison to Upper Continental Crust (UCC, Rudnick and Gao, 2003), for all studied Tethyan Mesozoic sedimentary rocks from Epirus, as well as the exceptional U anomaly of sample PER2B, are shown in Fig. 5. It is also obvious that the rocks are considerably enriched in Cd, a minor heavy metal which could be associated to apatites. The U-enrichment of Epirus phosphatized limestones, among phosphatized limestones and/or sedimentary phosphorites in the world, is also evident in Figs. 6 and 7 including data about the “average phosphorite” (Li and Schoonmaker, 2003) and characteristic phosphorites and phosphatized limestones from eastern Mediterranean and the rest of the world (Baturin and Kokenov, 2001; Bech et al., 2010). At the same time, it is demonstrated that all phosphorites and phosphatized limestones are highly enriched in Cd and Se (Bech et al., 2010). The REE + Y content is also high, as well as the content of Cd, due to involvement in the crystal structure of apatite (Pasero et al., 2010).

The chemical composition of the phosphorites and phosphatized limestones depends on conditions during genesis, the lithology, the stratigraphy, and the geographical provenance (e.g. Bech et al., 2010). It is notable that in most of the deposits, which have been studied around the world, there is always almost a triple sequence of phosphates-containing sediments, SiO2-containing sediments (cherts), and sediments rich in organic matter. It has been recently stated that phosphorite and/or phosphatized limestone deposits are in fact marine biogenic materials, due to bacterial activity producing bio-apatite and particularly carbonate apatite/francolite (Benmore et al., 1983; Diaz et al., 2008; Goldhammer et al., 1991). However, the partitioning of U in different (bio)minerals and phases constituting marine phosphorites and/or phosphatized limestones is not completely resolved.

The studied Epirus U-bearing phosphatized limestones are mineralogically rather simple, and the powder-XRD investigation showed only calcite (CaCO3) and apatite supergroup minerals (Ca5(PO4)3[F,Cl,OH]) in the bulk. In particular, the organic-rich part (PER2B), hosting the highest U concentration (648 ppm), contains also calcite and apatite as crystalline phases (Fig. 8). The apatite crystals are not visible, for all samples, under the optical microscope (Fig. 9a-c), due to their “cryptocrystalline” nature (the so-called “collophane”), but some of them are detectable by SEM–EDS (Fig. 9d-f). The phosphatized limestone, DRYM1 (Fig. 9a & 9d), is characterized as micritic and pelmicritic due to its calcitic and phosphatic grains. The sample PER1 (Fig. 9b & 9e) is a typical chert, consisting mainly of microcrystalline quartz (individual

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<td>Major and trace elements in the studied sedimentary rocks.</td>
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<td>MF</td>
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<td>SiO2</td>
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<td>P2O5</td>
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<td>MnO</td>
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<td>Lu</td>
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Fig. 4. Uranium concentrations in the studied rocks as resulted from gamma-ray spectroscopy and ICP-MS analyses.

| Fig. 4. Uranium concentrations in the studied rocks as resulted from gamma-ray spectroscopy and ICP-MS analyses. |
crystals not visible in optical microscope) alternating with calcite-rich layers. The carbonate part of the rock is characterized as biomicrite enriched in radiolarian and diatoms. Moreover, it is observed that in the examined sample the cracks are filled with diagenetic calcite. In addition the radiolaria have been replaced internally by chalcedony and microcrystalline calcite. The sample PER2 (Fig. 9c & 9f), is a brecciated phosphatized limestone rich in organic matter, filling all the discontinuities and the cracks, and it is therefore optically tectonized/re-

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**Fig. 5.** UCC (Rudnick and Gao, 2003)-normalized multielement geochemical spidergrams concerning the studied rocks.

