Δελτίο της Ελληνικής Γεωλογικής Εταιρίας, 2010
Πρακτικά 12ου Διεθνούς Συνεδρίου
Πάτρα, Μάιος 2010

Bulletin of the Geological Society of Greece, 2010
Proceedings of the 12th International Congress
Patras, May, 2010

THE GENETIC HYPOTHESIS OF THE URANIFERUS MINERALIZATION, EASTERN CHALKIDIKI (NORTHERN GREECE)

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Abstract

This paper presents the genetic hypothesis of αn uranium mineralization observed in Eastern Chalkidiki-Greece.

In the area of Stratoni (location Asprochomata) a uranium mineralization is expressing by disseminated primary (orthobrannerite) and secondary (torbernite) U minerals, in the granodioritic body of this area. Genetically it may be the result of uranium redistribution, which occurs in the resisting accecory minerals (e.g monazite) of the granodiorite, by magmatic or meteoric hydrothermal fluids of low temperature. The mineralized granodiorite of Stratoni gives no evidence of a metalliferous pluton, based on the study of hydrothermally altered samples and this ascertainment is a fact that should be confronted with a lot of carefull thought.

In the granite of Arnea area, uranium mineralization is in generally absent, excluding some poor one's, located along the contacts of the granite with small remnants of the hosting rock, expressed in the form of impregnations or veinlets. The possible cause for its formation being the interaction of a secondary low temperature hydrothermal system mainly of meteoric water participation (convective hydrothermal system) with the granite and the hosting wall-rock minerals. The granite of Arnea indicates all the characteristics of a metalliferous granitoid.

Key words: *Uranium redistribution, orthobrannerite, metalliferous granitoid, hydrothermal fluids, Chalkidiki, Northern Greece.*

1. Introduction

In Chalkidiki area, in the granodiorite of Stratoni, which does not present the characteristics of one metalliferous magmatic body, are observed a primary (orthobrannerite), as well as a secondary (trovernite) uranium mineralization resulting from the redistribution of uranium existing in the granodiorite accesory minerals (e.g. Monazite), by low temperature, magmatic or meteoric, hydrothermal fluids. On the contrary, the Arnea area's granite, although this magmatic intrusion presents characters of a metalliferous granitoide, uranium mineralization is not observed.

This study attempts the presentation of the uranium mineralization and the determination of its genesis. The mineral composition, the geochemical characteristics, the age, the geotectonic environment and the metallogenetic evolution of the two plutonic bodies are examined. For this reason thin polished sections of the samples from these areas were prepared, on which was used the method of

Fig. 1: Geological map of Chalkidiki.

autoradiography, with the purpose to detect and study the uraniferous minerals concentration.

2. Petrography - Mineralogy

The magmatic body of Stratoni area, known as Stratoni granodiorite, is a fine to coarse-grained rock with a composition changing from quatz diorite – monzonite to granodiorite – adamellite, with most common phase the granodiorite (Kalogeropoulos et al., 1988; Gerouki et al., 1988).

The main minerals are quartz, potassium feldspar, plagioclase, titaniferous biotite and as secondaries muscovite (sericite), hornblende, pyroxene (diopside), epidote, titanite, calcite, magnetite and pyrite are found. The main hydrothermal alterations are the biotite chloritization and the sericitization of the plagioclases.

The magmatic body of Arnea is a medium to coarse-grained leucogranite, which the composition presents small fluctuations. The main minerals are quartz, plagioclase, potassium feldspar, muscovite and biotite. As secondary minerals chlorite, epidotes, magnetite, +/-titanite, +/-allanite are found.

The comparison of the mineral composition of these two bodies shows that: a) the quartz is more abundant in the leucogranite of Arnea, b) the plagioclases are more abundant and more basic in the Stratoni granodiorite than in the Arnea leucogranite, while alkali feldspar are more abundant in the Arnea body, c) the micas content is low in both bodies, d) in the Arnea, leucogranite the content of muscovite and biotite is the same, but in the Stratoni granodiorite biotite is prevaling, e) the biotites of the Stratoni's granodiorite are rich in titanium, while those of the Arneas' leucogranite, are poor ones, f) femic minerals, like horneplende and pyroxenes, are observed only in the Stratoni body.

