Supergene alteration of a refractory epithermal gold mineralization: The Perama Hill deposit, NE Greece

Triantafyllidis S. National Technical University of Athens. School of Mining and Metallurgical Engineering. Section of Geologic Sciences

Skarpelis N. Faculty of Geology and Geoenvironment

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Triantafyllidis S.¹, Skarpelis N.²

¹School of Mining and Metallurgical Engineering, Section of Geologic Sciences, National Technical University of Athens, 9 Iroon Polytechniou str., 157 80, Zografou, Athens, Greece
²Faculty of Geology and Geoenvironment, Panepistimiopoli 157 84, Zografou, Athens, Greece
Tel.: 210-7724468, email: striantafyllidis@metal.ntua.gr

Abstract
Supergene alteration phenomena have affected the upper part of the Perama Hill epithermal mineralization hosted in the felsic sandstone (oxide sector). The very low acid buffering capacity of the porous sandstone combined with the disseminated character of pyrite and sulfosalts, resulted in extensive weathering. Goethite and hematite predominate in the upper part of the mineralized sandstone revealing pervasive oxidation and leaching of heavy metals. A transitional zone to the refractory sulfide mineralization is detected close to the underlying andesitic breccia. Free Au grains are identified in the upper, oxide sector of the deposit, with the highest Au grades being observed at the upper and lower part of the sandstone, the latter located close to the transition zone with the underlying andesitic breccia. Acid rock drainage identified in both surface and ground water samples in the vicinity of the Perama Hill epithermal deposit indicates active oxidation of the sulfide sector of the deposit.

Key words: Intermediate sulfidation, disseminated ore, oxidation, native Au

Περίληψη
Το κοίτασμα χρυσού του λόφου του Περάματος βρίσκεται περίπου 30 χλμ δυτικά-βορειοδυτικά της πόλης της Αλεξανδρούπολης και εντοπίζεται κατά μήκος μιας ΒΒΑ διεύθυνσης ρηξιγενούς ζώνης που καθορίζει το βορειοανατολικό όριο της τάφρου των Πετρώτων και η οποία φέρνει σε επαφή τους Καινοζωικούς ηφαιστειο-ιζηματογενείς σχηματισμούς της Μαρώνειας με Μεσοζωικής ηλικίας μεταμορφωμένα πετρώματα της Περιροδοπικής. Το κοίτασμα φιλοξενεί της Ελληνικής Γεωλογικής Εταιρίας τομ. XLIX, 59 - 75, 2015

Τριανταφυλλίδης Σ., Σκαρπέλης Ν.
Τριανταφυλλίδης Σ., Σκαρπελής Ν.

tησαν κατά την οξείδωσή της και τελικά στο σχηματισμό κόκκων ελεύθερου χρυσού. Συλλέχθηκαν δείγματα πυρήνων από 15 γεωτρήσεις κατά μήκος του άξονα B-N του κοιτάσματος, μέχρι βάθους 262 m από την επιφάνεια. Τα δείγματα μελετήθηκαν με Ηλεκτρονικό Μικροσκόπιο Σάρωσης με Ανιχνευτή Διασποράς Ενέργειας, με Περιθλασιμένη Ακτίνων-Χ και Οπτική Μικροσκοπία, για την αναγνώριση των υπογενετικών και υπεργενετικών ορυκτολογικών φάσεων. Ταυτόχρονα, γειτονικά του κοιτάσματος συλλέχθηκαν δείγματα επιφανειακών υδάτων (ρέμματα) και υπεδαφικών υδάτων (πηγάδια) για μελέτη πιθανής επίδρασης σύγχρονων φαινομένων υπεργενετικής αλλοίωσης και υποβάθμισης της ποιότητας των απορροφών ιστολογικών χαρακτηριστικών. Ταυτόχρονα, γειτονικά του κοιτάσματος συλλέχθηκαν δείγματα επιφανειακών υδάτων (ρέμματα) και υπεδαφικών υδάτων (πηγάδια) για μελέτη πιθανής επίδρασης σύγχρονων φαινομένων υπεργενετικής αλλοίωσης και υποβάθμισης της ποιότητας των απορροφών ιστολογικών χαρακτηριστικών.
1. Introduction
A significant number of epithermal systems occur in several parts of the Tertiary volcanosedimentary basin of Thrace, NE Greece. Exploration for gold is still carried out to this day, recognising the Tertiary Thrace basin as a Au-rich terrain (Skarpelis, et al., 1987; Michael et al., 1988; Michael et al., 1989; Michael et al., 1995; Bridges et al., 1997; Skarpelis, et al., 1999; Voudouris et al., 2003) due to favourable structures and magmatism. Several epithermal Au prospects were investigated during the last 15 years in the area with those of Perama and Saptes being the most important, verifying the Au potential of Thrace (Bordon et al., 1999; McAlister et al., 1999; Shaw and Constantinides, 2001; Lescuyer et al., 2003). The aim of the present paper is to determine the effect of supergene alteration of the epithermal mineralization at Perama hill and to identify the physicochemical conditions that prevailed during supergene alteration which led to free Au formation.

