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## GEOLOGICA MACEDONICA

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## TYPES OF HYDROTHERMAL ALTERATION WITHIN THE ILOVITZA DEPOSIT

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**A b s t r a c t:** As a result of the recent detailed explorations, Ilovitza deposit is separated to the polymetallic Cu-Au-Mo porphyry deposit, located within Tertiary intrusive complex, whose mineralization is closely related to intensive hydrothermal alterations of surrounding rocks. This deposit represents a part of several porphyry systems in eastern Macedonia and northern Greece, which are in association with igneous complexes and is one of deposits of the type of the deposit Bukovič–Kadiica in Macedonia and Scouries in Greece. Hydrothermal alterations, as a special mark of the deposit, with our laboratory examinations, were determined as an alteration that characterizes porphyry systems. Between them are distinguished neobiotitization, quartz–sericitization, silicification, argillitization et al one of the most intensive alteration is silicification (around 49 %), which in association with alunization (around 40%), encompasses the apical parts of intrusive complex.

**Key words:** porphyry system; intrusive complex; neobiotitization; quartz–sericitization; silicification; argillitization

### INTRODUCTION

From the historical aspect, Ilovitza deposit, which is located in eastern Macedonia, in the vicinity of Strumica city, have always been interesting for exploring, as indicated by the data in the form of travel notes, as well as numerous papers submitted by Томич, 1936; Шоптрајанова, 1957; Стојанов, 1966; Stojanović, 1972 etc.. Recent investigation which started in 2004 were made by the company *Phelps Dodge*, and today, extended from the company *EuroMax*, on whose basis Ilovitza deposit is separated as deposit whit porphyry type of Cu-Au-Mo mineralization (Aleksandrov and Bombol, 2008). Shows characteristics of the connection with Tertiary magmatism and the same is considered as deposit of the type of deposits from the zone Lece-Chalkidiki (Serafimovski, 1990,

1993). Examinations which include X-ray and microscopic examinations of the samples, proved the presence of hydrothermal alterations which is closely related to the porphyry mineralization (Рогожарева, 2010). Between them could be separated: supergene sulphide alteration, weak propylitic alteration, advanced argillic alteration, quartz-sericite-pyrite (“phyllic”) alteration and potassium metasomatism with the presence of intermediate argillic alteration. In addition, in view of the mineralization especially are interesting deeper parts of the deposit, especially zones and their contact parts where the quartz-sericite-pyrite alteration is developed and potassium metasomatism with the presence of intermediate argillic alteration.

### REGIONAL GEOLOGY, GEOTECTONIC AND METALLOGENIC POSITION

In the Republic of Macedonia even and broader, “Ilovitza” deposit represents one of the more significant porphyry deposits of Cu-Au-Mo.

It is located on the territory of the Republic of Macedonia, more precisely in its southeastern part, at about 17 km at a distance from Strumica city, in the immediate vicinity of the Ilovitza village.

In view of the regional geotectonic position, “Ilovitza” deposit belongs to Serbian-Macedonian Massif (Zagorchev et al. 2008) and the Serbian-Macedonian Metallogenic Zone (Janković, 1977; Serafimovski, 1990), in belt, in whose geological construction participate late Proterozoic to Palaeozoic metasediments and granitoids (Figure 1).