**Fig. 6.** UCC (Rudnick and Gao, 2003)-normalized multielement geochemical spidergrams concerning the U-bearing samples compared to global phosphorite (Li and Schoonmaker, 2003).
processed. It seems to be a debris flow, matrix supported and poorly sorted monomictic breccia produced by rock fragmentation related to faulting or other tectonic processes affected by a steep slope submarine area in a pelagic environment. It has angular sand or gravel to boulder-sized (fine to very coarse) clasts cemented together in a matrix. The matrix consists primarily of the cementing material, but it also contains sand and/or silt sized clasts cemented together among the coarser clasts. The cement that binds the clasts consists of black organophosphate material (organic matter + apatite) as well as of sparitic calcite. The clasts are also rich in fossils and other allochem ingredients like peloids and extraclasts. Calcite appears as either primary (micritic) or as sparite (secondary) as well as biomicrite (rich in biogenic elements). In addition, frambooidal pyrite aggregates, in fact goethite (FeOOH) pseudomorphs after oxidized pyrite (FeS2), are also visible, specifically in sample DRYM1, indicating marine Tethyan paleo-environment poor in O2 related to anoxic conditions in the depositional environment. The above evidence for anoxic conditions during the formation of Epirus phosphorites and/or phosphatized limestones supports the presence of U which precipitates in such physicochemical conditions (e.g. Anderson et al., 1989; Klinkhammer and Palmer, 1991). It should be emphasized that there are no distinct U minerals or phases, containing U as major element, identified either by optical microscopy or SEM–EDS in microscale. Thus, U in the sample possessing the highest content of the actinide element (PER2B) must be contained as trace element and/or impurity in phosphate and carbonate minerals or, most likely, in organic matter (O.M.) (Fig. 10).

The possible phases hosting U in the studied phosphatized limestones (Fig. 10) may fundamentally be minerals of the apatite supergroup and organic matter (O.M., i.e. bitumens). Calcite may also host traces of the actinide metal. Minor metallic minerals and detrital silicate/aluminosilicate phases are much less probably related to the U presence in the rocks.

There are numerous studies with regard to the structure of the apatite supergroup, reporting that the lattice of these phosphate minerals favours extended trace-element ionic substitutions (e.g. Hughes and Rakovan, 2002; Luo et al., 2009; Pan and Fleet, 2002; Pasero et al., 2010; Rakovan et al., 2002). The crystal chemistry of trace metals in the apatite supergroup minerals \([Ca_5(PO_4)_3[F,Cl,OH]]\) is of considerable significance in geology, biology, materials and environmental sciences. Apatite can accommodate several foreign elements, including actinides, showing environmental concern. Monovalent (Na+, K⁰⁺), divalent (Sr²⁺, Pb²⁺, Ba²⁺, Mn²⁺, Cd²⁺), trivalent (REE³⁺), as well as tetravalent (Th⁴⁺, U⁴⁺) and hexavalent cations (U⁶⁺) have been reported to substitute into Ca sites in the apatite structure (Luo et al., 2009; Pan and Fleet, 2002; Rakovan and Hughes, 2000; Rakovan et al., 2002). According to the reported structural refinements in natural near-end-member fluorapatite, chlorapatite, and hydroxyapatite, there are two Ca-polyhedra in the apatite structure that are hexagonally disposed about a central \([001]\) hexad (Hughes and Rakovan, 2002). The position Ca1 is coordinated to nine O atoms in a tricapped trigonal prism. On the other hand Ca2 bonds to six O atoms and one column anion. Thus, the two Ca positions in apatite offer quite different stereochemical environments and are able to accommodate a variety of cations as substituents. In an EXAFS study Rakovan et al. (2002) found U⁶⁺ substitutes into the Ca1 site in synthetic apatite grown at 1350 °C. The substitution causes a decrease in the Ca1–O1 and Ca1–O2 bond lengths and EXAFS data indicate a weaker Ca1–O3 interaction. They also speculated that a likely distortion is the rotation of O1 and O2 triads to approximate an octahedral geometry around U⁶⁺ (Rakovan et al., 2002). According to the study by Luo et al. (2011), also based on EXAFS data, U⁶⁺ may also incorporate in Ca-sites into the structure of apatites. All the above indicate that apatite supergroup minerals can fundamentally host U, and therefore U concentrated in phosphatized limestones and/or sedimentary phosphorites may be partially due to
apatite. Furthermore, there is positive correlation between U (in ppm) and P2O5 (in wt.%) for Mesozoic phosphorites from Epirus, Greece (Koukouzas et al., 1978; Skounakis, 1979) and for relevant phosphorites from Negev, Israel (Soudry et al., 2002), as shown in Fig. 11 (data from the present study are also included). Previous attempts to explain the presence of U in sedimentary apatite (e.g. Baturin and Kochenov, 2001) are based on the similarity of elements’ ionic radii and also on the assumption that U may substitute some Ca in the carbonate apatite/francolite lattice. However, a typical U concentration in pure non-sedimentary apatite (Durango-type fluorapatite) has been reported to be 8.88 ppm (Trotter and Eggins, 2006). Thus, much higher concentrations, and particularly hundreds of ppm, in phosphorites and/or phosphatised limestones, can hardly be explained only on the basis of apatite supergroup minerals. At this point, it should also be emphasized that all the studies about U in apatite structure concern fluorapatites and chloroapatites (Luo et al., 2009; Rakovan et al., 2002) and there are no specific studies about U in carbonate apatite/francolite (\([Ca_5(PO_4, CO_3)_{3}(F,OH)]\)) occurring, together with fluor- and hydroxy-apatite, in phosphorites and/or phosphatised limestones. Nevertheless, it is herein argued that in the studied Epirus U-bearing rocks, apatite may contain a portion of U (in the form of both U⁶⁺ and U⁴⁺), but a high percentage of the concentration of the element should be related to other materials (most likely to the contained, powder XRD-amorphous, organic matter/O.M.).