2. Geological setting– ore deposit geology
The Perama Hill gold deposit is located 30 km west-northwest of the city of Alexandroupolis, Thrace, NE Greece (Fig. 1A). The topography of the region consists of low altitude hills, with height ranging between 250 and 300 m above sea level. Vegetation is sparse comprising mainly thorn and scrub bushes and oak trees, and the climate is characterized as Mediterranean with mean annual rainfall of 560 mm (Juras et al., 2010).

The Perama Hill epithermal system is controlled by a NNE trending fault zone that defines the northeastern border of the Petrola graben and brings in contact the Cenozoic volcano-sedimentary formation of the Marionia basin with strongly deformed and drag folded Mesozoic marbles, greenschists and calc-schists of the Circum-Rhodope Belt (Lescuyer et al., 2003) (Fig. 1B). Transtensional opening of the graben during Late Eocene-Oligocene facilitated intrusion of calc-alkaline to high-K calc-alkaline magma bodies (Eleftheriadis, 1990; Christofides et al., 1998) with formation of extrusive and shallow level intrusive volcanic suites. Pecskay et al. (2003) distinguished two main periods of volcanic activity in the region, an Oligocene (33.5 - 25.4 Ma) and a Lower Miocene (22.0 - 19.6 Ma), based on K/Ar ages obtained from whole rock (lavas and tuffs) and biotite separates. During Oligocene, sinistral strike-slip reactivation of basement faults and graben margins is considered synchronous with the hydrothermal activity that led to the formation of the mineralization (Lescuyer et al., 2003).

The deposit is hosted in felsic volcanoclastic conglomerate unit with ranging thickness marks the transition be-
between the two formations.
The sandstone is considered coeval with felsic eruptions at the western part of the graben and the presence of worm tubes and wood fragments indicate palustrine environment (Les-cuyer et al., 2003).

The deposit is mushroom shaped and extends 750 m in a north-south direction and up to 300 m in an east-west direction with thickness varying from 15 m to 20 m at the borders and up to 125 m at the centre (Juras et al., 2010).

![Geological maps of Eastern Macedonia - Thrace, NE Greece](http://epublishing.ekt.gr)
Hypogene mineralization is under tectonic control and occurs in distinct subvertical feeder zones, whereas in the overlying sandstone is mostly disseminated. The deposit is characterized as intermediate sulfidation (Skarpelis et al., 2006) or as high sulfidation overprinted by a later intermediate sulfidation stage (Voudouris et al., 2007). Stable and radiogenic isotope data studies revealed the high to intermediate sulfidation character of the mineralization (Marschik et al., 2011). The deposit has been deeply oxidized and fine grained free gold mineralization is hosted in the sandstone (Skarpelis et al., 2006). Hence, two major sectors may be recognized in the Perahma deposit: the upper, oxide sector with free gold which is the target for mineral exploitation by application of cyanide extraction technique, and the lower, sulfide sector. The calculated reserves (proven and probable) are 9.4 Mt with average grade 3.20 gr/tn Au and 3.75 gr/tn Ag. In the oxidized ore Au grades range between 5 and 10 g/tn whereas in the underlying sulfide sector Au grades are below 1 g/tn (Juras et al., 2010).

