

Evolution of Mineralizing Fluid in the Porphyry Copper System of the Skouries Deposit, Northeast Chalkidiki (Greece): Evidence from Combined Pb-Sr and Stable Isotope Data

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Abstract

The porphyritic syenite of the Skouries deposit intruded the metamorphic basement of the Serbomacedonian Massif in the northeast Chalkidiki peninsula at 19 Ma. The final emplacement was controlled by dominantly northeast-southwest-trending steep faults that created pathways for the deep-seated magma to rise to shallow crustal levels. Following its emplacement (stage I), the porphyritic syenite suffered a pervasive potassic alteration (stage II, ~590°–640°C). Two later veining stages with propylitic characteristics (stage IIIA, ~480°C; stage IIIB, ~380°C) brought in most of the Cu, which was deposited in the form of chalcopyrite. Quartz sulfide-(calcite) veins transect the porphyritic syenite as well as the country rocks in a narrow (<50 m wide) halo around the stock only. The range of $\delta^{18}\text{O}$ values from 3.5 to 7.6 per mil for the fluids in equilibrium with vein quartz is within the typical range of early ore-forming fluids associated with porphyries, representing magmatic fluids that may, to some extent, have interacted with the igneous wall rock. A subsequent late propylitic alteration (stage IV, ~210°C), more localized and patchy, affected the country rocks and the porphyritic syenite and deposited disseminated pyrite and chalcopyrite. The $\delta^{34}\text{S}$ values from vein and disseminated sulfides range from -2.1 to +0.3 per mil, indicative of a magmatic origin for the sulfur.

The $^{207}\text{Pb}/^{204}\text{Pb}$ ratios from pyrite and chalcopyrite deposited in stage IIIA (early) and stage IIIB (late) veins (15.683–15.687) are markedly lower than those from disseminated sulfides related to stage IV (15.696–15.734) and lie within the range of 15.672 to 15.696 defined by feldspars from the porphyritic syenite. The Pb isotopes therefore indicate an evolution of the fluid composition from one characterized by magmatic components to one dominated by the country rocks, whereas ore hosted in veinlets (stage III) contains lead from both sources. Furthermore they suggest that the lead in the ores developed in continental crustal environments with high μ_2 and W_2 values and evolved in a reservoir with high Th/Pb and low U/Pb ratios.

Age-corrected $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from inclusion fluids in vein quartz range from 0.7086 to 0.7099 for veins within the country rock and from 0.7061 to 0.7080 in veins transecting the porphyritic syenite. Values for porphyry feldspars range from 0.7079 to 0.7081 and country rock from 0.7135 to 0.7342. These data confirm the Pb isotope trends and indicate that Sr contamination took place where the veins crosscut the country rocks. Fluids in veins within the porphyry could ascend rapidly from deeper levels without reacting with the porphyry and thus show an unaffected magmatic Sr isotope signature.

Pb and Sr isotopes in inclusion fluids are shown to be extremely sensitive tracers for elucidating the hypogene leaching processes in the Skouries porphyry system.

Introduction

ALTERATION and mineralization in porphyry copper systems depend on various complex processes among which fracturing, hydrothermal activity, and weathering are of prime importance. Furthermore, the change of physical and chemical conditions (such as pressure release, progressive cooling of the hydrothermal fluids, pH fluctuations, and oxygen and sulfur fugacity changes) are of basic significance for ore deposition and alteration. Due to the frequent spatial superposition of hydrothermal stages in and around porphyry copper systems, discrete alteration zones can rarely be discerned, thus making it difficult to sample an alteration mineral assemblage belonging to a single hydrothermal stage. Furthermore, the host rocks to the mineralization exert a profound control on the alteration mineral paragenesis inasmuch as they influence the chemical evolution of the alteration fluids. Among the numerous investigations of porphyry copper deposits, those focusing on the effects of magmatic assimilation of

crustal rocks and hydrothermal leaching of the country rocks around them and on the evolution of the mineralizing fluids are the most prominent.

Lead isotope investigations of mineralization related to Tertiary magmatic activity in the Serbomacedonian metallogenic province (Jankovic, 1977; Fig. 1) have led to controversial results with respect to possible genetic models applicable to ore deposits of this belt. Based on structural criteria and homogeneous Pb isotope data, Nesbitt et al. (1988) suggest that faults acted as pathways for metalliferous fluids in hydrothermal systems driven by the Tertiary magmatism and circulating through a large rock volume. Similar investigations in the Yugoslavian and Bulgarian part of the Serbomacedonian metallogenic province (Amov et al., 1974; Jankovic, 1978) indicate some variation in the isotopic composition of Pb from some Tertiary Pb-Zn deposits. First, isotopic scatter may derive first from primary magmatic variations, which will produce fluids containing isotopically distinct leads. Second, an observed isotopic scatter can result directly from distinct local sources, which contributed isotopically different Pb to the scavenging metalliferous fluids during late-magmatic, hydrothermal stages. In this case the isotopic composition of the ore minerals is mainly dependent on the isotopic composi-

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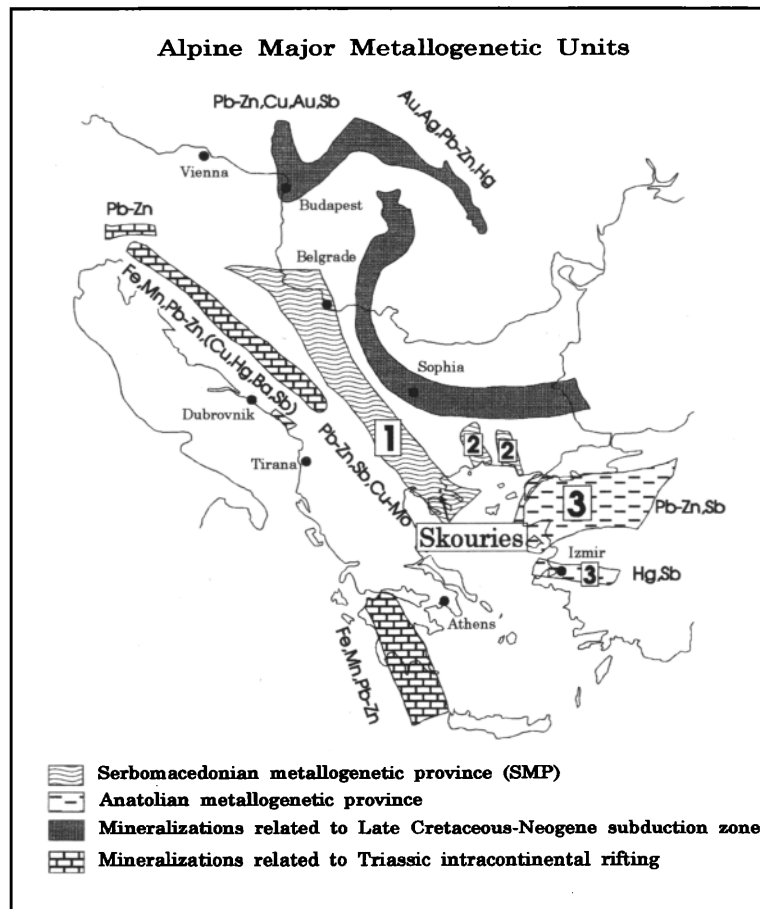


FIG. 1. Simplified map showing the main Alpine metallogenetic units in the Balkan peninsula and in western Turkey (adapted from Jankovic, 1977, and slightly modified). The Skouries porphyry occurs within the Serbomacedonian metallogenetic province. 1 and 2 = a large northwest-southeast-trending belt, which comprises dominantly Pb-Zn, Sb, and Mo-Cu deposits. These are related to Tertiary volcanic-intrusive complexes. 3 = the Anatolian metallogenetic province which forms the eastern extension of the Serbomacedonian metallogenetic province.

tion of the original fluid, the degree of interaction of the fluid with country rocks, and on the isotopic composition of the latter.

