Sci. Annals, Fac. Phys. & Mathem., Univ. Thessaloniki, **15,** 89, (1975).

REMARKS ON THE PORPHYRY COPPER DEPOSIT OF THE SKOURIES AREA OF CHALKIDIKI (GREECE)

by

A. PAPADAKIS

(Laboratory of Mineralogy and Petrography
University of Thessaloniki)

(Received 16.5.75)

Abstracts : *In the Skouries area of Chalkidiki occurs the only so far identified exploitable porphyry copper deposit in Greece. The host rock morphologically belongs to the vertically submerged oval to pipelike cylinder type with small dimensions (axis* 140 × 120*m) extending to unknown depth. The metallogenesis reaches the depth of* 600*m at least and consists mainly of chalcopyrite and pyrite. The characterization of the rock by ZAHOS*(1963)*and GUNLACH et al (*1971*) respectively as trachyte and quartz dioritic porphyry is not correct. The host rock, as it appears saturated with quartz and other components of the hypogene alteration, gives a composition of granitic porphyry. This is confirmed also by the treatment of the chemical analysis data. The original, unaffected rock was very probably a syenitic porphyry. In the potassic alteration zone of the rock, the following interesting facts, not mentioned in the literature of other porphyry ore deposits, are observed: The plagioclase phenocrysts are often selectively biotitized according to two modes.* 1) *The alteration biotite follows in the deposits the cleavage direction (*001*) and (*010*) of the host mineral.* 2) *The biotite replaces a whole plagioclase zone, either the core or any other zone, the boundary included. The first mode may be explained with the easy intrusion of the solution in the cleavage. The selective biotitization of certain zones of the crystal, different in every case, and consequently of different chemical composition, is very difficult to explain. As a possible explanation is suggested the existence of structural defects in the replaced zones.*

THE PORPHYRY COPPER DEPOSIT OF SKOURIES, CHALKIDIKI.

In the eastern Chalkidiki, in the metamorphic Serbomacedonian mass and in the Vertiskos Series *Kockel and Walther* (1938) occurs near the break of Megali Panagia a metallogenesis of copper in the form of stockwerk veinlets and igneous rock saturations. This ore deposit was known in ancient times and was greatly exploited, as the huge mass of useless material and slags indicates. In the literature it is first mentioned by *Zahos* (1973), who recognized its economic importance. According to him the host rock is a hydrothermally altered trachyte in the form of a dome enlarged towards the base. This trachytic dome is strongly broken in all directions. The thick net of breaks and fissures is filled with copper minerals or quartz or both. As primary metallic minerals he mentions chalcopyrite, pyrite and hornite. He reports 7.500.000 tons of measured ore deposit of 1-1,5% copper composition and 7.500.000 tons of possible stocks. According to *Gunlach* et al (1971), who first identified the deposit as a porphyry copper ore the host rock is a biotite-quartz-dioritic porphyry. It intrudes the crystalline rock in the form of a vertical cylinder. They estimate the reserves as 7.500.000 tons of only 0.7% copper. The thicknesses of the supergene alteration zones are: The oxidation zone 15-30m with malachite, azourite, limonite and jarossite and the enrichment zone 2-3m (according to *Zahos* up to 10m) containing mainly chalcosite.

According to our observations and information provided by the geologist Moundrakis, who worked at the drillings, the deposit is a porphyry copper of the verticaly submerged oval cylinder type. The cylinder is oval in shape, with an axis 140×120m, extending to an unknown depth and side branches in different depths. The drillings, which were made down to a depth of 600m, gave an average composition of 0.7%Cu, so the positive reserves amount to 145.000 tons of metallic copper. Obviously, because of the deposit form, a part only of this quantity can be extracted by means of excavation. A large part of the enrichment zone was mined out in the past. The metallogenesis in the primary zone occurs as stockwerk veinlets of quartz, pyrite and chalcopyrite of the same rock.

THE HOST ROCK.