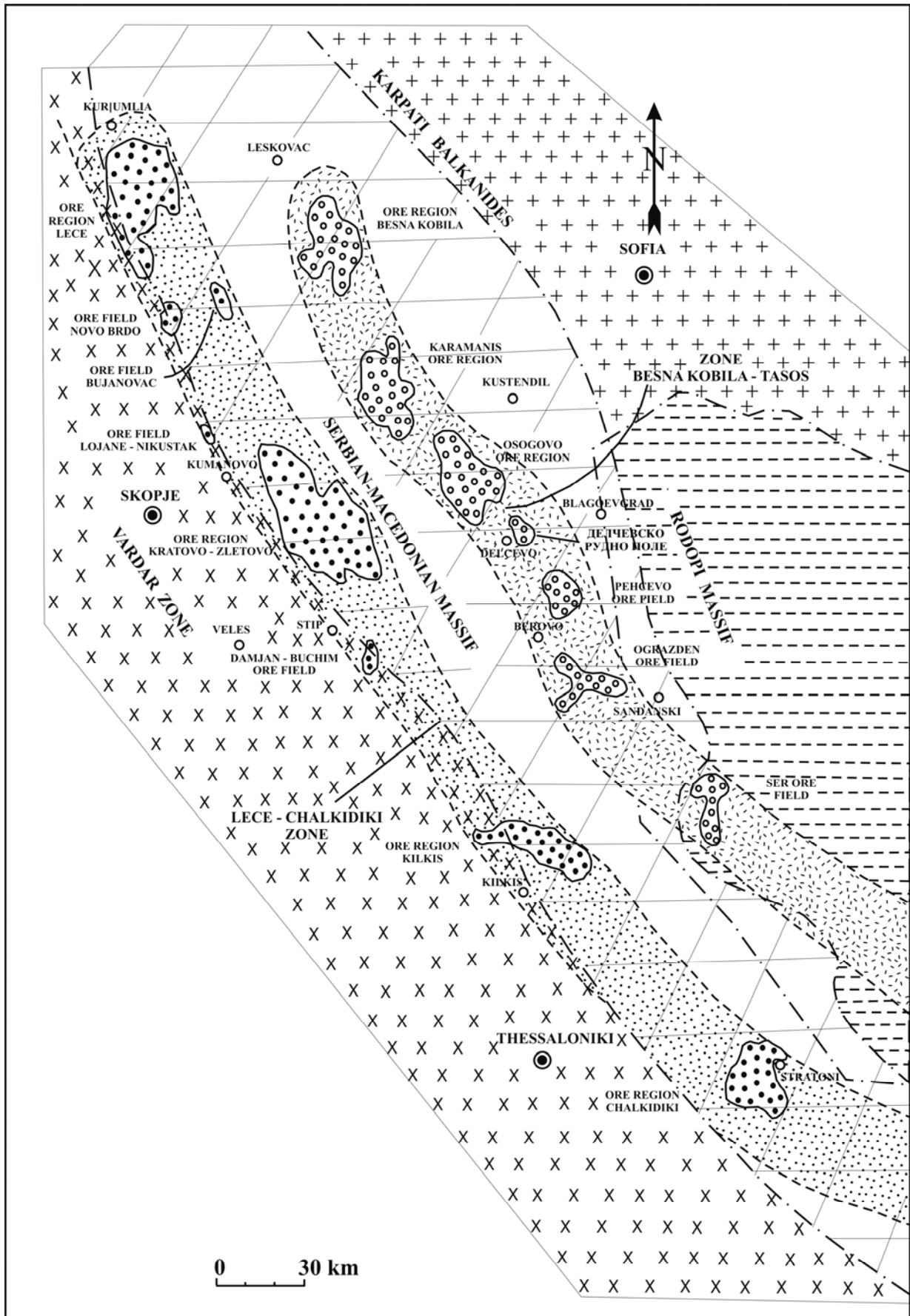


Fig. 1. Regional position of the “Ilovitza” deposit (Serafimovski, 1990)

The processes that took place in the frame of the SMM have caused structure of the volcanic apparatus, domes and regional dislocations, as the Tupal dislocation and dislocation Besna Kobila-Osogovo (Serafimovski, 1990; Aleksandrov, 1992). These regional dislocations are separated as very important in the structural control on the intrusive complexes of granitoides (Ракичевик et al. 1980; Janković et al. 1995; Janković and Serafi-

movski, 1997). Actually, creation and spatial distribution of the magmatism and the ore are in function of the structural factor of a control or disjunctive-depth structures that are present in the Ogražden granite massif and have direction along the borders of the basic geotectonic units: Serbian-Macedonian Massif and the Vardar Zone (Serafimovski, 1990).

## GEOLOGICAL CHARACTERISTICS OF THE BROADER AREA

The Ogražden granite massif is located in the southeast part of the Republic of Macedonia, in to large-scale geotectonic unit of the Serbian-Macedonian Massif (Figure 2). The fundament in which the broken the Palaeozoic Variscan granite massif is represented by Precambrian and Rif-Cambrian rocks. The Precambrian lithological is represented by gneisses (the two mica, the biotite, the muscovite, the porphyroblastic) micashists, amphibolites. The Rif-Cambrian is represented by the amphibole and epidote-quartz-sericite-chlorite shists. From the structural aspect, the massif Ogražden represent a batholite, which during the Variscan orogen phase was intrude in the fundament and is characterized by intense disjunctive tectonic or fault shape with general direction NW-SE.

During the Tertiary, along rupture structures in the consolidated Ogražden granite masses in the gneisses had volcanic acts that contributed to creation of dacite and andesite with which is connected hydrothermal changes. They represent subvolcanic to volcanic disruption in the granite and gneisses (Ilovitza, Dvorište, Štuka, Sušica).

Mineralogical-petrographic characteristics of the Ogražden massif indicate that is it quite heterogeneous and is basically represented by calcalkaline granites. These granites shall occupy the central parts of the mountain Ogražden and is represented by: biotite coarse-grained granites, leucocrate coarse-grained granites, granitoporphyrates, muskovite leucocrate granites, two mica medium grain granites, biotite porphyry granites and granodiorite, leucocrate schist granites.

From mineralogical aspect, the Ogražden massif is represented by large crystals of feldspar, a large amount of biotite and quartz. From petrographic aspect, the same are characterized by alotriomorphic grain to porphyry structure with massive, and sometimes the weaker schists texture.