This paper, in a combined stable and radiogenic isotope approach, deals with the complexity of alteration and mineralization in a well-defined, small porphyry copper system located in the northeast Chalkidiki peninsula (Greece; Fig. 1). The advantage of the Skouries porphyry system is that it exhibits clearly discernable alteration stages. Thus, it is a suitable deposit for detailed isotopic studies on the introduction and removal of chemical components during alteration processes, for tracing the evolutionary path of the mineralizing fluids, and for constraining the range of possible sources of the metals. With these goals in mind, samples were carefully selected on the basis of a detailed inspection of a larger number of samples. Analyses reported in this study therefore are deemed representative for characterizing the different alteration stages in the syenite porphyry of Skouries.

Geologic Setting

According to Jankovic (1978), the Balkan peninsula is dominated by three major metallogenetic provinces; the Serbomacedonian and Anatolian metallogenetic province (Pb-Zn, Sb,

Mo-Cu), the late Cretaceous-Neogene subduction zone (Pb-Zn, Cu, Au, Sb, Ag, Hg), and Triassic intracontinental rifting (Fe, Mn, Pb-Zn, \pm Cu, Hg, Ba, Sb), in which ore deposits are mainly related to Late Cretaceous to Tertiary volcanic-intrusive complexes. The Skouries porphyry copper deposit occurs within the Serbomacedonian metallogenetic province, a generally northwest-southeast-trending belt, which comprises dominantly Pb-Zn replacement, fracture-controlled Sb vein, Cu-Mo porphyry, and stratiform volcano-sedimentary deposits (Fig. 1). The mineral occurrences in the Rhodope Massif (2, Fig. 1) and in Anatolia (3, Fig. 1) show paragenetic similarities to the mineralizations in the Serbomacedonian metallogenetic province and are also closely associated with Tertiary intrusions. They are therefore believed to form an east-southeast-trending extension of the Serbomacedonian metallogenetic province. Fytikas et al. (1980), Channell and Horvath (1976), and Dewey et al. (1973) propose plate tectonic models to explain the initialization of the Tertiary magmatism in the Serbomacedonian metallogenetic province and suggest contemporaneous ore-forming processes in this belt. This hypothesis is supported by investigations of Tertiary mineralization in the Rhodope Massif of northern Greece (Nesbitt et al., 1988). These authors favor a dynamic model in which

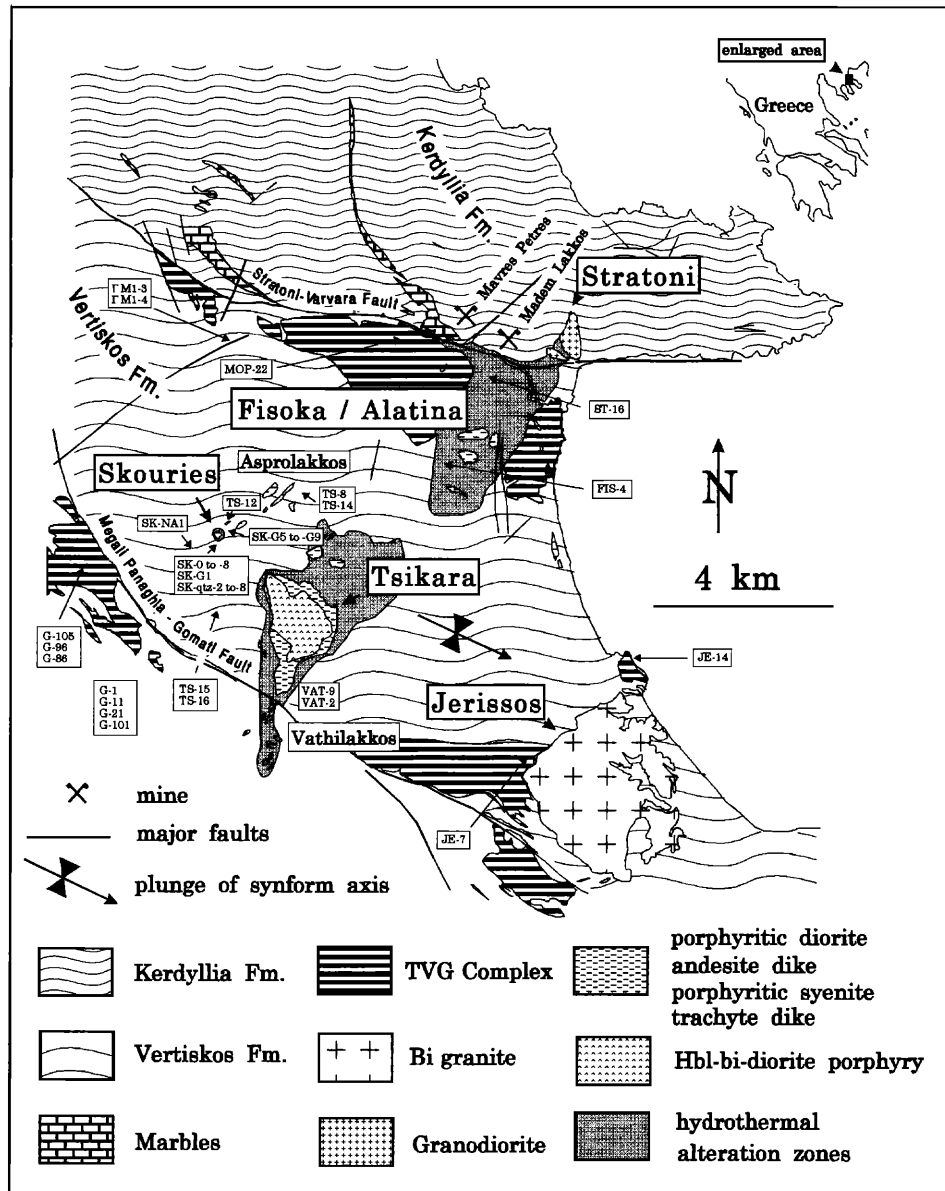


FIG. 2. Geologic map of northeast Chalkidiki (Greece) with the location of the Skouries porphyry and the trachitic dike swarm in the Asprolakkos area. Sample locations are given in the square boxes. Porphyry copper-type intrusions also occur in the Fisoka-Alatina and Tsikara areas. They are genetically associated with carbonate-hosted, gold-bearing massive sulfide replacement deposits at Madem Lakkos and Mavres Petres. A possible contact between Therma-Volvi-Gomati Complex rocks beneath the Vertiskos Formation in the area between the Stratoni-Varvara and the Megali Panaghia-Gomati fault (synformal structure) is suggested.

extensional tectonics associated with arc magmatism resulted in hydrothermal solutions migrating through well-defined fracture systems. Metals scavenged from the basement and cover sequences were subsequently dumped in chemically and physically favorable environments such as marble horizons or into actively depositing basins.

The Skouries porphyry belongs to a series of dominantly dioritic to andesitic porphyritic dikes and stocks (Fig. 2) emplaced in a northeast-southwest-trending intrusive belt in northeast Chalkidiki (Greece). Within this Tertiary intrusive belt a number of stocks bear typical porphyry copper-type mineralization. The most prominent porphyry copper stocks

are diorite porphyries in the Fisoka-Alatina area to the south of the two important carbonate-hosted, gold-bearing massive sulfide replacement deposits of Madem Lakkos and Mavres Petres (Neubauer, 1957; Nicolaou, 1960, 1964, 1969; Kalogeropoulou et al., 1989; Nebel et al., 1991; Gilg, 1993; Gilg and Frei, 1994). More or less barren diorite and andesite porphyries occur in the Tsikara area, whereas mineralized and barren porphyritic syenite to trachyte porphyries are emplaced in the Skouries-Asprolakkos and Stratoni area. The diorite porphyries of Fisoka and Tsikara produced a large phyllic alteration zone that predominantly affected the gneisses and schists of the Vertiskos Formation, the Therma-

Volvi-Gomati Complex, and the Kerdyllia Formation of the Serbomacedonian Massif. The porphyries are bound to mainly northeast-southwest-trending normal faults, indicating that extensional tectonics have triggered the emplacement of the various subvolcanic intrusions.