The obvious difference of opinion between *Zahos* (1963) and *Gunlach* et al (1971) regarding the nature of the host rock, necessitated a thorough investigation of the subject. The precise determination of a hypogene altered porphyry rock presents difficulties, because of the usual allochemichal alteration due to transfer of substances in hydrothermal solutions. A secure determination can only be made on samples of unaffected rock. Such samples were not found in the deposit of Skouries. So we were obliged to examine the altered rock and especially that of the potassic alteration zone. Macroscopically the rock shows a smoky grey colour with feldspar phenocrysts up to 4 cm. Thin veinlets traverse the rock and consist either of K-feldspar or quartz with copper minerals and biotite. Under the microscope it shows a typical porphyry structure Fig. 1, with two generations of crystallization. The first consists of hornblende phenocrysts usually altered to biotite or chlorite and phenocrysts of biotite K-feldspar, plagioclase or rarely augite. The phenocrysts size of the first generation ranges between 1 and 2,5mm but sometimes over 1cm. The second generation of crystallization is also crystalline but consists of minerals with much smaller dimensions, 0,05-0,1mm at most. In it were identified biotite, K-feldspar and quartz. As secondary minerals occur in the rock apatite (sometimes in large crystals), sphene, magnetite, and zircon. The intrusive veinlets consist either of K-feldspar only, or of quartz, in the crystal boundaries of which biotite is attached. The quartz veinlets and the rock are saturated with chalcopyrite and pyrite. The K-feldspar phenocrysts are always orthoclase with a few exsolutions of microperthitic albite. It shows frequently zonal structure, the optic axial angle was measured on a section vertical to the acute bisectrix in conoscopic observation on the universal stage and was found to be (-) $2v = 57^{0} — 59^{0}$. Consequently it is a high - orthoclase according to *Marfunin* (1961). It usually appears in Carlsbad twins, or single crystals. In some cases it includes plagioclases. Common alteration form is kaolinization. Apart from the phenocrysts, the orthoclase appears in a large amount also in the microcrystalline mass,

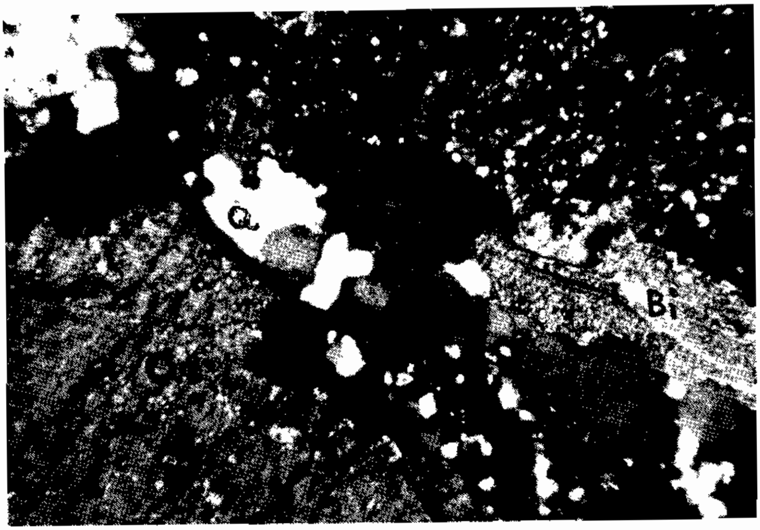

Fig. 1. Granite porphyry of Skouries, Chalkidiki.
Or = orthoclase Q = quartz B = biotite Pl = plagioclase.

The plagioclases, occuring only in phenocrysts, are always euhedral and tabular on (010). Inclusions of other minerals are rare. They show zonal structure, but only a slight difference in An - composition between the zones is observed. Their optical elements, measured on the universal stage, are: optic axial angle (-) $2v = 88^0$ $r > v$ average. An content 18% (sodic plagioclase). Using the V. d. Kaaden charts *Troeger*, (1971) we found that their predominating twin laws are Albite - Carlsbad, Albite, Carlsbad and Pericline. The plagioclases are selectively replaced and with a certain regularity by secondary biotite. This interesting subject is dealt with in the next chapter.