3. Chemism – Geotectonic environment – Age

The changing composition of the Stratoni granodiorite means complex magmatic conditions of genesis. In combination with the fact that it presents a metaluminous and a peraluminous character, this signifies a hybrid origin with the participation of both, mantle's components (I - type) as well as sialic components (S - type). Its composition is also fluctuating from cafemic to alumino-cafemic types.

It presents a wide range of SiO_2 values and a differentiation tendency which is expressed with an almost linear negative correlation for SiO_2 / TiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, MgO, CaO, Na_2O ratios and a positive one for SiO_2 / K_2O. The dispersion of the values is due to the hydrothermical alterations.

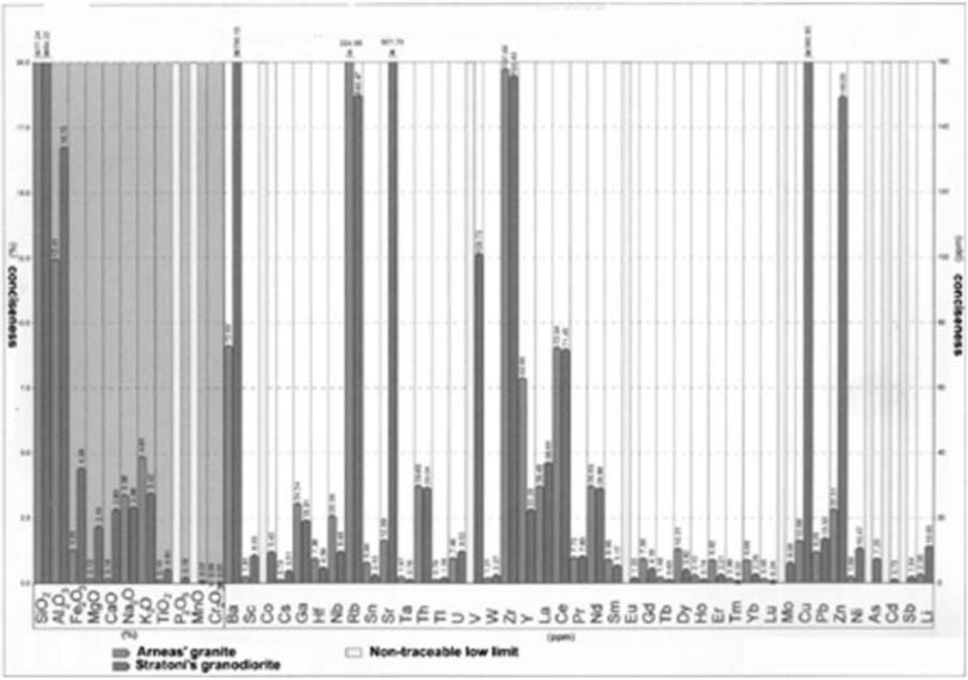

Fig. 2: Standard deviation graph for majors and trace elements in samples of Arneas' granite and Stratoni's granodiorite.

The leucogranite of Arnea has mainly a peralouminous character and presents small fluctuations of its composition, meaning that sialic components (S - type) have the major role in its genesis, but, on the other hand, the presence of magnetite indicates the participation also of a mantle's component (I – type).

Both bodies present a calcalkaline character and it seams that are formed in a subduction environment of high pressure.

The method of K/Ar in biotite gives an age of 29,6 ± 1,4 million years (Tertiary) for the Stratoni area granodiorite, (Alther et al., 1976), while the granite of Arnea's area, dated with the method of U/Pb in zircon, gives a Mesozoic age of 212 million years, (Frei, Gerouki pers. com., 1987).