The area shown in Figure 2 is characterized by two such northwest-southeast-trending faults, the Stratonii-Varvara and the Megali Panaghia-Gomati faults. These faults dip 30° to the south or southwest, have a minor strike-slip component, and form the loci of ongoing seismic activity (Pavlidis and Tranos, 1991). They define the southwest and northeast boundaries of a large synformal structure, in which mostly gneisses and schists of the Paleozoic or older Vertiskos Formation predominate. Amphibolites and peridotites of the Jurassic Therma-Volvi-Gomati Complex occur along the hinges of the synform and appear to underlie tectonically the Vertiskos schists. The country-rocks belong to the so-called Serbomacedonian Massif, a broadly northwest-southeast-trending tectonic belt referred to as the basement, which extends from south of Belgrade (Yugoslavia) to northeast Chalkidiki (Greece).

The Skouries porphyry itself occurs as a pipelike, mineralized subvolcanic body with surface dimensions of 180 m north-south and 200 m east-west with a vertical extent of at least 700 m. The intrusion age was determined at 19 ± 1 Ma on zircon and uranohorite fractions (Frei, 1992). The age is in accordance with K-Ar whole-rock ages of 20.5 ± 1.0 and 20.6 ± 1.0 Ma reported by Tompouoglou (1981). The composition of the porphyry has been the subject of various debates. Zachos (1963) refers to it as "porphyritic rock with trachytic origin," whereas Papadakis (1971) argues for a silicified syenitic or dioritic porphyry that was potassically altered. On the basis of several drilling campaigns the ore reserves of this deposit were estimated by Billiton International Metals (1981) as 72 M tons of 0.5 percent Cu, 0.7 g/t Au, and 2.5 g/t Ag, at a 0.25 percent Cu cut-off grade, or 27.2 M tons of 0.78 percent Cu, 1.4 g/t Au, and 4.5 g/t Ag at a cut-off for Cu of 0.50 percent (Kalogeropoulos et al., 1991). Eliopoulos and Economou-Eliopoulos (1991) report elevated platinum-group element concentrations, mainly of Pd, Pt, and Ru. On the basis of factor analysis they conclude that the occurrence of Au, Ag, Pd, and Te is coupled with elevated silica contents and therefore correlated with silicification rather than with potassic alteration. A low correlation of Te and Pd with Cu, in the opinion of these authors, may suggest that these metals, and to a lesser extent Cu, were redistributed during the late stages of evolution of the Skouries porphyry system. Approximately 300 to 400 m to the northeast of the main stock, in the Asprolakkos area, a swarm of mainly southwest-northeast-trending trachytic to andesitic barren dikes occurs (Fig. 2). Based on geochemical, structural, mineralogical, and isotopic compositional similarities of the latter to the Skouries porphyry, it is assumed that the subvolcanic intrusions in the Skouries-Asprolakkos area are genetically linked and were emplaced contemporaneously in the early to middle Miocene.

Country Rocks

The country rocks at Skouries belong to the Vertiskos Formation and comprise various types of biotite gneisses, which have undergone lower amphibolite facies metamorphism (Sakellariou, 1989). Retrograde mineral assemblages in these

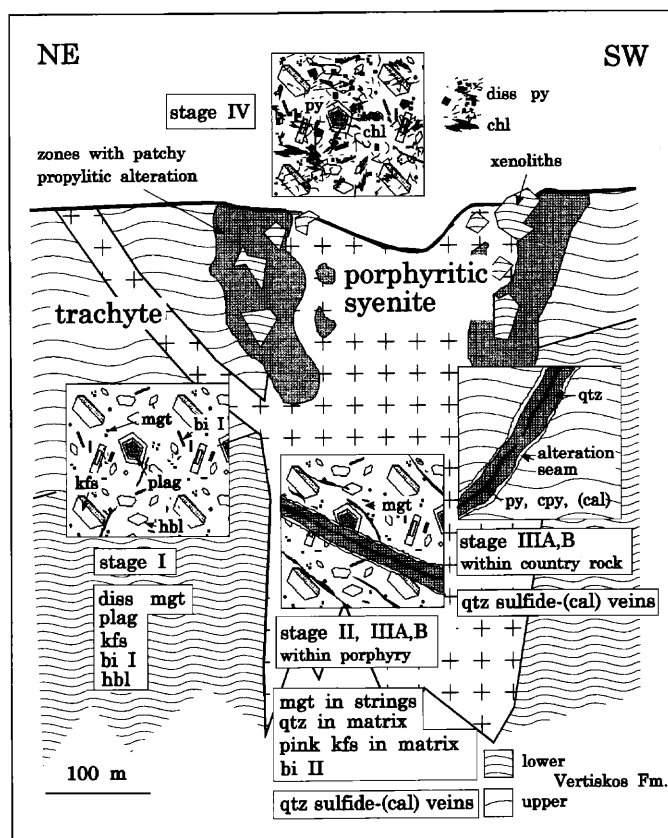


FIG. 3. Schematic profile across the Skouries porphyry and the genetically related unaltered trachyte dike with insets of the main host- and country-rock alteration features pertaining to stage I (fresh, magmatic), stage II (pervasive potassic), vein stage IIIA and B (early propylitic), and stage IV (patchy late propylitic). Characteristic mineral paragenesis is listed below the corresponding inset. Abbreviations: bi = biotite, cal = calcite, chl = chlorite, cpy = chalcopyrite, diss = disseminated, hbl = hornblende, kfs = K feldspar, mgt = magnetite, plag = plagioclase, py = pyrite, qtz = quartz.

gneisses and schists point to a later (Paleozoic or Alpidic) thermal event. Olive-green biotite and biotite-amphibole gneisses appear to prevail in the lower parts of the metamorphic country-rock pile, because they dominate in drill cores and also occur as xenoliths in the border zone of the porphyry (Fig. 3). Gray biotite gneisses and biotite-muscovite gneisses, some of which are garnetiferous, prevail at the surface. Both types of gneisses have been propylitically altered within only a narrow (approx 50 m wide) contact halo around the stock. Three spatially related mafic and ultramafic bodies within the Vertiskos Formation, referred to as the Therma-Volvi-Gomati Complex (Dixon and Dimitriadis, 1984), have been metamorphosed to high-grade amphibolite facies. They are interpreted as belonging to a dismembered, presumably Jurassic, ophiolite sequence (Dixon and Dimitriadis, 1984). The high-grade metamorphism and deformation events recorded in the Therma-Volvi-Gomati Complex are not observed in the surrounding Vertiskos metasediments. This implies a tectonic emplacement of the Therma-Volvi-Gomati Complex. The three main bodies are confined to and exposed along the two main northwest-southeast-trending Megali Panaghia-Gomati and Stratonii-Varvara faults. This, together with the regional trend of strike and dip of schistosity within the Vertiskos

gneisses and the Therma-Volvi-Gomati Complex indicating a synformal structure (1:50,000 geologic map of Greece, Stratoni sheet, Institute of Geology and Mining Research, 1988), suggests a possible contact of the Therma-Volvi-Gomati Complex beneath the Vertiskos pile in the area between these two major faults.

Mineralogy of the Porphyry and Trachyte

The mineralized porphyritic syenite at Skouries and the barren, unaltered trachyte from Asprolakkos both show a microgranular porphyritic structure. The phenocryst mineralogy consists of rare edenitic hornblende, a first generation biotite (biotite I, 2–20 vol %), zoned plagioclase (20–45 vol %), and potassium feldspar (10–40 vol %). The matrix, comprising 45 to 55 vol percent, consists of secondary pink albite and K feldspar (together up to 80 vol %), minor quartz, \pm chloritized secondary biotite (biotite II), and disseminated magnetite. In the purely potassically altered porphyritic syenite, magnetite occurs in strings (5 vol %) and secondary biotite (biotite II, up to 5 vol %) occurs as fresh laths. The latter is partly transformed to felty chlorite aggregates in propylitically altered parts. Apatite, zircon, sphene, anatase, and tellurides are accessory phases.

Alteration and Mineralization

Following emplacement, which in the following is referred to as stage I, three main alteration stages (II, IIIA and B, and IV) are recognized within the porphyry and the country rocks. They are schematically depicted in Figure 3.