The hornblende is the common green hornblende with strong pleochroism. Its optical constants are $c: n\gamma = 13^0$ and (—) $2v = 85^0$. Usually it alters to biotite or chlorite. Augite is common augite with green colour and slight pleochroism $c: n\gamma = 45^0$.

Biotite occurs in two modes: as primary with euhedral crystals and often altered to chlorite and as secondary, replacing hornblende, intruding in plagioclases or spreading in the rock groundmass. This secondary biotite shows an increased optic axial angle approximately (—) $2v = 10^0$.

Quartz never occurs as phenocrysts. It is limited to very small grains in the microcrystalline mass or to larger crystals in the secondary veinlets with biotite, chalcopyrite and pyrite. Taking into account the mineral composition and the structure of the rock, we conclude that in its altered form (potassic alteration in the examined samples), it must be characterized as granite porphyry. To the same conclusion leads the processing of the chemical analysis results of the rock according to the Niggli method, as is shown in the following tables.

TABLE 1

Chemical analysis of a host rock sample (Skouries)

S_iO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO
70,89	12,49	4,39	1,70	0,01	0,79	0,91

Na_2O	K_2O	TiO_2	P_2O_5	H_2O	CO_2	Total
3,15	4,59	0,24	0,09	0,75	0,02	100,07

Analyser: Bundesanstalt für Bodenforschung - Hannover.

TABLE II

Niggli figures of the Skouries host rock.

Si	al	fm	c	alk	ti	p	h	K
349,1	36,4	29,3	4,7	29,6	1,2	0,3	12,4	0,44

mg	w	qz	al - alk	$\frac{2alk}{al + alk}$	Magma
0,2	0,7	132,8	6,8	0,9	(Si)tasnagranitisch.

TABLE III

Calculation of the base of the Skouries host rock.

Cp	Ru	Kp	Ne	Cal	Sp	Fs	Fa	Fo	Q
0,1	0,2	16,9	17,5	2,6	1,3	4,8	2,1	1,0	53,5

TABLE IV

L, M, Q, π, γ, μ values of the Skouries host rock.

L	M	Q	π	γ	μ
17,0	9,5	53,5	0,7	0	0,13

TABLE V

Norm composition of the Skouries host rock.

Q	Cp	Ru	Or	Ab	An	En	Cord	Mt	Hm
29,7	0,1	0,2	28,2	29,2	4,3	1,3	2,4	4,2	0,4

From these tables and supposing that the chemical composition of the rock was not changed afterwards, we conclude that the magma was granitic (si - tasnagranitisch) and so the rock must be characterized as a granite porphyry. However, if we take into account that the original rock was allochemically altered to a large extend, mainly through the transfer of quartz and othoclase, we are led to the conclusion that the composition of the magma and consequently of the unaffected rock was different.

As no sample of the unaffected rock was found, only through arguments we can reach conclusions as regards its nature. Theoretically the following kinds of acid rocks can alter to granitic porphyry by means of quartz and orthoclase transfer: a) granite porphyry b) syenite porphyry c) granodiorite porphyry d) diorite porphyry e) quartz - dioritic porphyry. In cases a, c, and e, however the original rock ought to contain, even in small quantities, quartz phenocrysts of the first generation of crystallization, which is not observed here.

Consequently only cases b and d are left for discussion. Case d (diorite porphyry) is very improbable since the plagioclases in the rock are very acid (18% An) and they can hardly explain a dioritic magmatic origin. The occurence in the nearby Tsikara area of a dioritic mass with dioritic porphyry in the boundaries can not be correlated to the host rock of Skouries, because its plagioclases are very different (45%-48% An) and the percentage of the mafic components much greater. So we come to the conclusion that the original host rock of Skouries was a syenitic porphyry, which later, by the addition of quartz changed into a rock of granitic porphyry composition.

SELECTIVE BIOTITIZATION OF PLAGIOCLASES.