Hydrothermal changes in the dacite-andesite caused almost completely destroyed primary structure and changes in the mineral composition. These changes are manifested in the form of silicification, sericitization, alunization, kaolinitization and some places opalitzation and chloritization.

The zone of intensive silicification and sericitization space is expressed on the west side of the dacite-andesite disruption.

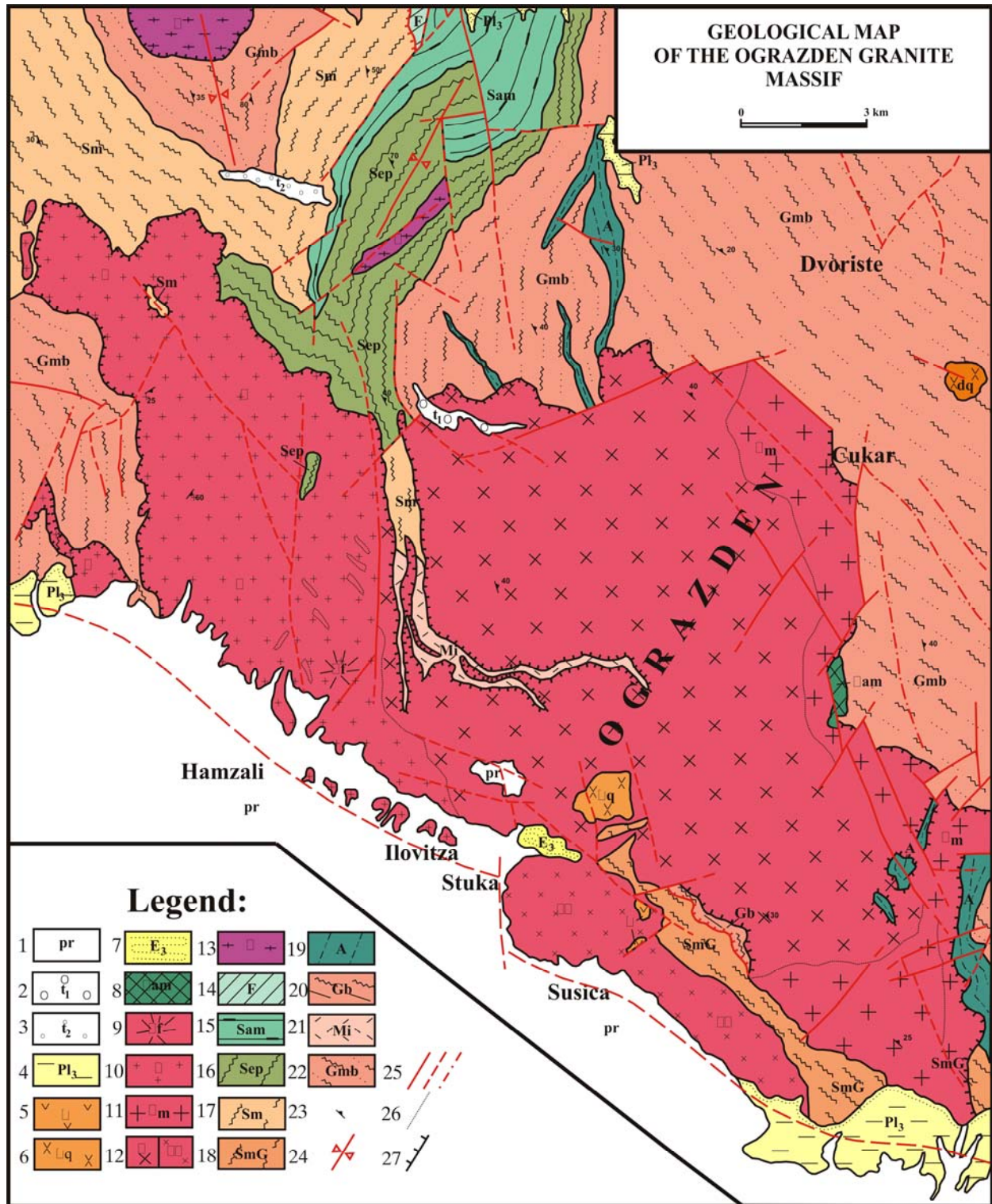
The zone of intensive silicification and alunization space is expressed on the east part of the dacite-andesite disruption, in which the presence of alunite varies from 20-50%.

Noticed that in the parts where alunite contains are moving within the limits of 20-48%, sulphide mineralization is missing, similar as well as in Plavica polymetallic systems (Stojanov, 1980) and Dudica (Ivanov and Ivanova, 1980). However, in the parts of intensive silicification and alunization are registered and certain contents of gold (over 19 g/t), which mark one epithermal area, where the mineral components are products of acidly sulfate solutions (Serafimovski and Aleksandrov, 1995).