Calcite, representing the other major crystalline phase in the studied U-bearing rocks, is not a strong candidate for accommodation of high U amount, either. The average abundance of U in carbonate sedimentary rocks is 2.2 ppm (Mason and Moore, 1982) whereas the concentration of U in relevant Tethyan rocks from SE Europe and the Middle East is reported to be in the range of 1–10 ppm (Ehrenberg et al., 2008). Unusually elevated amounts of U (up to ca. 53 ppm) have been measured in typical marine carbonates originating in the Tethys paleo-ocean (organic-rich calcitic limestone and tectonized/weathered dolomitic limestone) of Triassic age from Mt. Kithaeron, central Greece (Göttlicher et al., 2009). In the above case, Synchrotron-based µ-XRF and µ-XANES spectroscopy indicated the existence of U⁴⁺ in Ca-rich regions of the rocks, corresponding to calcite, around distinct Mn-oxide phases. Also, Sturchio et al. (1998), in a similar Synchrotron-based study, had mentioned U⁴⁺ in a 35 Ma-old spar calcite (5–35 ppm U) from a Mississippi Valley-type zinc ore deposit. As a consequence, calcite in the Epirus U-bearing phosphatised limestones may also contain traces of U (most likely in the form of U⁴⁺) without, however, significant contribution to the overall content.

It is therefore reasonable to argue that the majority of U in the organic-rich part of the phosphatised limestone (sample PER2B) is associated to the organic matter (O.M.). This geological material is powder XRD-amorphous, but it can be identified by distinct peaks (Calderon et al., 2011; Ellerbrock and Gerke, 2004) in the corresponding FT-IR spectra (Fig. 10). Besides, the CO₃²⁻ and PO₄³⁻ peaks, corresponding to calcite and apatite, were also resolved (Pasteris et al., 2004). The broad absorbance band at ~3451 cm⁻¹ corresponds to O–H stretching vibrations in water and hydroxyl groups in various organic and inorganic substances (Ellerbrock and Gerke, 2004; Gerzabek et al., 2006). Minor bands of low intensity at 2926 and 2854 cm⁻¹ arise from C–H stretching vibrations in aliphatic hydrocarbon. These bands along with the vibrations at 2357 cm⁻¹ and 2919 cm⁻¹ indicate the presence of organic material (Calderon et al., 2011). The FT-IR spectrum is also characterized by a strong band at ~1427 cm⁻¹ (ν₃ vibration) and a band of medium strength
at ~873 cm$^{-1}$ ($\nu_1$ vibration). These absorption bands are related to vibrations in the carbonate radical. The band at ~873 cm$^{-1}$ is specific to calcium carbonate and is commonly used to determine the presence of calcite in phosphate minerals (Fleet, 2009). Several more or less intensive bands are caused by the presence of calcite (CaCO$_3$) at 2517, 1428, 874, and 711 cm$^{-1}$. The vibrations at ~477 cm$^{-1}$ ($\nu_2$), 579 cm$^{-1}$ ($\nu_4$), 603 cm$^{-1}$ ($\nu_4$) and 1050 cm$^{-1}$ ($\nu_3$) are characteristic of the PO$_4$ groups indicating the presence of apatite (Pasteris et al., 2004).