Potassic alteration (stage II)

The porphyritic syenite has been affected by pervasive potassic alteration. Previous studies of porphyry copper systems have shown that the potassic alteration in such deposits is co- to late-magmatic and usually terminates at the time of final and complete crystallization of the emplaced magma. In the host rock of the Skouries deposit this stage is characterized by the alteration of edenitic hornblende to biotite II as well as by overgrowths of biotite II on biotite I. This process is often associated with deposition of martitized magnetite. Fine-grained, pink, secondary K feldspar and quartz predominate in the matrix. According to Tompouloglou (1981) the composition of secondary K feldspar ($an_0, or_{89.2}, ab_{10.8}$) is very similar to the composition of overgrowths on primary

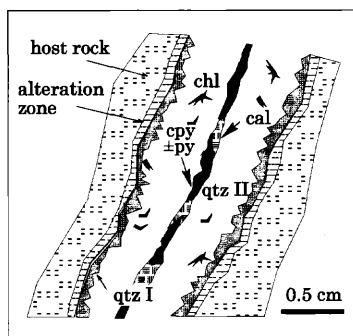


FIG. 4. Schematic sketch depicting an early (stage IIIB) propylitic vein, which typically transects the porphyry as well as the country rocks within a narrow alteration zone around the stock. Abbreviations: cal = calcite, chl = chlorite, cpy = chalcopyrite, py = pyrite, qtz = quartz.

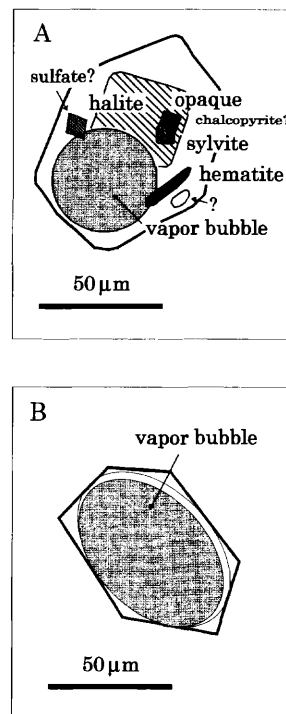


FIG. 5. Sketch showing a typical high-salinity, multiphase fluid inclusion (A) that coexists with vapor-rich inclusions (B) along growth zones in quartz from stage IIIA veins. The highly saline inclusions contain several daughter phases, among which halite, sylvite, and hematite, together with an opaque phase (possibly chalcopyrite?), a highly birefringent daughter mineral (possibly a sulfate?), and another unidentified phase are present.

phenocrysts. Stringers of magnetite, representing first generation fracture fillings, are confined to this alteration stage.

Early propylitic alteration (stage IIIA and B)

This alteration is confined to a major vein stage during which most of the Cu was deposited. Quartz sulfide-(calcite) veins of up to 1 cm in thickness transect the porphyry as well as the country rocks in a very narrow (<50 m wide) alteration zone. From the wall rock to the center, these consist of idiomorphic quartz that grew perpendicularly on the fracture surfaces, a later generation of quartz with interstitial chlorite, and a seam of sulfides and calcite (Fig. 4). In a narrow alteration zone (2–5 mm) around the veins, felty chlorite replaces both biotite generations (biotite I and biotite II). Two generations of veins are recognized.

First generation (stage IIIA) veins consist of quartz with chalcopyrite and pyrite in the center. Second generation (stage IIIB) veins consist mainly of quartz with an inner seam of chalcopyrite, pyrite, and calcite as the last deposited vein phases. The coexistence of quartz, chlorite, and calcite together with pyrite points to a typical propylitic assemblage. The mineralizing fluids are well preserved in high-salinity inclusions in quartz (Fig. 5). These are arranged along quartz growth zones, which indicates a primary origin. The coexistence of high-salinity inclusions (up to five daughter minerals) and vapor-rich inclusions in stage IIIA quartz growth zones, their constant liquid/vapor ratios, and the consistent phase ratios in the high-salinity inclusions indicate that the mineralizing fluid may have boiled during the early veining.

TABLE 1. Geochemical Analyses (XRF data) of Trachyte from Asprolakkos and Porphyritic Syenite from Skouries

	Trachyte					Porphyritic syenite						
	TS-12	A-246	A-332	A-333	2-64	SK-1	SK-3A	SK-5A	SK-0	A234	A231	SK-G1
Weight percent												
SiO ₂	64.37	64.32	65.29	66.11	65.32	66.38	63.89	67.42	65.06	64.67	64.31	61.23
TiO ₂	0.40	0.38	0.40	0.40	0.40	0.31	0.48	0.31	0.38	0.34	0.39	0.24
Al ₂ O ₃	14.79	14.68	14.92	16.00	15.00	15.00	15.49	14.44	16.32	15.65	14.97	14.63
Fe ₂ O ₃	3.44	3.17	3.21	3.29	3.47	6.42	6.79	6.15	5.55	5.05	5.08	9.76
MnO	0.05	0.06	0.06	0.07	bdl	0.02	0.03	0.00	0.02	0.04	0.03	0.01
MgO	2.04	1.28	1.76	1.41	1.77	0.99	1.88	0.95	1.32	1.26	0.82	0.78
CaO	3.54	3.32	3.44	2.85	3.79	1.52	1.59	1.05	0.71	1.69	2.17	0.59
Na ₂ O	3.24	3.41	3.47	4.21	4.01	3.87	3.21	3.50	3.30	3.91	4.02	2.20
K ₂ O	3.27	3.34	3.39	4.01	3.62	5.20	4.31	4.72	4.73	5.14	4.63	8.21
P ₂ O ₅	0.20	0.16	0.18	0.26	0.24	0.20	0.33	0.17	0.27	0.28	0.20	0.23
L.O.I.	3.01	1.63	1.40	0.98	1.32	0.49	2.67	1.29	2.50	1.09	0.98	0.46
Total	98.35	95.75	97.52	99.59	98.94	100.40	100.67	100.00	100.16	99.12	97.60	98.34
Parts per million												
F	789	na	na	na	na	na	na	na	na	na	na	668
Ba	1,358	1,381	1,305	1,199	na	1,991	1,912	1,874	1,853	2,071	1,859	2,293
Rb	92	113	107	179	na	124	86	108	117	144	123	177
Sr	1,025	1,060	982	909	na	1,065	813	874	780	1,131	1,114	637
Pb	33	na	na	na	na	38	5	43	6	na	na	36
Th	<5	na	na	na	na	27	5	27	25	na	na	49
U	<10	na	na	na	na	13	10	10	10	na	na	10
Nb	<4	na	na	na	na	<4	<4	<4	4	na	na	<4
La	<20	na	na	na	na	<20	65	32	104	na	na	<20
Ce	55	na	na	na	na	77	142	93	174	na	na	23
Nd	<25	na	na	na	na	26	59	29	67	na	na	<25
Y	<3	na	na	na	na	11	6	12	14	na	na	3
Zr	244	na	na	na	na	267	227	268	278	na	na	272
V	70	110	114	104	na	57	112	69	89	108	129	84
Cr	18	41	60	96	na	11	18	12	8	98	108	14
Ni	18	166	245	448	na	9	15	7	4	32	10	27
Co	7	20	21	22	na	7	15	13	9	17	10	19
Cu	6	<10	<10	<10	na	1,437	9,700	1,886	719	468	460	176
Zn	28	na	na	na	na	37	55	33	27	na	na	22
Hf	na	na	na	na	na	na	na	na	na	na	na	na
Ga	na	na	na	na	na	17	10	15	15	na	na	na
Sc	7	na	na	na	na	4	11	4	8	na	na	6
S	<50	na	na	na	na	834	<50	<50	<50	na	na	428

Samples A-231, A-232, A-233, A234, and A-246 from Tompouloglou (1981), sample 2-64 from Kockel et al. (1977); TS-12: unaltered trachyte; SK-1, SK-3A, SK-5A, SK-0: potassically altered porphyritic syenite; SK-G1: propylitically overprinted porphyritic syenite
bdl = below detection limit, na = not analyzed, L.O.I. = loss on ignition

Late propylitic alteration (stage IV)

The effects of a patchy propylitic alteration, which is superimposed on the vein-type alteration, can be observed within the porphyritic syenite and within a narrow halo in the country rocks. Textural evidence of a superposition is given by the occurrence of disseminated pyrite developed on alteration zones around veins within patchy propylitic areas, whereas it is absent in patches that have not been affected by stage IV. This stage is characterized by the breakdown of mafic components in the matrix to felty chlorite aggregates and calcite. Along with this alteration finely dispersed pyrite and minor chalcopyrite and molybdenite were deposited. Plagioclase suffered weak sericitization and saussuritization.