4. Depth and temperature of emplacement.

The granodioritic magma of Stratoni was placed at a temperature of about 900^{o} C and was solidified at a pressure between 1 and >5 kb. It presents a potassium tendency, fact meaning that the magma was firstly saturated in water. The wide range of pressure's values proves a gradual, slow crystallization of this granodiorite. So, the gradual falling of the pressure during the crystallization, would free water and metallic elements in the fluid phase, and this would help the magma ascent to highest levels in the crust (Eugster, 1985).

The leucogranite of Arnea seems to be crystallized in pressures values between ~1kb to <0.5 kb, meaning that its crystallization took place nearest to the crust surface, than the Stratoni body, and for this reason it was not characterized by sufficient water content.

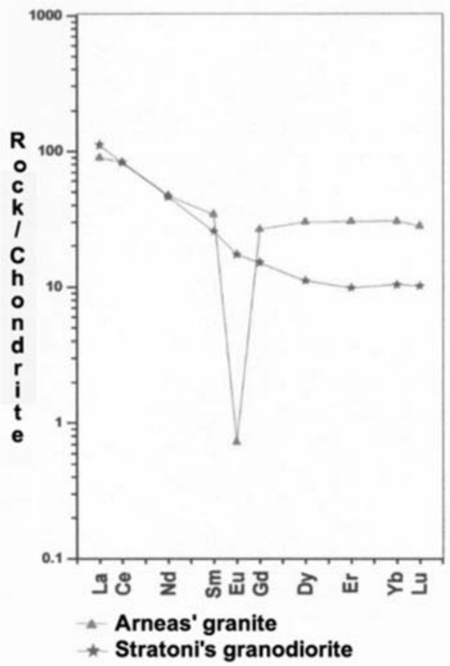

Fig. 3: The REE patterns of Arnea's granitic and Stratoni's granodioritic samples, normalized for 10 ordinary chondrites.

5. Cheochemical characteristics

The L.O.I. of the Stratoni samples is great (2.8), in contrary with these of Arnea samples (0,8), fact that is due to the hydrothermal alteration of the Stratoni´s samples, which must be examined with care.

The comparison of the mean concentration values of the major, as well as for the trace elements, make obvious the differences of the two bodies, (Fig.2).

The uranium content in the Arneas' granite fluctuates between 5 and 14 ppm, with a mean value of 7,5 ppm (σ=2), while the Th content changes from 23 to 40 ppm with a mean value of 29,6 ppm (σ=3,8). In the Stratoni granodiorite, the U content changes between 4-19 ppm with a mean value of 9,5 ppm (σ=3,4), and respectively the Th between 11-36 ppm with a mean value 29 ppm (σ=6). These values are highers than those usualy found in the granites, (3-5 ppm U and 10-12 ppm Th – Adams et al., 1959).

The granite of Arnea, except the high content of U and Th, also presents high values of other incompatiple elements, like the Rb, K, Sn, Nb, Y, Ta, while the content in Ba, Sr, Mg and Ti are low, so the ratios Rb/Sr, K/Ba, Cs/Ba are high and the ratio Sr/Y low.

The Stratoni granodiorite presents exactly the opposite image, with just a little augmentation in Cs and Li content. This results in high values of the Cs/K ratio and a small augmentation in this of U/Th.

In Figure 3 the REE patterns of Arnea's granitic and Stratoni's granodioritic samples, normalized for 10 ordinary chondrites (Nakamura, 1974), are shown. It is observed: a) the enrichement of the light Rare Earth Elements in both plutonic bodies, b) the granite of Arnea presents an augmentation of the heavy Rare Earth Elements values and a significant negative Eu anomaly, c) in the contrary, the granodiorite of Stratoni presents just a little increase in the values of the heavy Rare Earth Elements and a small negative irregularity in Eu.