Organic matter in sedimentary rocks, generally known as kerogen (Forsman and Hunt, 1958) is mainly represented by bitumen which is composed of asphaltenes + resins and hydrocarbons (Killops and Killops, 2005). Asphaltenes and resins are heavy N, S, O-containing molecules (molecular weight > 500), whereas the hydrocarbons are usually of lower molecular weights. The hydrocarbon fractions can be separated into aliphatic and aromatic hydrocarbon subfractions, again on the basis of the greater polarity of the aromatics. Traditionally, the aliphatic hydrocarbons (or saturates) are described in terms of their paraffinic (acyclic alkane) and naphthenic (cycloalkane) content. Uranium in sediments interacts intensively with organic matter and fundamentally forms compounds with organo-metallic bonding (Parnell, 1988; Rouzaud et al., 1980). According to Leventhal and Daws (1986) in sedimentary rocks with low U content, the actinide element is related to hydroxyls and molecules with both aliphatic and aromatic C-atoms. Otherwise, when the U content is high, the element is mostly associated to aromatic C-atoms. Therefore when U interacts with organic matter, there are two principal processes which can be identified: complexation and reduction (Landais, 1996). During complexation by ionic exchange, the carboxyl functional groups of humic acids, coals, and kerogens are responsible for the complexation of uranium by organic matter (Munier-Lamy et al., 1986). The chemical reactions describing this phenomenon involve in fact the uranyl cation (UO$_2^{2+}$) and a dehydrogenation of the organic matter:

$$2\text{R-COOH} + \text{UO}_2^{2+} \rightarrow \text{RCOO}^-(\text{UO}_2^-)\text{OCR} + 2\text{H}^+$$

The reduction of U$^{6+}$ to U$^{4+}$ has been experimentally investigated by Andreyev and Chumachenko (1964) and Nakashima et al. (1984). They have reported that the following chemical reaction describes the oxidation of organic matter during the reduction of uranium:

$$2(\text{RH}) + \text{UO}_2^{2+} \rightarrow 2\text{R}^+ + 2\text{H}^+ + \text{UO}_2.$$
can be reduced to $\text{U}^{4+}$ oxides. The $\text{UO}_2^{2+}$ cation may then be complexed with carboxylate groups of the humic acids (Nash et al., 1981). Alternatively $\text{UO}_2^{2+}$ ions may combine with electron donor free radicals within organic material (Rouzaud et al., 1980). Thus, adsorption and reduction to precipitate uraninite ($\text{UO}_2$) could occur in a single stage. In addition, most of the mineralized carbonaceous materials contain microcrystals of uraninite, while some other material contains uraniferous organometallic complexes that were detectable by SEM–EDS (Rouzaud et al., 1980).

Fig. 10. Phases hosting U in the studied U-bearing (648 ppm) phosphatized limestone; the FT-IR spectrum of the material indicating the presence of organic matter along with apatite and calcite.
Consequently, complex and/or organometallic compounds of \( \text{UO}_2^{2+} \) with carboxylate groups (most likely of humic acids), as well as reduced U in the form of uraninite (Parnell and Eakin, 1987), can be considered to be predominantly responsible for the presence of the element in the Mesozoic U-bearing phosphatized limestones of NW Greece (Epirus). It should be noted that uraninite, if existent, must occur in the form of nanocrystals, inasmuch as the SEM–EDS study did not reveal any U-phase in microscale.