The existence of hypogene alteration zones in the host rocks of the porphyry copper deposits is beyond *Lowell and Guilbert* (1970) special studies on the potassic alteration zone *Henley and Jones* (1970), place it to the postmagmatic or early hydrothermal deuteric environment. In such a process the solutions penetrating the rock bring quartz, K-feldspar, biotite and rarely anhydrite and alter the feldspars partly to sericite and kaolinite and the primary mafic minerals partly to chlorite. From the study of the potassic alteration zones in 27 extended ore deposits of North and South America *Lowell and Guilbert* (1970), results that the addition of K-feldspar and biotite to the host rock is not at random, but follows certain laws. The K-feldspar replaces an older K-feldspar or intrudes into the plagioclaces along the twin planes, or replaces some of their zones in the form of rings. Biotite grows in four main ways: 1) as fillings of veinlets in the form of fishbone, along with chalcopyrite, alteration silicates and anhydrite; 2) as sparse or massive replacement of plagioclase phenocrysts; 3) as bright black euhedral units megascopically nearly identical to primary rock biotite; and 4) as local replacement through the diffusion connecting the feldspars. In the examined host rock of the Skouries porphyry copper ore the biotitization of the feldspars differs from the above laws and follows a special regularity.

The penetration of biotite in the plagioclases and the replacement of the latter in the potassic alteration zone of the rock can be described as follows.

1) Penetration along the cleavage. Fig. 2.

The penetrating biotite constantly follows only two crystallographic directions of the plagioclase crystals: the (001) and (010) cleavage directions. This phenomenon is better observed in the case of beginning biotitization, when the replacement of the mineral is limited to the above two directions. With advancing biotitization deviations from this rule appear and the orientation of the deposited biotite gradually departs from the original ideal directions. It is apparent that the original intrusion of the solution causing biotitization, is made solely in the above mentioned directions of cleavages (001) and (010). It seems that when the plagioclase is soaked by a surplus quantity of solutions, these can cause corrosion of the crystal even along directions which do not necessary coincide with the original ones.

Fig. 2. Plagioclase crystal. Biotitization along the cleavages (001) *and* (010), *72×.*

2) Replacement in a certain plagioclase zone. Fig. 3,4.

Biotite replaces part of a zonal plagioclase and occupy the place of a whole zone of it resulting in a ring like appearance in thin sections. Usually, replaced zone is next to the boundary, often, however, is the core and sometimes the boundary or any intermediate zone. The phenomenon is sometimes related to case number 1 mentioned above, i.e. the biotite is deposited at the same time in both directions of cleavage, but

Fig. 3. Plagioclase crystal aggregate in granite porphyry with biotitized outer zones, 72×.

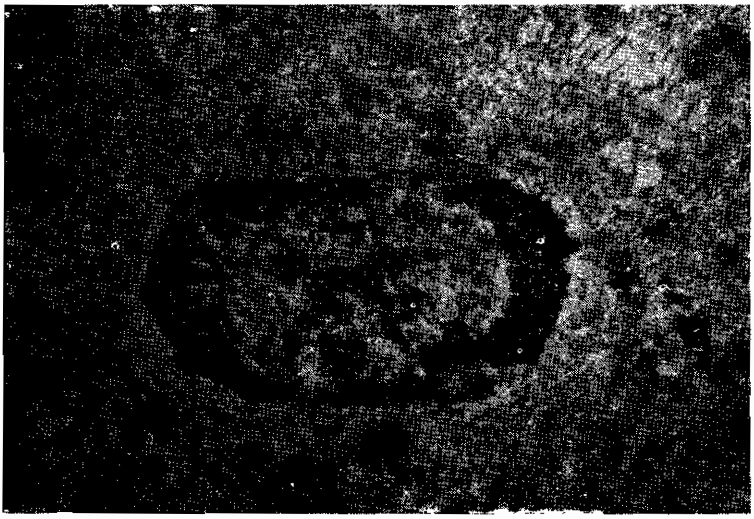

Fig. 4. Plagioclase crystal in granite porphyry.
Characteristic biotitization of a certain zone of the plagioclase, 72×.

sometimes only the zonal replacement occurs. In the second case we must accept that the solutions intrude again through the cleavage but without depositing microscopical distinguishable biotite. Worth observing is the fact that in the same rock sample biotite replaces always the same plagioclase zone. This regularity of biotite to replace a certain zone reminds of the phenomenon of K-feldspar replacing a certain zone of plagioclase described by *Lowell and Guilbert* (1968) with the difference that here it refers to biotite and not to the K-feldspar.