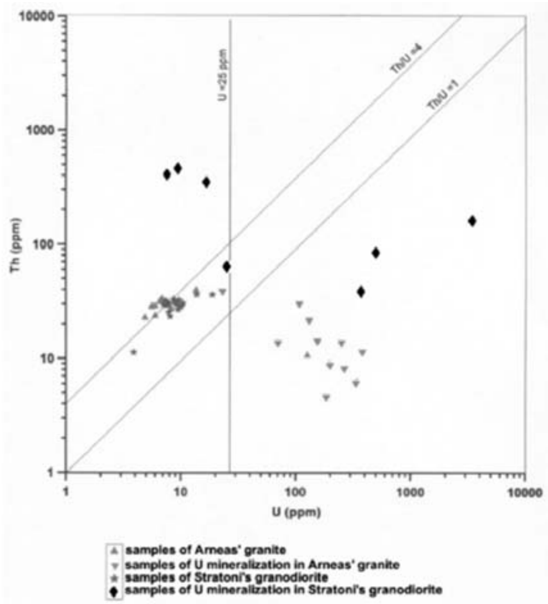

Fig. 4: Th versus U, for mineralized, unaltered and U mineralised samples from Arneas' granite and Stratoni's granodiorite.

The comparison of the chemical data from the two bodies shows that the granite of Arnea, except the Li content, presents all the characteristics of a metalliferous granitoide. On the contrary, the Stratoni granodiorite, except for the U and the Th, seems that does not present this tendency (Howarth et al., 1981).

6. Metallogenetic evolution

It is considered that the main supply sources for metallic elements are three. A) The magmatic fluids, which contribute to the circulating hydrothermal fluids, combinated with events in the silicate melt, like freezing, crystallization, and pressure or permeability changes. B) The reactions between the hydrothermal fluids (magmatic or meteoric), and the solidified crust of the plutonite and C) the interaction between hydrothermal fluids and the minerals of the hosting rock. The temperatures related with the hydrothermal events B and C, usually does not exceed the 500^0C (Eugster, 1985).

This hydrothermal action may be primary or secondary. The primary (magmatic) is related with the last phases of the plutonite crystallization, especially, if this one is saturated in water, while the secondary is developed by the meteoric waters with the creation of an hydrothermal convective system, usually inside an extended system of discontinuities, like the faults, which facilitate the heating and the water circulation. The high concetrations of the radioactive elements, U, Th and K, which heat some parts of the rock, can maintain such hydrothermal systems. In these metal-bearing systems, underground waters are leaching metals and volatic componets from the granite, after his emplacement, especially during periods of higher thermal flows from the mantle, like the Tertiary (Simpson et al., 1979).

The metal bearing granite of Arnea does not present a marked Uranium mineralization, except a small one, observed at the contacts of the granite with some remnants of the hosting rocks inside the granite (of some decade meters), which have a composition of two micas gneisses, or two micas schists with garnet, or phyllites. These contacts sometimes are of tectonic origin and the mineralization is developed at the crossing of NW-SE faults, with faults of E-W direction. The type of this mineralization depends from the kind of the hosting rock and usually it is expressed like veinlets or like impregnations, but always inside the hosting rock and near the contact. The absence of mineralization in the granite is propably due to a lack of water, caused by the high or medium degree of metamorphism of the hosting rocks. On the contrary at the contacts of the granite with the hosting rocks, with the help of the faults and the high concentration of radioactive elements (U, Th, K), seems that a secondary hydrothermal system was developed and maintained, from waters of meteoric origin or waters from the hosting rock. The interaction of the hydrothermal fluids with the solidified part of the granite and the minerals of the hosting rock, propably is the formation source of the uranium mineralization in the area.

The mineralization in the Stratoni area appears inside the granodiorite at the crossing of two fault systems, of NNW-SSE and NW-SE directions respectively. It is expressed by disseminated primary and secondary uranium mineralizations, located in a small surface of Asprochomata in Stratoni area. This mineralization seems resulting from the redistribution of the uranium included inside the granodiorite's secondaries resistant minerals. It is accomplished with the help of magmatic and meteoric hydrothermal fluids. These fluids result from the water sufficiency characterizing the granodiorite, the high concentration of radioactive elements (U, Th, K) and the faults, which cut the area.