## TYPES OF HYDROTHERMAL ALTERATIONS

According typomorphic minerals and on the basis of the results derived from X-ray examination of samples, as well as so far, the degree of ex-

plorations, within the Ilovitza deposit may be separated the following types of hydrothermal alterations (Figure 3).



**Fig. 2.** Structural-geological map of the Ogražden granitoid massif

Quaternary – 1. Proluvium; 2. Lower terrace; 3. Higher terrace. Tertiary – 4. Clays; 5. Andesites; 6. Dacites; 7. Volcanic sediment sandstones, conglomerates and tuffs. Lower Palaeozoic – 8. Amphibole gabbro; 9. Leucocrate coarse-grained granites (metasomatic); 10. Aplitoide granites; 11. Muscovite leucocrate granites; 12a. Biotite porphyry granites; 12b. Biotite porphyry granodiotites; 13. Leucocrate shist granites; 14. Phyllites. Riphean-Cambrian – 15. Amphibole shists; 16. Epidote-quartz-sericite chlorite shists. Precambrian – 17. Micashists; 18. Micashists and leptinolites; 19. Amphibolites; 20. Biotite gneisses; 21. Migmatite (porphyryblastic gneisses); 22. Two mica fibre gneisses; 23. Elements of the decline in the foliation; 24. Axis of syncline; 25. Faults (set, covered and fotogeological); 26. Gradual transition; 27. Lump of the flakes



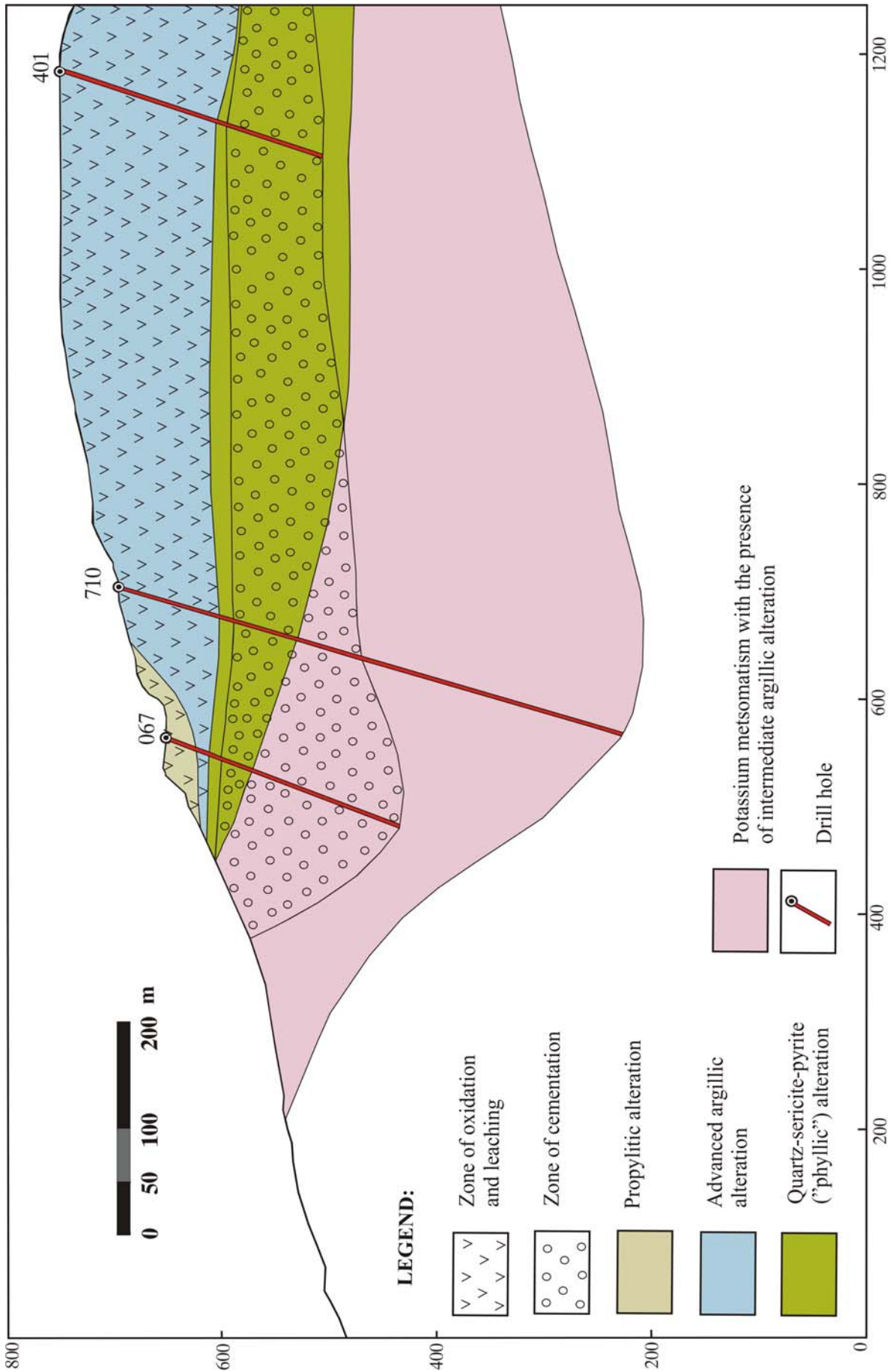


Fig. 3. Development of the types of the hydrochemical alterations in "Ilovitza" deposit