3. Sampling – Analytical methods
Drill core samples from 15 bore holes (Fig. 1B) along a N-S axis to depths down to 262 m were collected and used for the mineralogical investigation of both hypogene refractory mineralization and supergene mineral phases. Sampling was focused on those parts of drill cores where high in Au and base metals ore was detected, based on geochemical profiles and the grades provided by the company. A total number of 35 thin and polished sections were prepared, and a part from each sample was pulverized and homogenized for X-Ray diffraction. Mineral identification was carried out by combined optical microscopy, X-ray diffractometry and Scanning Electron Microscopy (SEM). X-ray diffractometry was carried out by using a SIE-MENS D5005 X-ray diffractometer with Cu(ka) radiation at 40 kV/20 mA operating conditions. Scanning electron microscopy was performed using a Jeol JSM 5600 scanning electron microscope combined with energy dispersive X-ray spectrometry (OXFORD ISIS Link electron microprobe) and equipped with a Jeol Analytical back-scattered electron detector at the Laboratory of Economic Geology and Geochemistry, University of Athens. Operating conditions for the SEM were 20 kV accelerating voltage and 0.5 nA beam current. Counting time for each analysis was 50 sec, with 15 sec dead time. Several geochemical profiles of selected heavy metals of the studied boreholes were provided by courtesy of Thracean Gold Mining S.A. and used for the mineralogical and textural investigation (Fig. 2).
Stream and groundwater samples from the vicinity of the deposit were collected in order to investigate whether supergene alteration phenomena are active, affecting surface drainage and underground waters. Sampling was carried out in June and October 2003 applying standard sampling techniques. Water samples were commercially analyzed for cations contents. Concentrations of Fe, Mn, Cu, Pb, Zn, Cd, Ni, Co, As, Hg, and Sb were determined by an inductively coupled...
plasma atomic emission spectrometer (ICP-AES). For Hg, the Hydride/Cold vapor technique was applied in order to further lower the detection limit below 0.01 mg/L. Temperature, pH and Eh were measured on site while sulphate concentrations were measured at the Laboratory of Economic Geology and Geochemistry, University of Athens, by spectrophotometry (Hach DR 2000).

4. RESULTS
4.1. Hypogene mineralogy – Sulfide sector
Pyrite is the predominant sulfide mineral in the Perama Hill deposit with its concentrations increasing along with depth (Tabl. 1, Fig. 2). Pyrite is mostly disseminated and rarely forms patches and aggregates. Marcasite usually occurs in crystal sizes ranging between 5 and 10μm. Marcasite aggregates are observed along with pyrite. Tennantite and enargite participate in moderate proportions (Tables 1 and 2). Minor anglesite, sphalerite (mainly as inclusions in pyrite), Pb-sulfosalts and tellurides are identified as well. In the sulfide sector, Au-bearing phases include Au and Ag-Au tellurides in association with hessite and Ag-Bi tellurides. No primary silicates besides quartz are observed, indicating hydrothermal alteration and replacement by silica and to a lesser degree by kaolinite. Svanbergite-woodhouseite series phases are found in samples from both the oxide and the sulfide sector of the deposit (Tabl. 1). These phases are fine-grained forming aggregates and patches with kaolinite and euhedral unaltered pyrite and may indicate hypogene origin related to development of advance argillic alteration (Dill, 2001). Svanbergite-woodhouseite phases are members of the alunite – jarosite supergroup – APS with a general formula \( \text{AB}_2(\text{XO}_4)\text{2(OH)}_6 \). The anion \( \text{XO}_4 \) is occupied either by S or P (Struntz and Tennyson, 1982; Scott, 1987; Jambor, 1999) with alunite being the most common phase. Late stage acidic fluids with increased P content may change alunite composition through coupled substitutions of [\( \text{K}^+ + \text{SO}_4^{2-} \)] by [(\( \text{Ca}, \text{Sr} \))\text{2} + \text{PO}_4^{3-}] towards svanbergite-woodhouseite solid solutions (Dill, 2001). No supergene alteration is observed and primary sulfides and sulfosalts still remain (Fig. 3A).

### Tabl. 1. Semiquantitative analyses of minerals identified by optical microscopy, X-ray diffraction and Scanning Electron Microscopy from drill core samples of the Perama hill Au deposit.