In many cases the phenomenon is accompanied by sericitization of the plagioclase. Even this proccess takes place along the two cleavage directions and specially that of (001). Total change of whole mineral zones to sericite was not observed. The phenomenon of sericitization is later than that of biotitization, because in some sections sericite, occurring along the cleavage traverses the biotitic ring of the original plagioclase zone.

To explain the phenomenon of selective biotitization of plagioclases we must take into account the formation of biotite from the intruding solutions. It seems plausible that they should follow directions of easiest penetration, that is, the cleavage directions and any fissures of the mineral. In the case where the solutions intruded through fissures the occurring biotite must appear at random and irregular directions. This is not observed in the examined rock, except in very few cases. Consequently we must accept that the rock plagioclases lack essentially fissures. This means that after their original crystallization the plagioclases have not suffered any stresses from the magma. Moreover, the solidified rock was not affected, before the rising of the solutions, by such strong forces as to cause fissures in the plagioclases. Such an acceptance might probably be an explanation to the difference between the plagioclase biotitization in other porphyry copper deposits and the above observed case of selective biotitization.

Greater are the difficulties in explaining the phenomenon of the replacement of a certain plagioclase zone by biotite. The difference in the chemical composition between the various zones does not seem to be the cause, since in the different samples of the rock different zones appear to be replaced and not always the same as might be expected. Possibly the reason is a slight difference in structure and mainly slight deffects of the crystal in a certain zone, which favour a selective intrusion.

REFERENCES

H. Gunlach, Kockel F., Mollat H., Walther H., Antoniadis P., Ioannidis K., Mitsaki T., (1971): Prospektion auf Kupfer in Porphyritstöcken der östlichen Chalkidiki. Bundesanstalt fur Bodenforschung und ΙΓΕΥ p 1-46 Hannover.

J.J. Hemley and Jones W.R. (1964): Chemical aspects of hydrothermal alteration with emphasis on hydrogen metasomatism. Econ. Geol. 59 p. 538-564.

F. Kockel und Walther H.W. (1968): Zur geologischen Enwicklung des südlichen Serbomakedonischen Massivs (Nordgriechenland). Bulg. Akad. Sc. Bull. Geol. Instr. Ser. Geot. Strat. Lyth. KHXVII p. 133-142.

D. Lowell and Guilbert J. (1970): Lateral and Vertical Alteration - Mineralization Zoning in Porphyry Ore Deposits. Econ. Geol. 65 p. 373-408.

A.S. Marfunin (1961): The relation between structure and optical orientation in potasch soda feldspars. Instituto Lncas mallada (Espana). Cursillos y conferecius fasc 8, p. 47-109.

W. E. Troeger (1971): Optische Bestimmung der gesteinsbildenden Minerale, 4. Auf. Stuttgart.

K. Zahos (1963): Discovering of copper ore deposit in Chalkidiki ΙΓΕΥ vol. VIH No I p. 1-26.

ΠΕΡΙΛΗΨΙΣ

ΠΑΡΑΤΗΡΗΣΕΙΣ ΕΠΙ ΤΟΥ ΚΟΙΤΑΣΜΑΤΟΣ ΠΟΡΦΥΡΙΤΙΚΟΥ ΧΑΛΚΟΥ ΕΙΣ ΣΚΟΥΡΙΕΣ ΧΑΛΚΙΔΙΚΗΣ (ΕΛΛΑΣ)

Ὑπὸ
Α. ΠΑΠΑΔΑΚΗ
(Ἐργαστήριον Ὀρυκτολογίας καὶ Πετρογραφίας τοῦ Πανεπιστημίου Θεσσαλονίκης)