Comparing the U/Th ratio in samples from the granite of Arnea and the granodiorite of Stratoni, as well as in uraniferous samples from these two areas, it is observed (fig.4) that the samples from the granite of Arnea and the granodiorite of Stratoni are projected along the line which is defined from the ratio Th/U=4 and till the limit of 25ppm with a positive correlation of the two elements (Wenrich, 1985). This indicates a magmatic differenciation with the uranium hosted to someone of the resistants primary minerals (monazite) and not in the uraninite. The uraniferous samples from Arnea and Stratoni are projected mainly in the field where the ratio Th/U is less than 1, with just a little bigger value for the Stratoni samples. This means that either, U rich fluids but not in thorium enriched the samples, or that the Th was removed. Because the Th is a relatively immobile element, is in generally accepted the first process for the mineralization, in which the mineralization was produced from low temperature hydrothermal fluids, usually of meteoric origin. Three samples of the uranium mineralization from Srtatoni area, are projected in the field, where the ratio Th/U is bigger than 4 (values between 21 and 54), and the U concentration has a value less than 25ppm. This means that high temperature hydrothermal fluids redistribute the Th, in the same time the U was leached by the hydrothemal alteration.

7. The Uranium Mineralization (Autoradiographies– mineralogy – mineral chemistry).

The study of the uranium mineralization was completed with the construction of a sufficient number (20) of polished thin sections from uraniferous samples, the examination of their autoradiographies, targeting to charting the α-radiation, which is mainly radiated from the U and Th minerals, and after their localization on the thin section surface, with their examination in the electronic microscope combinated with electron microprobe analyser, aiming to determine the chemical composition of these minerals.

The method of the autoradiography is based on the registretion of the α-radiation traces from the radioactive elements on a specialized detector. In the present study the used detector was a plastic material, known as CR-39, which was in a stable and constant contact with the thin polished sections surface for one month. After the month, to observe the radiation traces, the pieces of the detector were etching with NaOH 6N in a temperature of 80^0 C for 3 hours. From the whole number of the sam-

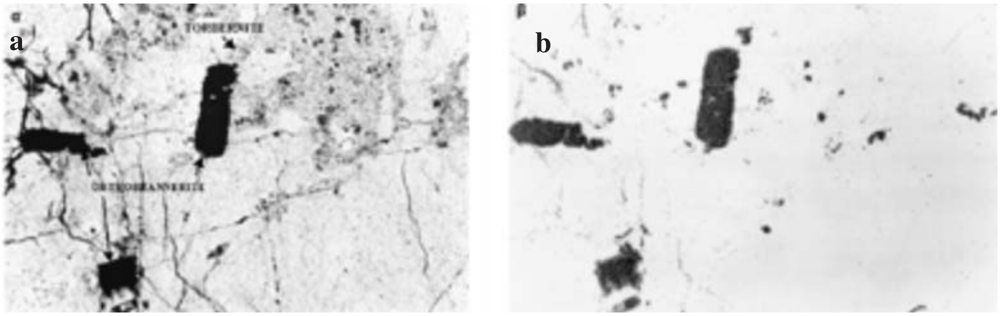

Fig. 5: Specimen AS-3 (thin section AS-3B) a. Microphotography of a thin section from Aspro-chomata, Stratoni area – East Chalikidiki, with Orthobrannerite and Torbernite crystals (Magnification x16. Nicols//). b. Microphotography of the autoradiography, on CR-39, of the thin section's same area (as the previous foto a), where the traces of a-particles from Orthobrannerite and Torbernite crystals are registered (Nicols //).

les, only seven autoradiographies, the more representatives, were selected, (with the corresponding thin polished sections). After the detection and localization of the radioactive minerals on the sections, it followed their study to the polarizing microscope as well as their electron microprobe analysis, mainly in the laboratories of N.C. S. R. "DEMOCRITOS", (SEM system PHILIPS 515 coupled with EDAX 9900). For the analysis were used an accelaration voltage of 25KeV, a ZAF correction program and the total error was less than 10% for the major elements. A smaller number of thin sections were examined in the SEM laboratory of IGME, (S.E.M. system JEOL JSM-5600 coupled with an E.D.S system of OXFORD INTRUMENTS), where the analysis conditions were 30KeV acceleration voltage, 3nA beam current and a spot diameter of 10-30 μm.