<table>
<thead>
<tr>
<th>Sulfides, sulfosalts, native metals</th>
<th>Gangue</th>
<th>Supergene phases</th>
<th>Detrital phases in the sandstone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>Quartz</td>
<td>Goethite</td>
<td>Rutile-anatase</td>
</tr>
<tr>
<td>Tennantite</td>
<td>K-feldspar</td>
<td>Hematite</td>
<td>Zircon</td>
</tr>
<tr>
<td>Enargite</td>
<td>Kaolinite</td>
<td>Jarosite</td>
<td>Monazite</td>
</tr>
<tr>
<td>Galena</td>
<td>Iillite</td>
<td>Anglesite</td>
<td>Limonite</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>Svanbergite-woodhouseite</td>
<td></td>
<td>Churhite</td>
</tr>
<tr>
<td>Pb-sulfosalts</td>
<td>Barite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Marcasite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hessite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetradymite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag-Bi tellurides</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au (±Ag) grains</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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4.2. Supergene mineralogy – Oxide sector

The Au distribution and mineralogy of borehole Pd10 is shown in Fig. 2. The location of the borehole along with the large number of drill core samples studied (ranging in depth from 40 m to 262 m from the surface) provide a reliable profile on the distribution of hypogene and supergene phases identified in the ore, and insights on the geochemical environment prevailing during oxidation relative to depth.

Goethite and hematite are the predominant secondary phases identified in the oxidation zone (Tabl. 1, Fig. 2). Major textural forms in the oxide sector include patches of fine-grained goethite and hematite associated with fine-grained kaolinite between quartz clasts. Scarce pseudomorphs of goethite after euhedral pyrite are also identified at lower levels of the oxide sector with minor anglesite (after galena) and other secondary hydrous Fe-sulfates (Tabl. 1). Jarosite is identified in the lower level of the oxide sector and is usually enriched in Al with ranging Na content (Tabl. 3). Jarosite is closely associated with pyrite oxidation, forming anhedral grains around pyrite crystals. In the oxide sector, quartz is the predominant gangue mineral (Tabl. 1) appearing in two major forms.

<table>
<thead>
<tr>
<th>Tabl. 2. Representative chemical analyses of tennantite (out of 125) and enargite (out of 83) from the Perama Hill deposit (results in wt%).</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mn</strong></td>
</tr>
<tr>
<td><strong>Fe</strong></td>
</tr>
<tr>
<td><strong>Cu</strong></td>
</tr>
<tr>
<td><strong>Zn</strong></td>
</tr>
<tr>
<td><strong>As</strong></td>
</tr>
<tr>
<td><strong>Sb</strong></td>
</tr>
<tr>
<td><strong>S</strong></td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Tabl. 3. Representative chemical analyses of jarosite (out of 65) from the Perama Hill deposit (results in wt%).</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>K2O</strong></td>
</tr>
<tr>
<td><strong>9.05</strong></td>
</tr>
<tr>
<td><strong>9.20</strong></td>
</tr>
<tr>
<td><strong>8.12</strong></td>
</tr>
<tr>
<td><strong>A site</strong></td>
</tr>
<tr>
<td><strong>B site</strong></td>
</tr>
<tr>
<td><strong>X site</strong></td>
</tr>
</tbody>
</table>

Structural formulas calculated on the basis of 29 and 8 atoms for tennantite and enargite respectively.

Compositions based on jarosite general formula AB3(XO4)2(OH)6 with XO4 normalized to 2.
Triantafyllidis S., Skarpelis N.

**Fig. 2.** Lithological, mineralogical and geochemical fingerprint of borehole PD10 (after Skarpelis et al., 2006 with modifications). The Au distribution with depth was provided by courtesy of Thracean Gold Mining S.A.