Geochemistry of the Mineralized Porphyritic Syenite and the Barren Trachyte

Table 1 presents XRF analyses of trachytes in the Asprolakkos area and the porphyritic syenite at Skouries. Unal-

tered trachytes (analyses from Tompouloglou, 1981, and Kockel et al., 1977), including sample TS-12, are plotted in a K₂O + Na₂O vs. SiO₂ diagram (Irvine and Baragar, 1971) in Figure 6. These trachytes can be characterized as belonging to a typical subalkaline suite, in accordance with the conclusion drawn by Kockel et al. (1975) for subvolcanic intrusions in the northeast Chalkidiki peninsula (shaded field). The lack of first generation quartz as well as the sodic nature of plagioclase (Papadakis, 1971) in all samples points to a syenitic rather than a dioritic composition for the subvolcanic intrusion at Skouries prior to potassic alteration. Six unveined, potassically altered porphyritic syenite samples from Skouries (samples A234 and A231 taken from Tompouloglou, 1981) are plotted in the same diagram of Figure 6 together with one propylitically altered sample (SK-G1). Despite potassic alteration, samples of the Skouries porphyritic syenite still plot within the northeast Chalkidiki porphyry field. Elevated K₂O + Na₂O contents relative to the fresh trachyte and Fe₂O₃

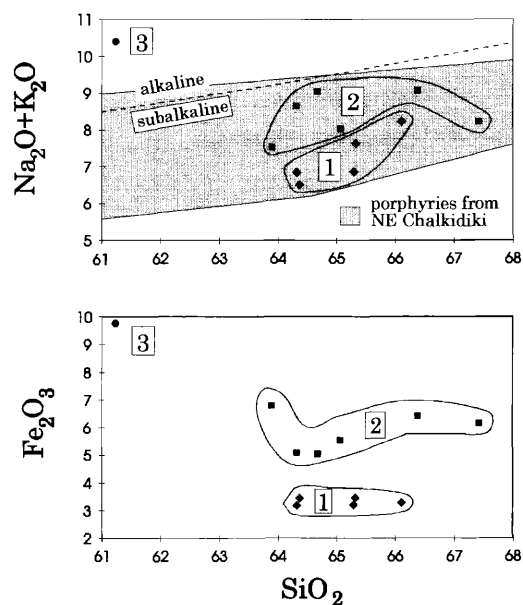


FIG. 6. SiO_2 vs. $\text{K}_2\text{O} + \text{Na}_2\text{O}$ and Fe_2O_3 plots of unaltered trachytes (diamonds) from Asprolakkos (data from Tomouloglou, 1981, and Kockel et al., 1977, including sample TS-12), potassically altered porphyritic syenite samples (squares), and one propylitically overprinted porphyry sample (SK-G1, circle) from Skouries. The shaded field comprises data from porphyries of the eastern Chalkidiki (Kockel et al., 1975). The subvolcanic intrusions show subalkaline characteristics and are typical of a calc-alkaline suite. The effect of potassic alteration (data field 2) can be seen in the elevated content of $\text{K}_2\text{O} + \text{Na}_2\text{O}$ relative to unaltered trachyte (data field 1), whereas late propylitic alteration introduced Fe mainly in the form of pyrite (data point 3, sample SK-G1). Discrimination of an alkaline from a subalkaline trend is according to Irvine and Baragar (1971).

(total Fe) of the propylitically altered sample relative to the potassically altered ones are mainly due to the development of secondary K feldspar and pyrite, which are, respectively, direct indications for pervasive potassic and onset of propylitic alteration. In potassically altered porphyry samples the amount of K increased by 20 to 36 percent over the original content. SiO_2 contents in the potassically altered samples are quite variable, in accordance with results reported by Eliopoulos and Economou-Eliopoulos (1991). The variation of Si is not systematically correlated to increases or depletions of other elements. The elevated Fe content in the potassically altered samples relative to the fresh trachytes is mainly due to magnetite (disseminated and stringy) introduced during late-magmatic alteration. The relative concentrations of more or less immobile elements such as Al, Ti, and Zr, plotted in a triangular diagram (Fig. 7), are narrowly clustered. This is an indication of a close genetic relationship between the porphyritic syenite at Skouries and the unaltered trachyte at Asprolakkos.

Analytical Techniques

Pb isotope analyses were performed on 300 to 500 mg of powdered whole-rock samples. They were dissolved in HF and HNO_3 . Pb was separated by standard DOWEX AG-1 X8[®] anion exchange columns in a mixed HBr-HCl medium. Vein samples were separated from the host rock with a miniature diamond saw. Vein seams were successfully separated from the rest of the vein material by the same technique. Separation of plagioclase and K feldspar demanded magnetic and heavy liquid techniques prior to handpicking. Sulfides from the 50- to 80- μm grain size fraction were handpicked from heavy liquid concentrates of carefully selected samples. Inclusion fluids were released by hand crushing of 2 to 3 g of pure vein quartz in 25 ml of triply distilled H_2O . After rinsing and evaporation, the sample was passed through miniaturized teflon columns charged with anion exchange resin and Pb was separated using the standard HBr-HCl recipe. The total Pb blank of the procedure for analyzing the inclusion fluids amounted to 200 pg, where it was on the order of 800 pg for the whole-rock samples and mineral separates. Sr isotope analyses were performed on similar sample amounts, whereby Sr was separated in 20-ml quartz columns charged with DOWEX 50W-X8 cation exchange resin. The procedural Sr blank was on the order of 500 pg. Pb and Sr were measured on a MAT 261 spectrometer on single Re and Ta filaments, respectively. Rb and Sr concentrations were analyzed by isotope dilution. Fractionation for Pb amounted to 0.15 per mil per atomic mass unit and a factor of 1.002 for $^{85}\text{Rb}/^{87}\text{Rb}$ was applied to the Rb ratio. The reproducibility of the NBS 981 common Pb standard during the time of this study was $^{206}\text{Pb}/^{204}\text{Pb} = 0.12$ percent, $^{207}\text{Pb}/^{204}\text{Pb} = 0.15$ percent, and $^{208}\text{Pb}/^{204}\text{Pb} = 0.23$ percent ($n = 43$, 2σ level, 95% confidence). The $^{87}\text{Sr}/^{86}\text{Sr}$ values were corrected for fractionation and normalized to $^{88}\text{Sr}/^{86}\text{Sr} = 8.37521$. The reproducibility of the NBS 987 Sr standard for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was better than 0.03 percent ($n = 5$, 2σ). Errors of the $^{87}\text{Rb}/^{86}\text{Sr}$ ratios are below 1 percent (2σ). Runs were usually terminated after 100 and 200 scans for Pb and Sr, respectively. Oxygen isotopes were analyzed at the Institute for the Study of the Earth's Interior (ISEI), Misasa, Japan. Using standard techniques, oxygen was extracted from quartz, feldspar, and magnetite by the BrF_5 (Clayton and Mayeda, 1963) and carbon reduction methods. The CO_2 samples were analyzed on a VG ISOGAS mass spectrometer. The reproducibility of the NBS 28 quartz standard at ISEI is better than 0.1 per mil in the usual delta notation. Sulfur isotopes were measured on about 50 mg of handpicked, pure sulfide phases, which were dissolved in 4 ml of HNO_3 and a few drops of Br_2 to transform S^{2-} to SO_4^{2-} . After passing the sample through a cation exchange column (precleaning stage), a 0.1 M BaCl_2 solution was added and the BaSO_4 precipitate was fully decomposed to SO_2 according to the method of Yanagisawa and Sakai (1983). Sulfur isotope analyses were performed on an automated SIRA-10 mass spectrometer. Mass fractionation was