### *Supergene sulphide alteration*

One of the important features of the "Ilovitza" porphyry Cu-Au-Mo deposits is the presence of the deep supergene sulphide zone of alteration, which locally reaches a depth more than 150 m, similar to the appearances in the polymetallic system Bukovik-Kadiica (Tasev, 2010).

Is characterized by oxidation, leaching and intensive argillitization and includes the appearances of pyritization, limonitization and secondary sulphide enrichment.

Oxidized and leached zones on the surface are recognized by the "coverage" of metals in the supergene clay minerals, limonite (goethite, hematite and jarosite) and residual quartz. The secondary (supergene) zones containing chalcocite, covelline and other  $\text{Cu}_2\text{S}$  minerals (digenite et al.), hrizokol, native copper and copper oxides, as well as carbonate and sulfate minerals (Panteleyev, 1995; Tasev, 2010).

Pyritization is a direct indicator that there were conditions for sulphide mineralization. Limonitization is widespread, especially in quartz-alunite-limonite breccias (Figure 4).



Fig. 4. The core of silica-alunite-limonite breccia

Is manifested with occurrence of hematite, goethite and jarosite, which mark the zone of oxidation. Their occurrence is noticed at the surface of the terrain and also by microscopic and X-ray examinations, when it is determined that limonite meet cracks of the tectonic weaken rocks, so all rock mass is filled with them and simultaneously making pigmenting of the silica which is present in the rock (Figure 5).

In the products which occurred after the formation of the primary mineralization, and as a result of supergene sulphide oxidation is among the secondary sulphide enrichment, occur in the area

of the oxidation-reduction zone (Emmons, 1917; Garrels, 1954; Čifliganec, 1993; Tasev, 2010). This area on the secondary sulphide ore in "Ilovitza" deposit, which in some parts is possible over and above 100 m (locally over 150 m) was built by chalcocite and covelline and the same has no particular economic significance.



Fig. 5. Intensely altered core of the drill hole PDIC-04-01

### *Propylitic alteration*

This alteration phenomenon occurs in the end-edge areas of the zone of alteration and is characteristic of the andesite porphyry which are characterized by the presence of chlorite-epidote-clay with limonite veinlets and Mn oxides in outcrops (Donkova, 2006).

Occurs in the vicinity of the other alteration types and is characterized with very weak intensity associated with the zeolites, so in the individual parts almost is absent (Ivanov and Ivanova, 1980).

The zeolitization, which registered a low occurrence is manifested in the surface, more shallower parts of the terrain with appearance of analcime, who is the registered in PDIC-06-07 in sample number 1, with contents of 14 %.

### *Advanced argillic alteration*

Advanced argillic alteration is widespread, immediately over Cu-Au-Mo porphyry system in the peripheral parts of the intrusive, controlled by the presence of deep normal faults.

Includes kaolinite and quartz, as well as alunite, natroalunite, natrolite, ilite, sericite, limonite and pyrite.

Associated with silicification and alunitization, which are manifested with structurally-controlled appearance, in which the silicification and silica- or silica-alunite-sulphide-limonite alteration is surrounded by narrow zones of clay alteration and bleaching, hosted in both fractured zones within basement granite, or within dikes/pods of Tertiary tuff-breccia (Carter, 2007).

The alunization especially is characteristic for the apical parts of the intrusive, where it is developed silica-alunite litho-cap, while the process of alunization is related to the mineralization, and especially with the zones of stock-work mineralization.

The alunization also is registered in the core of drill hole, more precisely in drill hole PDIC-04-01, in which are determined the most contents of alunite presence in the sample number 1 (37%), where with the quartz represent the most dominant minerals in the sample (Table 1).