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Hypogene Mineralization</th>
<th>Supergene Mineralization</th>
<th>Hydrothermal Alteration and Gangue</th>
</tr>
</thead>
<tbody>
<tr>
<td>42</td>
<td>Gn +</td>
<td>Qz +</td>
<td>++</td>
</tr>
<tr>
<td>45</td>
<td>Gn +</td>
<td>Qz +</td>
<td>++</td>
</tr>
<tr>
<td>60</td>
<td>Py IIII</td>
<td>Qz IIII</td>
<td>++</td>
</tr>
<tr>
<td>80</td>
<td>Py IIII</td>
<td>Qz IIII</td>
<td>++</td>
</tr>
<tr>
<td>84</td>
<td>Tnt IIII</td>
<td>Qz IIII</td>
<td>++</td>
</tr>
<tr>
<td>85</td>
<td>Py IIII</td>
<td>Qz IIII</td>
<td>++</td>
</tr>
<tr>
<td>88</td>
<td>Tnt IIII</td>
<td>Qz IIII</td>
<td>++</td>
</tr>
<tr>
<td>90</td>
<td>Eng IIII</td>
<td>Qz IIII</td>
<td>++</td>
</tr>
<tr>
<td>100</td>
<td>Py ++</td>
<td>Qz IIII</td>
<td>++</td>
</tr>
<tr>
<td>108</td>
<td>Py IIII</td>
<td>Qz IIII</td>
<td>++</td>
</tr>
<tr>
<td>128</td>
<td>Py IIII</td>
<td>Qz IIII</td>
<td>++</td>
</tr>
<tr>
<td>170</td>
<td>Py IIII</td>
<td>Qz IIII</td>
<td>++</td>
</tr>
<tr>
<td>261</td>
<td>Tnt IIII</td>
<td>Qz IIII</td>
<td>++</td>
</tr>
</tbody>
</table>


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The mineralogy of samples studied by SEM, XRD and optical microscopy studies revealed that the physicochemical environment, related to the lower sulfide sector, changes rapidly at the transition zone between the andesitic breccia and the overlying sandstone. Secondary, supergene phases are present indicating that supergene alteration phenomena have affected the disseminated ore hosted in the felsic sandstone. Mineralogical studies of drill core samples reveal that the lower limit of the oxidation zone roughly follows the boundary between the andesitic breccia and the sandstone and reaches approximately 100 m at depth at the center (90 m for borehole Pd10, Fig. 2), whereas is limited at the sides of the deposit ranging from 20 to 25 m from the surface (Fig. 1C) (Skarpelis et al., 2006; Triantafyllidis, 2006).

Pervasive oxidation is identified in near surface samples with a maximum depth of 45 to 50 m at the center (Fig. 2). Liesegang bands, scarce remnants of pyrite and tennantite, significant load in secondary goethite and hematite as impregnations with fine-grained kaolinite (Fig. 3B) and disseminated native Au

Table 4. Physicochemical conditions and geochemical analyses of stream and underground water samples (sulfates and cation concentrations in mg/L, Eh in mV, conductivity – CND in µS/cm).

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Eh</th>
<th>CND</th>
<th>SO₄</th>
<th>As</th>
<th>Cd</th>
<th>Co</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>3.2</td>
<td>227</td>
<td>3570</td>
<td>1700</td>
<td>bdl</td>
<td>0.283</td>
<td>0.012</td>
<td>8.8</td>
<td>10.4</td>
<td>0.16</td>
<td>bdl</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>P2</td>
<td>4.1</td>
<td>171</td>
<td>5400</td>
<td>0.02</td>
<td>0.003</td>
<td>0.618</td>
<td>0.004</td>
<td>39.4</td>
<td>10.1</td>
<td>0.32</td>
<td>0.025</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>P3</td>
<td>4.1</td>
<td>170</td>
<td>3180</td>
<td>0.02</td>
<td>bdl</td>
<td>0.479</td>
<td>bdl</td>
<td>23.1</td>
<td>7.8</td>
<td>0.26</td>
<td>bdl</td>
<td>0.1</td>
<td></td>
</tr>
</tbody>
</table>

Detection limits:

<table>
<thead>
<tr>
<th></th>
<th>0.002</th>
<th>0.002</th>
<th>0.002</th>
<th>0.002</th>
<th>0.002</th>
<th>0.005</th>
<th>0.005</th>
<th>0.005</th>
<th>0.002</th>
</tr>
</thead>
</table>

Reproducibility (%):

<table>
<thead>
<tr>
<th>±0.01</th>
<th>±5.25</th>
<th>±0.02</th>
<th>±0.002</th>
<th>±0.006</th>
<th>±0.007</th>
<th>±2.21</th>
<th>±0.01</th>
<th>±0.07</th>
<th>±0.007</th>
<th>±0.04</th>
</tr>
</thead>
</table>