tion of plagioclase and K feldspar demanded magnetic and heavy liquid techniques prior to handpicking. Sulfides from the 50- to 80- μm grain size fraction were handpicked from heavy liquid concentrates of carefully selected samples. Inclusion fluids were released by hand crushing of 2 to 3 g of pure vein quartz in 25 ml of triply distilled H_2O . After rinsing and evaporation, the sample was passed through miniaturized teflon columns charged with anion exchange resin and Pb was separated using the standard HBr-HCl recipe. The total Pb blank of the procedure for analyzing the inclusion fluids amounted to 200 pg, where it was on the order of 800 pg for the whole-rock samples and mineral separates. Sr isotope analyses were performed on similar sample amounts, whereby Sr was separated in 20-ml quartz columns charged with DOWEX 50W-X8 cation exchange resin. The procedural Sr blank was on the order of 500 pg. Pb and Sr were measured on a MAT 261 spectrometer on single Re and Ta filaments, respectively. Rb and Sr concentrations were analyzed by isotope dilution. Fractionation for Pb amounted to 0.15 per mil per atomic mass unit and a factor of 1.002 for $^{85}\text{Rb}/^{87}\text{Rb}$ was applied to the Rb ratio. The reproducibility of the NBS 981 common Pb standard during the time of this study was $^{206}\text{Pb}/^{204}\text{Pb} = 0.12$ percent, $^{207}\text{Pb}/^{204}\text{Pb} = 0.15$ percent, and $^{208}\text{Pb}/^{204}\text{Pb} = 0.23$ percent ($n = 43$, 2σ level, 95% confidence). The $^{87}\text{Sr}/^{86}\text{Sr}$ values were corrected for fractionation and normalized to $^{88}\text{Sr}/^{86}\text{Sr} = 8.37521$. The reproducibility of the NBS 987 Sr standard for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was better than 0.03 percent ($n = 5$, 2σ). Errors of the $^{87}\text{Rb}/^{86}\text{Sr}$ ratios are below 1 percent (2σ). Runs were usually terminated after 100 and 200 scans for Pb and Sr, respectively. Oxygen isotopes were analyzed at the Institute for the Study of the Earth's Interior (ISEI), Misasa, Japan. Using standard techniques, oxygen was extracted from quartz, feldspar, and magnetite by the BrF_5 (Clayton and Mayeda, 1963) and carbon reduction methods. The CO_2 samples were analyzed on a VG ISOGAS mass spectrometer. The reproducibility of the NBS 28 quartz standard at ISEI is better than 0.1 per mil in the usual delta notation. Sulfur isotopes were measured on about 50 mg of handpicked, pure sulfide phases, which were dissolved in 4 ml of HNO_3 and a few drops of Br_2 to transform S^{2-} to SO_4^{2-} . After passing the sample through a cation exchange column (precleaning stage), a 0.1 M BaCl_2 solution was added and the BaSO_4 precipitate was fully decomposed to SO_2 according to the method of Yanagisawa and Sakai (1983). Sulfur isotope analyses were performed on an automated SIRA-10 mass spectrometer. Mass fractionation was

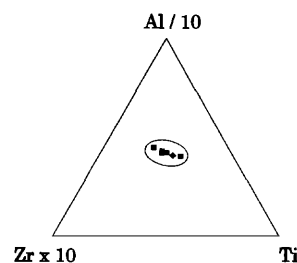


FIG. 7. Triangular plot of element concentrations of Al, Zr, and Ti in the five potassically altered porphyritic syenite samples (squares) and the unaltered trachyte sample TS-12 (diamond) from Skouries and Asprolakkos, respectively.

TABLE 2. Lead Isotope Ratios from Ore Minerals, Feldspars, and Vein Fluids from the Skouries Copper Porphyry Deposit

Sample no.	Phase	Type	Alteration	Location	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
Lead isotope ratios of feldspars from the intrusion							
SK-1	kfs	Porphyritic syenite	Stage II	Skouries, drill core	18.749	15.693	38.945
SK-1	kfs	Porphyritic syenite	Stage II	Skouries, drill core	18.737	15.683	38.917
SK-1	kfs	Porphyritic syenite	Stage II	Skouries, drill core	18.749	15.681	38.912
SK-1	kfs	Porphyritic syenite	Stage II	Skouries, drill core	18.752	15.691	38.933
SK-6	kfs	Porphyritic syenite	Stage II	Skouries, drill core	18.755	15.682	38.908
SK-8	kfs	Porphyritic syenite	Stage II	Skouries, drill core	18.746	15.697	38.956
SK-G1	kfs	Porphyritic syenite	Stage II	Skouries, drill core	18.749	15.693	38.954
SK-1	plag	Porphyritic syenite	Stage II	Skouries, drill core	18.748	15.685	38.907
SK-6	plag	Porphyritic syenite	Stage II	Skouries, drill core	18.754	15.672	38.874
SK-G1	plag	Porphyritic syenite	Stage II	Skouries, old adit, dump	18.751	15.696	38.980
TS-12	kfs	Trachyte	Stage I	Skouries-Asprolakkos	18.742	15.672	38.851
TS-12	plag	Trachyte	Stage I	Skouries-Asprolakkos	18.761	15.682	38.886
Lead isotopes ratios from disseminated ore minerals within the porphyry							
SK-1	cp	Porphyritic syenite	Stage IV	Skouries, drill core	18.763	15.711	39.013
SK-1	bn	Porphyritic syenite	Stage IV	Skouries, drill core	18.778	15.734	39.088
SK-2	cp	Porphyritic syenite	Stage IV	Skouries, drill core	18.749	15.696	38.965
SK-2	cp	Porphyritic syenite	Stage IV	Skouries, drill core	18.743	15.699	38.976
SK	cp	Porphyritic syenite	Stage IV	Skouries, drill core	18.748	15.700	38.965
SK-3	cp	Porphyritic syenite	Stage IV	Skouries, drill core	18.752	15.705	38.980
SK-G1	py	Porphyritic syenite	Stage IV	Skouries, old adit, dump	18.778	15.703	39.032
SK-8	py	Porphyritic syenite	Stage IV	Skouries, drill core	18.756	15.697	38.981
Lead isotope ratios from vein-related sulfides, calcite, and inclusion fluids in quartz							
SK	cp	Syenite porphyry	Stage IIIB	Skouries, drill core	18.733	15.684	38.911
SK-3	cp	Syenite porphyry	Stage IIIB	Skouries, drill core	18.733	15.683	38.908
SK-qtz-3	cp	Syenite porphyry	Stage IIIB	Skouries, drill core	18.760	15.687	38.942
SK	py	Syenite porphyry	Stage IIIA	Skouries, drill core	18.734	15.685	38.912
SK-qtz-4	Incl. fluid	Syenite porphyry	Stage IIIB	Skouries, drill core	18.764	15.672	38.882
SK-qtz-6	Incl. fluid	Country rock	Stage IIIA	Skouries, drill core	18.738	15.709	38.962
SK-qtz-4	cal	Syenite porphyry	Stage IIIB	Skouries, drill core	18.735	15.685	38.900

Reproducibility of NBS 981 lead standard during this study ($n = 43$) was 0.12% on $^{206}\text{Pb}/^{204}\text{Pb}$, 0.15% on $^{207}\text{Pb}/^{204}\text{Pb}$, and 0.23% on $^{208}\text{Pb}/^{204}\text{Pb}$ ratios at the 2σ level (95% confidence)

bn = bornite, cal = calcite, cp = chalcopyrite, fluid = inclusion fluid, kfs = K feldspar, plag = plagioclase, py = pyrite

controlled by internal laboratory standard BaSO_4 samples, and the reproducibility during the time of the study was better than 0.06 per mil ($n = 4$, 2σ) on two laboratory standard BaSO_4 samples.