Table 1

Results of X-ray analysis of the more significant minerals (%) of drill hole PDIC-04-01

| Number of sample | Content (%) |         |                |              |          |          |           |            |                        |           |           |        |                   |
|------------------|-------------|---------|----------------|--------------|----------|----------|-----------|------------|------------------------|-----------|-----------|--------|-------------------|
|                  | Quartz      | Alunite | Hidromuskovite | Fluorapatite | Anortite | Hematite | Anhydrite | Microcline | Muscovite type of mica | Muscovite | Kaolinite | Pyrite | Muscovite + ilite |
| 1                | 54          | 37      | 4              | 3            | -        | -        | -         | -          | -                      | -         | -         | -      | -                 |
| 2                | 59          | -       | 25             | -            | 7        | 5        | 2         | -          | -                      | -         | -         | -      | -                 |
| 3                | 46          | 10      | 27             | -            | 5        | 3        | -         | 7          | -                      | -         | -         | -      | -                 |
| 4                | 48          | 5       | 32             | -            | 4        | 7        | 2         | -          | -                      | -         | -         | -      | -                 |
| 5                | 52          | -       | -              | -            | 6        | 3        | 2         | -          | 35                     | -         | -         | -      | -                 |
| 6                | 53          | -       | -              | -            | 7        | 4        | 2         | -          | -                      | 22        | 10        | -      | -                 |
| 7                | 44          | -       | -              | -            | 6        | -        | 1         | -          | 24                     | -         | 12        | 11     | -                 |
| 8                | 42          | -       | -              | -            | 4        | -        | 1         | -          | -                      | -         | 17        | 13     | 21                |
| 9                | 50          | -       | 26             | -            | 6        | -        | 2         | -          | -                      | -         | 3         | 11     | -                 |

Among the rest, the intensity in his appearance shows and the silicification, which is probably a product of the completed leaching of the cations and the result of the decomposition of feldspars.

In the Ilovitza deposit, it is manifested by the presence of quartz in the form of two generations or more fine-grained, which appears in the base of the rock mass and than suppressed the primary mineralization and coarse-grained, in the form of vein-lets with varying thickness, which arise with fulfill of the cracks and fractures with silica matter.

#### Quartz-sericite-pyrite ("phyllitic") alteration

Quartz-sericite-pyrite ("phyllitic") alteration is located below the zone of the advanced argillic

alteration and is represented by intense quartz-sericite-clay-FeOx alteration, which contains which contains larger bodies of quartz-alunite alteration, and the same represents proximal zone of significant ore changes. As such shall be determined in hosted in both basement granite and Tertiary magmatic rocks (Carter, 2007).

This zone of alteration in the deeper parts is associated of stock-work quartz-pyrite-FeOx alteration and intense clay-sericite alteration largely confined to Tertiary dacitic breccia and dacite-granodiorite intrusive rocks (Carter, 2007).

The silicification is the companion of the phyllyte alteration and variable is influential in the most of part of stock-work and the most of the most of the dykes. The quartz veins show an environment of weak sericite halos.

The appearance of phyllyte alteration is characterized by an increase in the contains of muscovite, which arises by replacing of the orthoclase and plagioclase and the same has gradually transition towards other alterations.

Also, iron free from the alterations of iron-bearing minerals, as well as iron and sulphur additions of the fluid, can formed pyrite, which increases in the deeper levels of this zone.

He is present in the form of veins and impregnations, so the pyrite vein-lets reach a thickness of (8–10 mm) and in some places they are replaced by chalcopyrite. The numeral sulphide vein-lets formed a stock-work which is accompanied by quartz-sericite-pyrite and the traces of chalcopyrite alteration with some content of kaolinite (Figure 6).



Fig. 6. Quartz-sericite-pyrite alteration with intensive quartz and pyrite vein stock-work

In the deeper parts and closer to the core of the system, there are occurrence of intensive stock-



work with lateral quartz veins of older generation, crosscutting with younger quartz-pyrite and the youngest pure pyrite veins and vein-lets. Among the rest this zone is characterized by a higher degree of copper contents.

*Potassium metasomatism with the presence of intermediate argillic alteration*

Allocating of the potassium metasomatism with the presence of intermediate argillic alteration is a result of overlapping of these two alteration types.

Intermediate argillic alteration is characterized by the appearance of kaolin, which is determined and with the X-ray analysis. Arises as a result of the alteration changes of the plagioclase, which become replaced by kaolinite and appears near the ore body. The potassium feldspar is less afflicted with the processes of metasomatism, when it is formed sericite, while similar biotite formed chlorite. This alteration zone is represented by central quartz-magnetite-sulphide FeOx stock-work and dissemination, with matrix alteration of illite-sericite, chlorite (“intermediate argillic alteration”) containing patches of residual secondary biotite and K-feldspar, hosted in dacite-granodiorite porphyry, and minor andesite and latite-andesite porphyry dikes (Carter, 2007).

The shallow level of the alteration may be interpreted as supergene (zone of secondary sulphide enrichment) cover over the deposit, so it is not ex-

cluded and probability and deeper clay alterations of the feldspar to have the same origin. In this zone in individual parts and chalcocite occurs in the form of impregnations and vein-lets arise with the suppression of the chalcopyrite (Figure 7).