P1: N40°52’37.1”  E25°37’44.8”
P2: N40°54’34.9”  E25°38’02.8”
P3: N40°54’10.0”  E25°37’31.0”

Silver, Hg and Sb below detection limit for all samples analyzed

Sample coordinates:

The mineralogy of samples studied by SEM, XRD and optical microscopy studies revealed that the physicochemical environment, related to the lower sulfide sector, changes rapidly at the transition zone between the andesitic breccia and the overlying sandstone. Secondary, supergene phases are present indicating that supergene alteration phenomena have affected the disseminated ore hosted in the felsic sandstone. Mineralogical studies of drill core samples reveal that the lower limit of the oxidation zone roughly follows the boundary between the andesitic breccia and the sandstone and reaches approximately 100 m at depth at the center (90 m for borehole Pd10, Fig. 2), whereas is limited at the sides of the deposit ranging from 20 to 25 m from the surface (Fig. 1C) (Skarpelis et al., 2006; Triantafyllidis, 2006).

Pervasive oxidation is identified in near surface samples with a maximum depth of 45 to 50 m at the center (Fig. 2). Liesegang bands, scarce remnants of pyrite and tennantite, significant load in secondary goethite and hematite as impregnations with fine-grained kaolinite (Fig. 3B) and disseminated native Au
(Skarpelis et al., 2006) characterize the upper, extensively leached and oxidized part of the deposit. Highly insoluble anglesite replacing galena is the only supergene phase observed in the upper part of the oxide sector. At the lower levels of the Perama sandstone and up to the transition zone with the underlying andesitic breccia, supergene alteration phenomena are less extensive (Fig. 2). Goethite and hematite are present in fractures and fissures of the silicified sandstone, but also as aggregates and patches with kaolinite. Pyrite is locally replaced by jarosite (Fig. 3E).

**Fig. 3.** A. Tennantite in association with pyrite in the sulfide sector. B. Impregnations of goethite and hematite in kaolinite patches between angular-subangular quartz clasts in the upper, pervasively altered part of the oxide sector. C. Free Au grains from the upper part of the oxide sector. D. Free Au grain from the lower part of the oxide sector. E. Pyrite alteration to jarosite at the lower level of the oxide sector. F. Free Au grains from the lower part of the oxide sector near the transition zone.

**Εικ. 3.** Α. Τεναντίτης σε επαφή με σιδηροπυρίτη στο πυριτιωμένο ανδεσιτικό breccia. Β. Εμποτισμοί γκαιτίτη και αιματίτη σε μάζες καολινίτη μεταξύ γωνιώδων-υπογωνιώδων κλαστών χαλάζα από το ανώτερο, έντονα εξαλλοιωμένο τμήμα του ψαμμίτη. Κόκκοι Au από το ανώτερο τμήμα του ψαμμίτη του Περάματος. Δ. Κόκκοι Au από το κατώτερο τμήμα του ψαμμίτη. Ε. Οξείδωση σιδηροπυρίτη προς γιαροσίτη στο κατώτερο τμήμα του ψαμμίτη. Φ. Κόκκοι Au από το κατώτερο τμήμα του ψαμμίτη του Περάματος κοντά στη ζώνη μετάβασης.
Supergene alteration phenomena are active as it is proved by the quality of surface and ground water samples collected in the vicinity of the Perama Hill deposit. All samples fall into the quality range of waters draining several epithermal deposits globally (Koyanagi and Panteleyev, 1993; Plumlee et al., 1995; Skarpelis and Triantafyllidis, 2004). In particular, the drainage waters are characterized by increased Fe, Mn and Ni content and very low concentrations of Cu, Pb and As, whereas the Fe content decreases along with distance distance to the ore deposit (Tabl. 4). The surface and ground water samples collected in the vicinity of the Perama Hill deposit are characterized as acidic to extreme acidic with high metal load when plotted on a Ficklin diagram with pH values less than 5.5 and total heavy metal load higher than 1mg/L (Triantafyllidis, 2006).