Results

Lead isotopes

Lead isotope ratios of feldspars, disseminated ore minerals, vein-related sulfides, and inclusion fluids in quartz are listed in Table 2 and plotted in Figure 8. The overall Pb isotope pattern in Figure 8 is characterized by high $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios relative to $^{206}\text{Pb}/^{204}\text{Pb}$ ratios for feldspars and ore minerals associated with the porphyritic intrusion. Three fields can be distinguished. K feldspar (K) and plagioclase (P) from the porphyry define a field with the lowest $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios, representative for early stage I (unaltered feldspars from the trachyte sample TS-12) and stage II (K feldspars formed during the potassic alteration and plagioclase from potassically altered samples). The Pb isotope compositions of K feldspar and plagioclase from the propylitically overprinted sample SK-G1 mark the upper boundary of the feldspar field and overlap with the field de-

finied by disseminated sulfides in both diagrams. This suggests contamination of the feldspar lead by the $^{207}\text{Pb}/^{204}\text{Pb}$ -dominated propylitic fluids percolating during stage IV (see below). This stage is represented by the Pb isotope compositions of disseminated sulfides, i.e., chalcopyrite (5 samples), pyrite (2 samples), and bornite (1 sample) from propylitically overprinted samples of the porphyritic syenite. Lead isotope ratios of chalcopyrite (3 samples), pyrite (1 sample), and calcite (1 sample) from stage IIIA and B propylitic veins within the porphyry plot in a narrow field that overlaps the feldspar data but is characterized by lower $^{207}\text{Pb}/^{204}\text{Pb}$ ratios than the disseminated ore minerals (stage IV). Disseminated ore related to the late propylitic, patchy alteration (stage IV) is isotopically clearly distinguishable from vein-related ore characteristic of the earlier and main mineralizing stage IIIA and B.

"F" denotes two inclusion fluid analyses from quartz sulfide-(calcite) veins (stage IIIA and B). The one with the higher $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratio (i.e., SK-qtz-6) is from a vein transecting the biotite gneiss, whereas the other (i.e., SK-qtz-4) is from a vein within the porphyritic syenite itself.

Table 3 displays the whole-rock lead isotope results from country rocks of the Vertiskos Formation and the Therna-

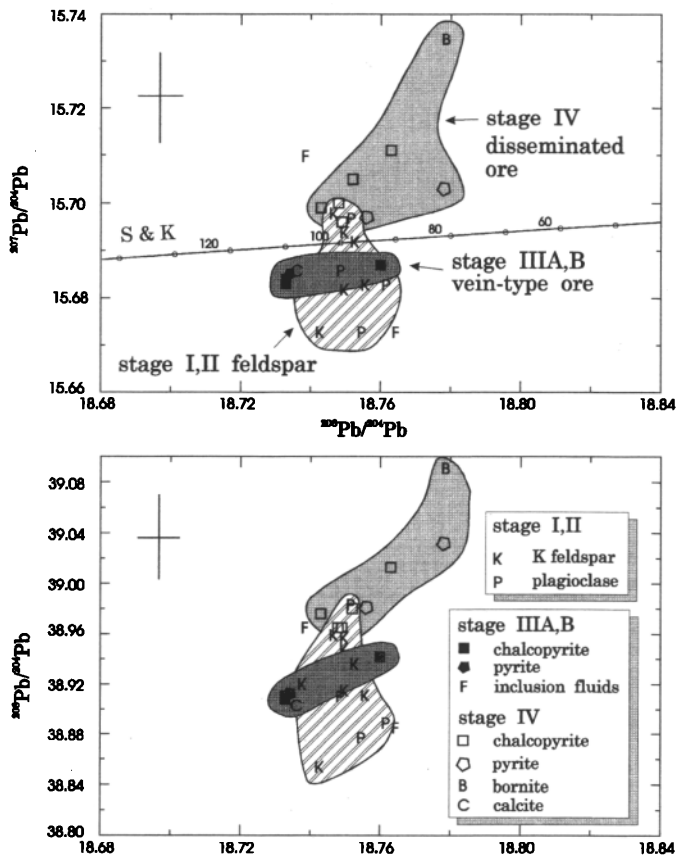


FIG. 8. Common lead isotope plots for feldspars, disseminated ore minerals, vein-related sulfides, and inclusion fluids from the Skouries porphyry and the associated trachyte dike. The three data fields characterize the three main hydrothermal stages, whereby the magmatic lead (stages I and II) is characterized by feldspar lead. Data fields characterizing early (stage IIIA and B), and late (stage IV) propylitic alteration stages correspond to the description in the text. The reference line (S and K) is according to the common lead evolution model ($\mu_2 = 9.74$) proposed by Stacey and Kramers (1975). The error crosses correspond to the reproducibility of the NBS 981 common Pb standard during the time of this study.

Volvi-Gomati Complex. These data are plotted in Figure 9. Country rocks from surface outcrops around the Skouries stock, mainly grayish biotite gneisses from the upper Vertiskos Formation, are characterized by high μ_2 values above 10.0 and high thorogenic lead components. In situ decay corrections for the whole-rock lead isotope analyses are insignificant for the time period of interest, i.e., for the time passed since the emplacement of the porphyry at 19 Ma. Therefore, the metamorphic country-rock leads can be directly compared to those of the porphyry system. Their data field completely overlaps with that defined by feldspar, ore, and inclusion fluid leads from the Skouries deposit. The country rock in the lower part of the Vertiskos Formation (cropping out in the Asprolakkos valley to the northeast of Skouries and occurring as xenoliths within the stock), consists of mainly greenish, partly amphibole-bearing biotite gneisses and has lower $^{207}\text{Pb}/^{204}\text{Pb}$ ratios. In the thorogenic diagram (Fig. 9), the overlap of data defined by rocks from the lower Vertiskos Formation with the low $^{208}\text{Pb}/^{204}\text{Pb}$ end of the field comprising the leads from the Skouries deposit can be seen. The lead isotope compositions of the country rock around the stock

are within the range of leads from Vertiskos country rocks in the northeast in both $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagrams. Whole-rock Pb isotope ratios of amphibolite and serpentinite from the Therma-Volvi-Gomati Complex are characterized by the least radiogenic values. Their field partly overlaps with the Vertiskos data field; in fact, the lead isotope compositions are similar to those of the biotite-amphibole gneisses of the lower Vertiskos Formation at Skouries.

Rubidium-strontium isotopes

Isotopic data are listed in Table 4 and plotted in Figure 10. Data comprise feldspar, apatite, and whole-rock analyses of the unaltered, genetically related trachyte (sample TS-12), the porphyritic syenite, and the country rocks. One leach analysis from vein calcite (stage IIIB) and several inclusion fluid analyses of vein quartz (stage IIIA and B) from veins transecting the porphyritic syenite and the Vertiskos country rocks are also listed. The data are corrected for 19 m.y. in situ Rb decay in order to compare $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at the time of emplacement of the stock. The unaltered trachyte yielded an initial whole-rock $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.70656 and an uncorrected value of 0.70669 for the apatite, whereas the porphyry is characterized by higher initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the range of 0.70793 to 0.70812 as indicated by K feldspar, plagioclase, apatite, and whole-rock analyses. Three biotite gneiss whole-rock analyses of surface samples from the upper Vertiskos Formation indicate an expected, more radiogenic signature of the country rocks. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are higher than 0.71351 and therefore are clearly distinguishable from those of the intrusion. Initial isotopic ratios from inclusion fluids in quartz from quartz sulfide-calcite veins transecting the country rocks are higher (0.70862–0.70993) than those from veins transecting the porphyritic syenite (0.70606–0.70799). A combined leach and crush experiment (leaching the sample for 1 hr with 25 ml of 1 N HCl; analysis of the leachate) was applied to sample SK-qtz-2 (vein within the stock). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for the vein leach (0.70658 \pm 18), dissolving calcite from the innermost vein seam, is within the error limits in accordance with the result of the subsequent crush experiment (0.70621 \pm 22) that released the fluids.