The origin and the formation conditions of the U-bearing brecciated phosphatized limestones can initially be approached by a Th/Sc vs. Zr/Sc discrimination diagram, as shown in Fig. 12a. The organic-rich part of the U-bearing phosphatized limestones (containing 648 ppm U) exhibits a considerable mafic–fundamentally igneous–trend, in contrast to the rest of the studied rocks (PER1, DRYM1) lying close to typical pelagic sediments. The organic-poor – calcitic – part (sample PER2A) has not been plotted in the same diagram due to the lack of significant Sc content. More information can be obtained by the use of rare earth elements (REE) which are suitable for the study of a wide range of geological processes. The geochemical behaviour, and generally the chemistry of REE, has been applied to study the origin of sediments (e.g. Taylor and McLennan, 1985), the chemical weathering (e.g. Hannigan and Sholkovitz, 2001) and the chemical composition of the ground water. The enrichment of phosphorites in REE was observed very early and described in detail by a number of researchers (e.g. Ilyin and Ratnikova 1976; McClure and Walsh 1984; Piper and Medrano 1995). The negative anomalies of Ce and Eu were used to characterize the environment of deposition, and particularly redox conditions (Eldering and Greaves, 1982). The most direct source of REE is water and all REEs are supposed to replace Ca. The Epirus U-bearing organic-rich phosphatized limestones illustrate enrichment in light-REE (LREE). The Eu and Ce anomalies, related to oxidation (\( \text{Ce}^{3+} \rightarrow \text{Ce}^{4+} \)) and reduction (\( \text{Eu}^{3+} \rightarrow \text{Eu}^{2+} \)), depend subsequently on redox conditions (Eldering and Greaves, 1982), and give important information about the depositional environment. Negative Ce anomalies have been reported to be common in phosphorites (Kidder et al., 2003; McClur and Walsh, 1984) whereas they have also been implied for Epirus phosphorites (Sovatzoglou-Skounaki and Skounakis, 1989).

However, by using a recent Eu/Eu* vs. Ce/Ce* discrimination diagram (Leybourne and Johannesson, 2008), in combination with SEM–EDS, it is proven that the organic-rich part of the U-bearing phosphatized limestones is a typical sedimentary material while the organic-poor (and also U-poor) – calcitic – part of the rock (PER2A) is secondary calcite related to surface waters (Fig. 12b). This observation proves that the studied geological material has been subjected to various surface diagenetic and weathering processes. However, these intense natural processes were not able to completely remove primary U from the sedimentary rocks, mostly in the form of uranyl carbonate anions (\( \text{UO}_2[\text{CO}_3]^{3-} \)), (Parnell and Eakin, 1987), resulting in long-term immobilization of U, most likely by the organic matter. Thus, it is worthy to make obvious that the uraniferous, P- and organic matter-rich, carbonate rocks of NW Greece (Epirus) might also be considered as natural analogue sites of areas with relevant rocks contaminated with actinide, and namely U, radioactive elements.

Conclusions

Sedimentary Mesozoic rocks from NW Greece (Epirus region), and particularly laminated phosphatized limestones and brecciated phosphatized limestones, show, on the basis of field measurements, increased natural radioactivity. On the other hand, neighbouring bedded chert-rich limestones show a non-radioactive typical behaviour.

Laboratory HR gamma-ray measurements showed elevated radioactivity (up to 7700 Bq/Kg), mainly attributed to \(^{238}\text{U}\)-series, in the case of dark organic-rich material hosted into the brecciated phosphatized limestones. Moreover, bulk geochemical analyses, using ICP-OES/MS, showed high U concentrations with a significant value of 648 ppm. To the best of our knowledge, we herein demonstrate one of the richest U-bearing phosphatized limestone and/or sedimentary phosphorite in the world.

Moreover, relatively high concentrations of Cd are measured in the rocks, probably related to apatite, though lower compared to the “average phosphorite”. On the other hand, there is a geochemical depletion in LILE (e.g. Cs, Rb, K), as well as in As, Sb and Se. Optical microscopy, together with powder-XRD, SEM–EDS and FTIR confirmed abundantapatite supergroup minerals, besides calcite, as well as organic compounds (organic matter/O.M.) which should be mainly associated to the high U content. Apatite, and calcite in lesser extent, may also host traces of the actinide element.

According to a Th/Sc vs. Zr/Sc discrimination diagram 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. The utilization of a recent Eu/Eu* vs. Ce/Ce* discrimination diagram, coupled with SEM–EDS, indicated that the above organic-rich (and also U-rich) part is a typical sedimentary material.
while the organic-poor (and also U-poor) part of the rock is secondary calcite related to surface waters.

All of the above lead us to argue that, despite various long-term surface diagenetic and weathering processes, U still remains immobilized in NW Greece P- and organic matter-rich carbonate rocks, which, in turn, could also be considered as natural analogue sites of geological environments contaminated with actinide elements.

Acknowledgements

Many thanks are due to the staff of the Epirus branch (Preveza) of IGME for valuable information concerning the field work and sampling.

References