4.3. Native Gold
Optical microscopy and SEM studies proved that native Au grains, with ranging Ag content, are present in the oxide sector of the Perama Hill epithermal deposit. Free Au predominates in the upper (depth up to 10m from the surface) and the lowermost part of the Perama sandstone, near the transition zone between the sandstone and the sulfidic ore. That observation is in line with Juras et al. (2010) who state that the highest gold grades are identified in drill core samples from the upper and the lower part of the oxide sector. In the oxide sector, native Au is either associated with Kaolinite and goethite, or it appears between quartz clasts with size ranging between 1 to 10μm (Figs 3C, 3D, 3F). On the other hand, mineralogical investigation of samples from the sulfide sector revealed no free Au grains.

5. Discussion
The distribution of secondary phases in the oxide sector provides insights on the physicochemical conditions and the maturity of the physicochemical environment of both the upper and the lower part of the deposit. Secondary Fe(III) phases goethite and hematite prevail in the upper part, whereas jarosite and other Fe-sulfates are present at lower levels (Fig. 2). According to Walton-Day (1999), Newbrough and Gammons (2002), Courtn-Nomade et al. (2003), and Fukushi et al. (2003) typical secondary phases in oxidation zones resulting from alteration of Fe-sulfides and sulfosalts include ferrhydrite, schwertmannite, jarosite, goethite and hematite. The stability of those minerals depends on the prevailing physicochemical conditions with increasing pH and decreasing sulfate load the series of replacement is as follows:

\[ \text{Jarosite} \rightarrow \text{schwertmannite} \rightarrow \text{ferrhydrite} \rightarrow \text{goethite} \rightarrow \text{hematite} \]

Goethite and hematite are the most stable secondary Fe(III) phases in mildly acidic to alkaline and oxidative conditions (Nordstrom and Alpers, 1999). It is therefore reasonable to assume that as supergene alteration phenomena progressed, the geochemical environment of the upper part of the oxide sector gradually changed from highly oxidative with increased sulfate load, to mildly acidic and oxidative with very low sulfate content. This pervasive oxidation of the ore is enhanced in the central part of the deposit reaching depths to 45m (Fig. 2). The presence of goethite and hematite combined with the absence of secondary sulfates (e.g. jarosite), and the depletion of most heavy metals, based on the geochemical profiles of
the bore-holes studied, indicate a mature physicochemical environment and progressively increasing pH and decreasing sulfate load. Liesegang bands also support the hypothesis of mature physicochemical conditions and limited advent flow, since the characteristic rings result from diffusion of oxygen with Fe-rich fluids in poorly lithified sediments (Balsamo et al., 2013; Stegena, 1983). The hypothesis on mature environment is also supported by the enrichment of goethite in As in near-surface samples. In slightly acidic to neutral conditions the concentration of soluble As is controlled by the presence of Fe oxides/hydroxides. Secondary Fe(III) phases show positive surface charge enabling adsorption of negatively charged anions and oxyanions of As (Smith, 1999; Sracek et al., 2004) with maximum adsorption in pH between 3 and 5 (Garcia-Sanchez and Alvarez-Ayuso, 2003).

During the early stages of supergene alteration, the mineralogy of the host sandstone combined with the disseminated mode of occurrence of hypogene minerals and the high potential of pyrite and tennantite to produce highly oxidative agents (Plumlee, 1999), enhanced oxidation phenomena resulting in liberation of microparticulate Au. In oxidative near-surface environments of sulfide deposits two major mechanisms of Au solubility exist, metastable thiosulfate (Webster, 1986; Renders and Seward, 1989) and chloride complexes (Mann, 1984; Webster and Mann, 1984; Stoffregen, 1986), where the Ag content of free Au may provide insights on the prevailing geochemical conditions. In the presence of chlorides, Ag is more readily dissolved relative to Au (Craw et al., 2015) resulting in Au grains with very low Ag content. Scanning Electron Microscopy study revealed that free Au grains in the oxide sector of the Perama deposit show a ranging Ag content (between 1 and 3 wt%) indicating co-deposition of Au with Ag. It means that thiosulphate-mediated dissolution of Au was most likely the major Au transport mechanism in early stages of supergene alteration. During the evolution of the upper part of the oxide sector of the Perama Hill deposit, the physicochemical environment changed from acidic and oxidative, to mature (near-neutral and oxidative). In such conditions, Au is highly insoluble and is mainly transported as elemental, colloidal Au (Krauskopf, 1951), favoring small scale migration, aggregation and re-deposition as free Au grains (Fig. 3C, 3F).