Εἰς τὴν τοποθεσίαν Σκουριὲς τῆς Χαλκιδικῆς ἐμφανίζεται τὸ μοναδικὸν μέχρι σήμερον διαπιστωθὲν ἐκμεταλλεύσιμον κοίτασμα πορφυριτικοῦ χαλκοῦ ἐν Ἑλλάδι. Τὸ φιλοξενοῦν πέτρωμα ἀνήκει μορφολογικῶς εἰς τὸν τύπον τοῦ κατακορύφως βυθιζομένου ἐλλειπτικοῦ κυλίνδρου μικρῶν σχετικῶς διαστάσεων (ἀξόνων 140x120m) ἐκτεινόμενον εἰς ἄγνωστον βάθος. Ἡ μεταλλοφορία φθάνει εἰς βάθος τουλάχιστον 600 μ. καὶ συνίσταται κυρίως ἀπὸ χαλκοπυρίτην καὶ σιδηροπυρίτην. Ὁ χαρακτηρισμὸς τοῦ πετρώματος ὑπὸ τῶν ἀσχοληθέντων μέχρι τοῦδε μὲ τὸ θέμα Ζάχου (1963) καὶ Gunlach κ.τ.λ. (1971) ὡς τραχείτου καὶ χαλαζιακοδιοριτικοῦ πορφύρου ἀντιστοίχως εἶναι ἐσφαλμένος. Τὸ φιλοξενοῦν πέτρωμα ὡς ἐμφανίζεται διαποτισμένον ὑπὸ χαλαζίου καὶ ἄλλων συστατικῶν τῆς ὑπογενοῦς ἐξαλοιώσεως παρουσιάζει σύστασιν γρανιτικοῦ πορφύρου. Τοῦτο ἐπιβεβαιοῦται καὶ ἐκ τῆς ἐπεξεργασίας τῶν δεδομένων χημικῆς ἀναλύσεως αὐτοῦ. Τὸ ἀρχικὸν ὑγιὲς πέτρωμα θὰ πρέπει νὰ ἦτο συηνιτικὸς πορφύρης. Ἐντὸς τῆς ζώνης ποτασσικῆς ἐξαλοιώσεως τοῦ κοιτάσματος παρουσιάζονται τὰ ἑξῆς ἐνδιαφέροντα φαινόμενα: Οἱ φαινοκρύσταλλοι τῶν πλαγιοκλάστων ἔχουν ὑποστῆ πολλάκις μίαν ἐκλεκτικὴν βιοτιτίωσιν ἡ ὁποία ἀκολουθεῖ δύο κανόνες. Κατὰ τὸν πρῶτον ἡ βιοτιτίωσις ἀκολουθεῖ ὑπὸ μορφὴν λεπτῶν ἀποθέσεων τὰς διευθύνσεις σχισμοῦ (001) καὶ (010) τοῦ ὀρυκτοῦ. Κατὰ τὸν δεύτερον ὁ βιοτίτης ἐκτοπίζει ὁλόκληρον ζώνην τοῦ πλαγιοκλάστου, ἡ ὁποία δυνατὸν νὰ εἶναι εἴτε ὁ πυρήν, εἴτε μία ἐνδιάμεσος ζώνη, εἴτε καὶ ἡ περιφερειακὴ ζώνη τοῦ κρυστάλλου. Προτείνεται ὡς ἐξήγησις διὰ τὴν βιοτιτίωσιν κατὰ τὴν διεύθυνσιν τοῦ σχισμοῦ ἡ εὔκολος διείσδυσις τῶν διαλυμάτων κατὰ μῆκος τοῦ σχισμοῦ. Ἡ περίπτωσις τῆς ἐκλεκτικῆς βιοτιτιώσεως ὡρισμένων ζωνῶν τοῦ κρυστάλλου, διαφόρων κατὰ περίπτωσιν, συνεπῶς διαφόρου χημικῆς συστάσεως εἶναι δυσχερέστερον νὰ ἑρμηνευθῆ. Ὡς πιθανὴ ἐξήγησις προτείνεται ἡ ὕπαρξις δομικῶν ἀτελειῶν ἐντὸς τῶν ὑποκαθιστουμένων ὑπὸ βιοτίτου ζωνῶν.