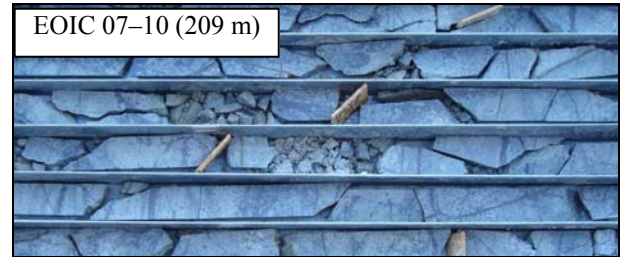


Fig. 7. Core of intensely altered stock-work with chalcocite in impregnations and veinlets

This zone is characterized by gradual transitions towards the potassium alteration, which represents the earliest and relatively high temperature alteration, which results in enrichment with potassium.

This type of alteration has a chance to be formed before the full crystallization of the magma, as indicates the presence of unrelated flexuous vein-lets.

Is represented by the appearance of orthoclase and secondary biotite, accompanied by a chlorite and sericite, but also we can notice the appearance of calcite and siderite in the deeper parts of the drill holes (Figure 8).

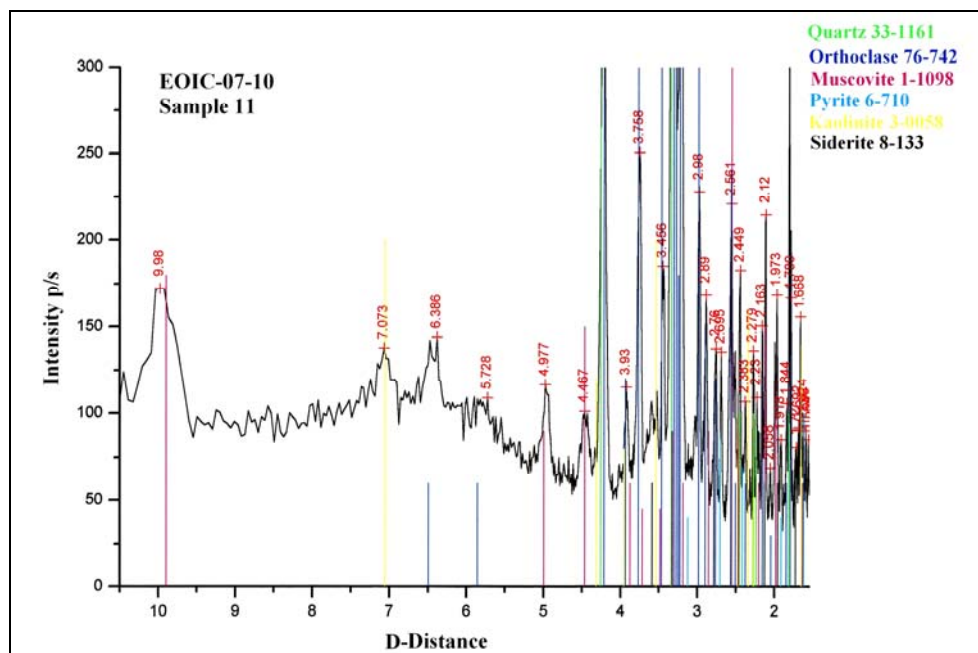


Fig. 8. Roentgenogram with the results of X-ray analysis of the sample number 11 of EOIC-07-10

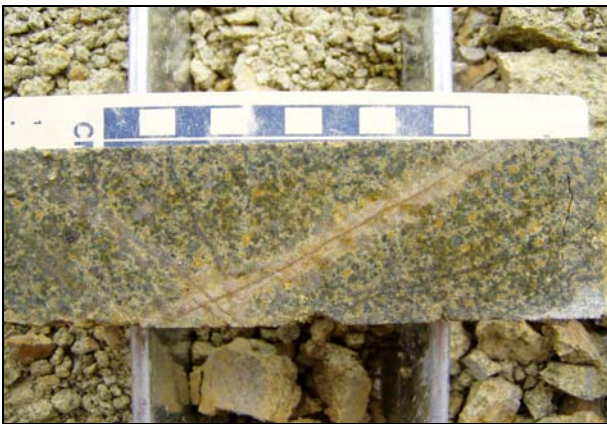
Based on the X-ray analysis of the core of the several drill holes is found that the level of the occurrence of the potassium metasomatism starts from about 165.00 m, what exactly is determined by the appearance of the orthoclase, whose appearance with variable contents is present until the end of examined drill holes.

Its genesis probably is a result of the metasomatism of the plagioclase in the K-feldspar, while secondary biotite with metasomatism of hornblende or chlorite.

Magnetite and hematite are general. The common sulphides are pyrite, molybdenite and chalcopyrite.

In the following are shown individually photographic images of the core of this zone, as well as mineralogical-alteration features of the core of the deeper parts of the drill holes.