At the lower levels of the oxide sector, the oxidation phenomena are still active but not pervasive. This view is supported by the varying degree of alteration of hypogene sulfides and sulfosalts. In several occasions pseudomorphs of goethite after pyrite and jarosite grains around pyrite crystals are observed (Fig. 3E). The presence of secondary Fe-sulfates indicates relatively immature environment, oxidative conditions and increased sulfate load (Walton-Day, 1999; Courtin-Nomade et al., 2003), an hypothesis supported by the acidic nature and the high metal load of surface and groundwaters draining the Perama sandstone (Tabl. 4). Meteoric waters penetrate the porous sandstone and still attack the disseminated ore comprising pyrite and tennantite resulting in very low quality drainage. It seems that the geochemical environment of the lower part resembles the conditions of the near-surface sector of the deposit during the early stages of supergene alteration. Oxidative, rich in sulfates fluids resulting from on-going oxidation of
sulfides and sulfosalts favor solubility of Au as thiosulfate complexes. As physicochemical conditions change near the transition zone between the oxide and the sulfide sector of the deposit, aggregation and reprerecipitation of native Au grains among quartz clasts occurs (Fig. 3D), resulting in enrichment of the lower part of the oxide sector in gold (Fig. 2). The mode of occurrence of Au in the oxide sector of the Perama Hill deposit is a combination of detrital, later hydrothermal and subsequent supergene alteration mineralogy. The Perama sandstone is characterized by uniform mineral assemblage with abundant quartz, kaolinite, minor illite and traces of K-feldspar. As stated by Lescuyer et al. (2003), the Perama sandstone contains angular to subangular fragments of the basement metamorphic rocks (quartz grains and polycrystalline quartz clasts and mica), as well as glass shards and pyroclastic fragments related to felsic eruptions of the Petrola graben. The immature, felsic sandstone is characterized by increased porosity (coarse, angular to subangular clasts, Fig. 3B). That porosity played a very important role when the sandstone was later affected by hydrothermal activity related to the original high sulfidation mineralogy and the final development of the intermediate sulfidation system. Acidic hydrothermal fluids followed feeders and conduits, and also diffused in the porous media, resulting in extensive hypogene alteration of detrital feldspars and micas to fine-grained kaolinite that filled voids and cracks in the Perama sandstone, providing the final assemblage with very low acid buffering capacity. Uplift and subsequent supergene alteration resulted in oxidation of hypogene disseminated sulfides and sulfosalts, liberation of microparticulate Au, migration, aggregation and deposition of free Au grains.

6. Conclusions
Extensive supergene alteration phenomena have affected the upper part of the Perama Hill epithermal mineralization hosted in the felsic sandstone, whereas oxidation is very limited at the lower sulfide sector. It seems that rock heterogeneity between the underlying andesitic breccia and the overlying porous sandstone played a critical role in development of the texture of the mineralization and the following geologic evolution. The disseminated nature of the ore, with pyrite being the predominant sulfide, combined with the texture and limited acid-buffering capacity of the host sandstone favored penetration of slightly acidic and oxidative meteoric waters and subsequent oxidation phenomena. Goethite and hematite predominate at the uppermost part of the deposit, whereas secondary phases of other heavy metals occur as minor constituents (e.g. anglesite), or are lacking (e.g. Cu and Zn) revealing pervasive supergene oxidation and leaching. At lower levels secondary Fe sulfates are identified, indicating locally highly acidic and oxidative conditions and immature geochemical environment. Free Au grains are observed in the upper and lowermost part of the oxide sector of the deposit, observation that is in line with statements by Juras et al. (2010). Oxidation phenomena still affect the disseminated ore and enrich the ore in free Au near the transition zone between the underlying andesitic breccia and the overlying sandstone. Supergene alteration phenomena are active till this day as proved by the acidic and oxidative and rich in heavy metals, surface and ground drainage at the Perama sandstone.
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