For each of the two studied areas the results are the following:

A. Stratoni area

In the area were observed the uranium minerals Orthobrannerite, Torbernite, Uranothorite and Cheralite. An opaque Fe-P uraniferous mineral, red in color, and coupled with the Cryptomelan was also found.

The radioactivity in the places of sampling reaches 2.500 c/s, while the sample from this area gave a content of 3428 ppm U and 162 ppm Th.

The Orthobrannerite is a primary U mineral with chemical formula $U^{4+}U^{6+}Ti_4O_{12}(OH)_2$ crystallizing in the orthorhombic system, which does not contain Rare Earth Elements, while the Brannerite (U, Ca, Y, Ce) $(Ti, Fe)_2O_6$ contains Rare Earth Elements and crystallizes in the monoclinic (Perroud, 1986, 1994, 1998). Standartless semiquantitative spot analysis of an Orthobrannerite crystal in the Electronic Microanalyser gave the following content in oxides (%): Al_2O_3=0.6 SiO_2=0.4 UO_2=54.4 TiO_2=37.4 και FeO=3.7.

The Torbernite is a secondary U mineral with chemical formula $Cu(UO_2)_2(PO_4)_2{\bullet}12H2O$, which crystallizes in rhombic system. Standartless semiquantitative spot analysis in the Electronic Microanalyser gave the following content in oxides (%): Al_2O_3=0.3 SiO_2=1.8 P_2O_5=20.1 UO_2=67.7 FeO =0.7 CuO=7.8 και As_2O_3=1.6.

The Uranothorite is a thorite ($ThSiO_4$) with more than 5% U content. Standartless semiquantitative

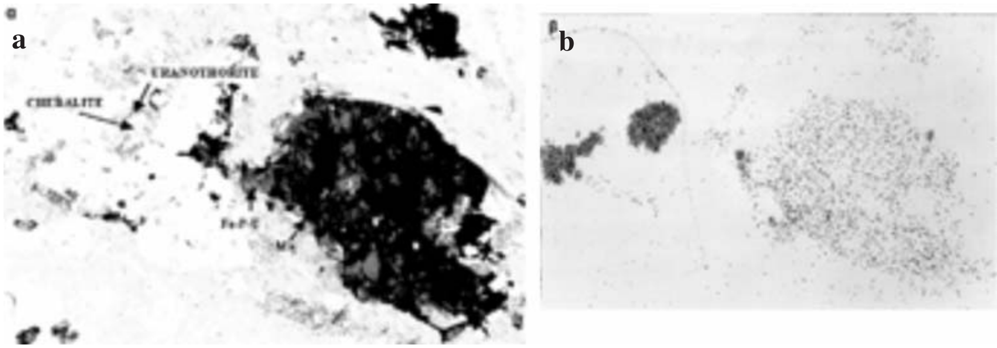

Fig. 6: Specimen AS-3 (thin section AS-3A) a. Microphotography of a thin section from Asprochomata, Stratoni area – East Chalikidiki, with Cheralite and Uranothorite crystals, as well as with uraniferous Fe-P-minerals closely linked with Mn minerals (Magnification x36. Nicols//). b. Microphotography of the autoradiography, on CR-39, of the thin section's same area (as the previous foto a), where the traces of a-particles from the Cheralite and Uranot-horite crystals, as well as from the uraniferous Fe-P-minerals closely linked with Mn minerals are registered (Nicols //).