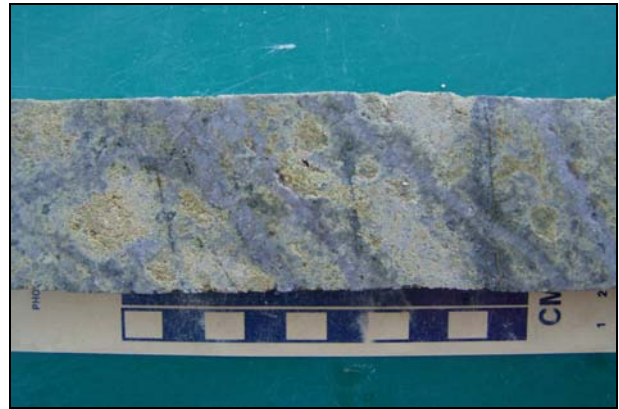
On Figure 9 is given chlorite-sericite-clay-magnetite alteration with the quartz-magnetite vein-lets. In the deep parts, chlorite and magnetite become stable. Originally, the rock is altered to chlorite and magnetite. Replacement of the plagioclase by dark brown montmorillonite to the rock gives yellow-brown appearance.



**Fig. 9.** Chlorite-sericite-clay-magnetite alteration with quartz-magnetite vein-lets

In the deepest levels of the examined drill holes biotite has been preserved. At this level, is present facies of quartz veins (Figure 10), but, should be said that the density of the veins was reduced than in the stock-work zone of the higher

level of the drill holes or the developed intensive stock-work go reaches its maximum in the periphery of the intrusive, while in the deeper parts more prevalent is the disseminated mineralization, which is accompanied by chlorite-sericite-magnetite-biotite alteration, which is covered with a late argillitization.



**Fig. 10.** Quartz veins with presence of argillitization of late stage

Among the rest, clearly can be noted that the deeper parts of the drill holes are characterized by late igneous occurrences as clasts of quartz veins, igneous breccias with quartz basis mass and some aplite structure. Also, should be said that at the top of this deep intrusive system is registered an appearance of typically developed system of alteration to the "worm-like" silicification.

Based on data derived from examinations and explorations, Ilovitza deposit by its characteristics can be set aside as copper porphyry deposit of type of deposit Scurries in Greece, which represents one of the first discovered porphyry deposits in Lecce-Chalcidice metallogenic zone.

Similar hydrothermal alterations, altered zones and mineralization which are present in Ilovitza deposit can meet and among many other porphyry deposits, such as Chukvikamata, Chile (Sinclair, 2009).

However, the characteristic mark of the Ilovitza deposit is its intense and widespread hydrothermal alterations, the deep zone of sulphide oxidation, leaching and argillitization.

## CONCLUSION

The recent detailed explorations and examinations of the "Ilovitza" deposit pointed out on the presence of the polymetallic Cu-Au-Mo porphyry deposit, located within Tertiary intrusive complex,

whose mineralization is closely related to intensive hydrothermal alterations of surrounding rocks.

The hydrothermal alterations are allocated on the basis of the typomorphic and characteristic fol-

low minerals. Between them can be separated the following types of hydrothermal alterations: supergene sulphide alteration, weak propylitic alteration, advanced argillic alteration, quartz-sericite-pyrite (“phyllitic”) alteration and potassium metasomatism with the presence of intermediate argillic alteration. The ore mineralization in the biggest part is related to the zones where is developed the quartz-

sericite-pyrite alteration and potassium metasomatism with the presence of intermediate argillic alteration, as well as in their contact parts. From aspect of the developed zones of hydrothermal alterations in “Ilovitza” deposit, may be noted that with him have can be developed the main zone of alterations that is also present almost in all porphyry deposits.

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Резиме

ТИПОВИ НА ХИДРОТЕРМАЛНИ АЛТЕРАЦИИ ВО НАОГАЛИШТЕТО „ИЛОВИЦА“

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**Клучни зборови:** порфирски систем; интрузивен комплекс; необититизација; кварц-серицитизација; силификација; аргилитизација

Како резултат на неодамнешните истражувања, наоѓалиштето „Иловица“ е издвоено како полиметалично порфирско наоѓалиште на Cu-Au-Mo, во рамките на Терциерниот интрузивен комплекс, чија минерализација пројавува карактеристики на тесна поврзаност со интензивните хидротермални алтерации на околните карпи. Ова наоѓалиште претставува дел од неколкуте порфирски системи во источна Македонија и северна Грција кои се во асоцијација со магматските комплекси и се вбројува во наоѓалиштата од типот на наоѓалиштето БуковиќКадница

во Република Македонија и Скуриес во Грција. Хидротермалните алтерации, како посебен белег на наоѓалиштето, со нашите лабораториски испитувања, беа одредени како алтерации кои ги карактеризираат порфирските системи. Помеѓу нив се издвојуваат необититизација, кварц-серицитизација, силификација, аргилитизација итн. Една од најинтензивните алтерациони промени е силификацијата (околу 49%), која во асоцијација со алунитизацијата (околу 40%), ги зафаќа апикалните делови на интрузивниот комплекс.