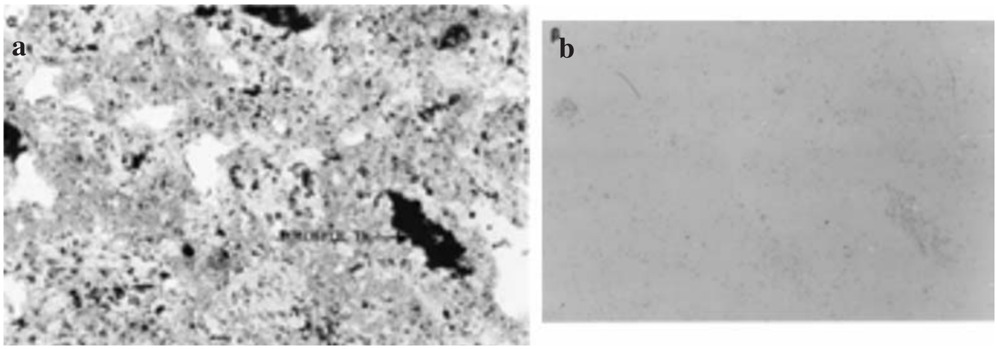

Fig. 7: Specimen AS-6 a. Microphotography of a polished thin section from Asprochomata, Stratoni area – East Chalikidiki, where we can see Jarosite crystals with Th (Magnification x16. Nicols//). b. Microphotography of the autoradiography, on CR-39, of the thin section's same area (as the previous foto a), where the traces of a-particles from the Jarosite crystals containing a little Th concentration are registered (Nicols //).

spot analysis in the Electronic Microanalyser gave the following content in oxides (%): SiO_2=13.8 ThO_2=57.8 και UO_2=28.3. Because its great UO_2 content it may be a Thorogoumite ($Th(SiO_4)_{1-x}(OH)_{4x}$), which contains UO_2 between 2.5-31.5% and ThO_2 from 18.2 to 50.8%.

The Cheralite has a chemical formula (Ce, La, Th, Ca, U)PO_4 SiO_4 with UO_2 content of 3.5-5.5% and ThO_2 between 25.9-27.7%. It is a mineral appartaining in the group of Monazite (they have the same structure), like the Huttonite ($ThSiO_4$) and the Brabantite ($CaTh(PO_4)_2$). Standartless semi-quantitative spot analysis in the Electronic Microanalyser gave the following content in oxides (%): SiO_2=2.6 P_2O_5=29.4 ThO_2=27 UO_2=7.9 CaO=4.9 La_2O_3=11.4 και Ce_2O_3=16.8.

The standartless semiquantitative spot analysis of the red opaque mineral with Fe and P, gave the following content in oxides (%): Al_2O_3=1.2% SiO_2=1.5% P_2O_5=14.2% SO_3=3% UO_2=0.5 CaO=1 MnO=1.5 FeO=75.8 and CuO=0.8. Probably the uranium is adsorbed in this mineral, or dispersed in the crystal lattice in a small quantity.

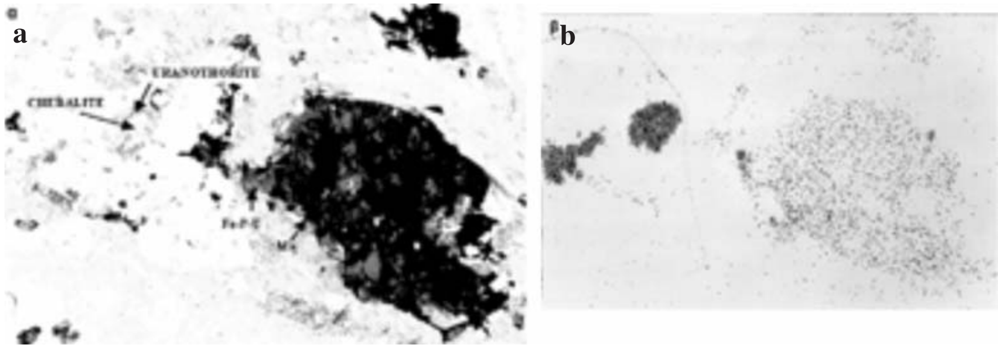

Fig. 8: Specimen AP-1 (thin section AP-1A) a. Microphotography of a thin section from Arnea area – East Chalikidiki, where we can see U-Ti-Fe-Mg oxides inside the cleavage surfaces of a mica crystal (Magnification x36. Nicols//). b. Microphotography of the autoradiography, on CR-39, of the thin section's same area (as the previous foto a), where the traces of a-particles from the U-Ti-Fe-Mg oxides inside the cleavage surfaces of the mica are registered (Nicols //).

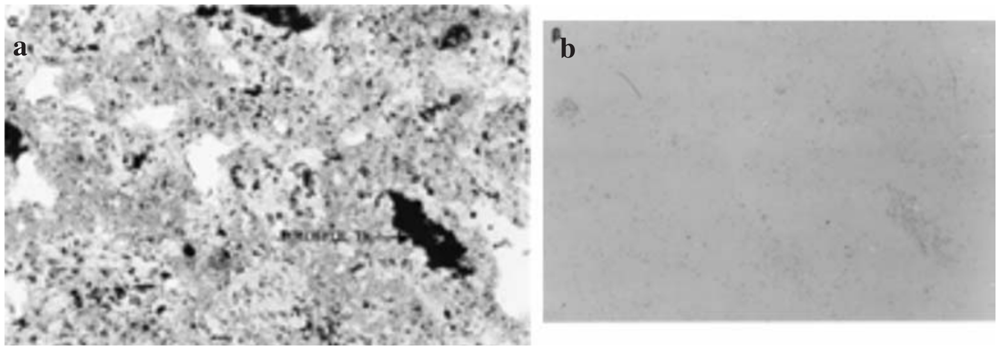

Fig. 9: Specimen AP-4 (thin section AP-4A) a. Microphotography of a polished thin section from Arnea area – East Chalikidiki, where we can see Xenotime crystals (Magnification x40. Nicols//). b. Microphotography of the autoradiography, on CR-39, of the thin section's same area (as the previous foto a), where the traces of a-particles from the Xenotime crystals are registered (Nicols //).

Finally at the sampling place AS-6 (thin polished section AS-6) was measured a radioactivity of 1200 c/s and a content of 9 and 451 ppm of U and Th respectively. The examination of the thin polished section in the E/M demonstrates that the Th, which is contained in the mineral Jarosite, causes the radioactivity. This mineral with chemical formula $KFe_3(SO_4)_2(OH)_6$ is very widespread and it appears in the oxidation zone of the iron sulfide deposits and especially of pyrite. Semiquantitative spot analysis in the Electronic Microanalyser gave the following content in oxides (%): P_2O_5=3.8 SO_3=34.6 ThO_2=0.7 K_2O=8.3 TiO_2=0.5 και FeO=51.6.

B. Arnea area

In the Arnea's area the radioactivity was detected from:

From crystals of Xenotime (YPO_4) in which the standartless semiquantitative analysis in the E/M gave the following contents in oxides (%): Al_2O_3=3.8 SiO_2=9.3 P_2O_5=42.2 UO_2=1.1 CaO=1.2 TiO_2=0.7 Gd_2O_3=1.3 Dy_2O_3=5.2 Er_2O_3=3.3 και Y_2O_3=30.8. The radioactivity on the sampling place was measured at 1000 c/s and the chemical analysis of the sample gave 262 ppm U and 8 ppm Th.

From U-Ti of Ferromanganese oxides in the clivage surfaces of the mica.

From a radioactive veinlet composed of P-Fe-Si-Y-U-Al-Ca-La-Nd oxides with a changing composition from point to point. The standartless semiquantitative spot analysis in a point of the veinlet gave the following content in oxides (%): Al_2O_3=1 SiO_2=32.3 P_2O_5=24.2 UO_2=7.5 CaO=1.6 Nd_2O_3=0.7 Fe_2O_3=11.9 and Y_2O_3=18.8. The radioactivity in the place where the sample was taken (1400c/s) is the bigger observed in the area of Arnea. The chemical analysis gave 343ppm for U and 6ppm for Th.

8. Conclusions

In the area of Stratoni (location Asprochomata) the Uranium mineralization is expressed in the granodioritic body of the area by disseminated primary (orthobrannerite) and secondary (torbernite) U minerals.

In the area of Arnea uranium mineralization is in generally not observed in the granite, except this poor one located along the contacts of the granite with small remnants of the hosting rock.

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