Sulfur isotopes

The sulfur isotope composition of six monomineralic concentrates (chalcopyrite, pyrite) from samples that are considered representative of the mineralization in time and space were analyzed. The results are listed in Table 5 in terms of conventional per mil deviations ($\delta^{34}\text{S}$) relative to CDT (Canyon Diablo troilite).

The $\delta^{34}\text{S}$ compositions of the six hypogene sulfides range from -2.14 to $+0.30$ per mil. It appears that the $\delta^{34}\text{S}$ values are related to the kind of alteration during which the sulfides were deposited. The $\delta^{34}\text{S}$ values of chalcopyrites decrease from vein stage IIIA to vein stage IIIB and to the pervasive propylitic stage IV, during which the sulfides were deposited as disseminations. The most pronounced decrease from -0.75 to -2.14 per mil occurs between stage IIIB and stage IV, possibly induced by the addition of light sulfur from the Vertiskos metasediments to the hydrothermal fluid during late propylitic alteration. This trend is also reflected by the decrease of $\delta^{34}\text{S}$ values from $+0.30$ to -0.23 per mil in pyrite from the corresponding pairs. The results from coexisting

TABLE 3. Lead Isotope Ratios from Country Rocks of the Vertiskos Formation and the Therma-Volvi-Gomati Complex

Sample no.	Phase	Type	Position	Location	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
Lead isotope ratios of Vertiskos rocks from Skouries							
SK-G5	wr	Bi gneiss	Upper Vertiskos Fm.	Skouries, profile	18.749	15.695	38.953
SK-G7	wr	Bi gneiss	Upper Vertiskos Fm.	Skouries, profile	18.750	15.696	38.955
SK-G8	wr	Bi gneiss	Upper Vertiskos Fm.	Skouries, profile	18.785	15.738	39.087
SK-G9	wr	Bi gneiss	Upper Vertiskos Fm.	Skouries, profile	18.764	15.718	39.021
SK-NA1	wr	Bi gneiss	Upper Vertiskos Fm.	1 km SW of Skouries	18.784	15.742	39.107
SK-5	wr	Bi gneiss	Upper Vertiskos Fm.	Skouries, profile	18.749	15.692	38.942
TS-8	wr	Bi-amph gneiss	Lower Vertiskos Fm.	Asprolakkos (Dambizi)	18.738	15.660	38.885
TS-14	wr	Bi-amph gneiss	Lower Vertiskos Fm.	Asprolakkos (Dambizi)	18.749	15.655	38.853
SK-4A	wr	Bi-amph gneiss	Lower Vertiskos Fm.	Skouries, xenolith	18.804	15.661	38.932
Lead isotope ratios of Vertiskos rocks in northeast Chalkidiki							
VAT-9	wr	Augen gneiss	Vertiskos Fm.	Vathilakkos	18.717	15.645	38.826
R-19	wr	Augen gneiss	Vertiskos Fm.	Pyragadikia	18.694	15.694	39.002
R-19	wr	Augen gneiss	Vertiskos Fm.	Pyragadikia	18.701	15.703	39.034
VAT-2	wr	Mus gneiss	Vertiskos Fm.	Vathilakkos	18.954	15.663	39.111
TS-15	wr	Mus gneiss	Vertiskos Fm.	Vathilakkos-Tsikara	18.857	15.668	39.093
TS-16	wr	Mus gneiss	Vertiskos Fm.	Vathilakkos-Tsikara	18.840	15.666	39.078
R-63	wr	Mus gneiss	Vertiskos Fm.	Metangitsi	18.918	15.685	39.104
R-62	wr	Mus gneiss	Vertiskos Fm.	Metangitsi	18.837	15.720	39.052
R-44	wr	Mus gneiss	Vertiskos Fm.	Metangitsi	18.812	15.658	39.055
G-21	wr	Mus gneiss	Vertiskos Fm.	H. Rachi-Megali Panaghia	18.662	15.654	38.742
G-101	wr	Mus gneiss	Vertiskos Fm.	H. Rachi-Megali Panaghia	18.882	15.668	39.158
R-58	wr	Mus gneiss	Vertiskos Fm.	Pyragadikia-Metangitsi	18.673	15.657	38.822
SK-VER	wr	Mus gneiss	Vertiskos Fm.	Megali Panaghia-Paleochori	18.617	15.650	38.798
G-38	wr	Mus-gar gneiss	Vertiskos Fm.	H. Rachi-Megali Panaghi	18.711	15.664	38.860
R-23	wr	Two mica schist	Vertiskos Fm.	Pyradikia	18.720	15.734	39.043
G-11	wr	Two mica schist	Vertiskos Fm.	H. Rachi-Megali Panaghia	18.639	15.676	39.089
G-1	wr	Two mica schist	Vertiskos Fm.	H. Rachi-Megali Panaghia	18.660	15.642	39.186
Lead isotope ratios of Therma-Volvi-Gomati rocks in northeast Chalkidiki							
G-105	wr	Amphibolite	TVG Complex	Megali Panaghia	18.674	15.662	38.785
G-96	wr	Amphibolite	TVG Complex	Megali Panaghia	18.726	15.646	38.845
G-86	wr	Amphibolite	TVG Complex	Megali Panaghia	18.688	15.635	38.619
AMPH	wr	Amphibolite	TVG Complex	Stratoni	18.637	15.600	38.610
MOP-22	wr	Amphibolite	TVG Complex	Morphouli, Stratoni	18.603	15.629	38.673
ST-16	wr	Amphibolite	TVG Complex	Stratoni	18.676	15.610	38.696
FIS-4	wr	Amphibolite	TVG Complex	Fisoka	18.692	15.628	38.743
JE-14	wr	Amphibolite	TVG Complex	Jerissos	18.569	15.593	38.639
JE-7	wr	Serpentinite	TVG Complex	Jerissos, Gomati	18.592	15.637	38.650
TM1-3	wr	Amphibolite	TVG Complex	Palaeochori-Varvara	18.762	15.657	38.843
TM1-4	wr	Amphibolite	TVG Complex	Palaeochori-Varvara	18.638	15.641	38.791

Reproducibility of NBS 981 lead standard during this study ($n = 43$) was 0.12% on $^{206}\text{Pb}/^{204}\text{Pb}$, 0.15% on $^{207}\text{Pb}/^{204}\text{Pb}$ and 0.23% on $^{208}\text{Pb}/^{204}\text{Pb}$ ratios at the 2σ level (95% confidence)

amph = amphibole, bi = biotite, gar = garnet, mus = muscovite, wr = whole rock; Fm. = Formation, H = Hondri

sulfide pairs are consistent with the ^{34}S increases in pyrite relative to chalcopyrite established from both theoretical and experimental studies (Sakai, 1968; Kajiwaru and Krouse, 1971). Temperatures have been determined from delta values of mineral pairs (Table 6) by utilizing the experimental fractionation curve for pyrite-chalcopyrite (Kajiwaru and Krouse, 1971) in order to see whether or not the isotopic trend is consistent with isotopic fractionation effects that are due to decreasing temperatures during the paragenetic evolution of mineralization-alteration. Early veining took place at temperatures of $\sim 484^\circ \pm 45^\circ\text{C}$, followed by a less tempered event at $\sim 380^\circ \pm 40^\circ\text{C}$ (coexistence of pyrite, chalcopyrite, chlorite, quartz, and calcite). The late propylitic alteration occurred at $\sim 213^\circ \pm 30^\circ\text{C}$. The overall temperature range of the propylitic stages is in agreement with the range of 200° to 500°C

for transitional- and late mineralization in porphyry copper deposits (Hunt, 1991). Further, the temperatures do not contradict field and thin section observations, from which a clear vein paragenetic sequence (calcite-bearing veins are younger than pure quartz veins) can be established and from which it is clear that a later propylitic event with disseminated sulfides was superimposed onto the vein stages.

Oxygen isotopes

The aim of the oxygen isotope investigation was to estimate the oxygen isotope composition of the ore-forming fluids responsible for the deposition of sulfides in quartz sulfide veins as well as to estimate the late-magmatic temperature conditions from quartz-potassium feldspar-magnetite fractionation. Results from the unaltered trachyte (sample TS-12) and the

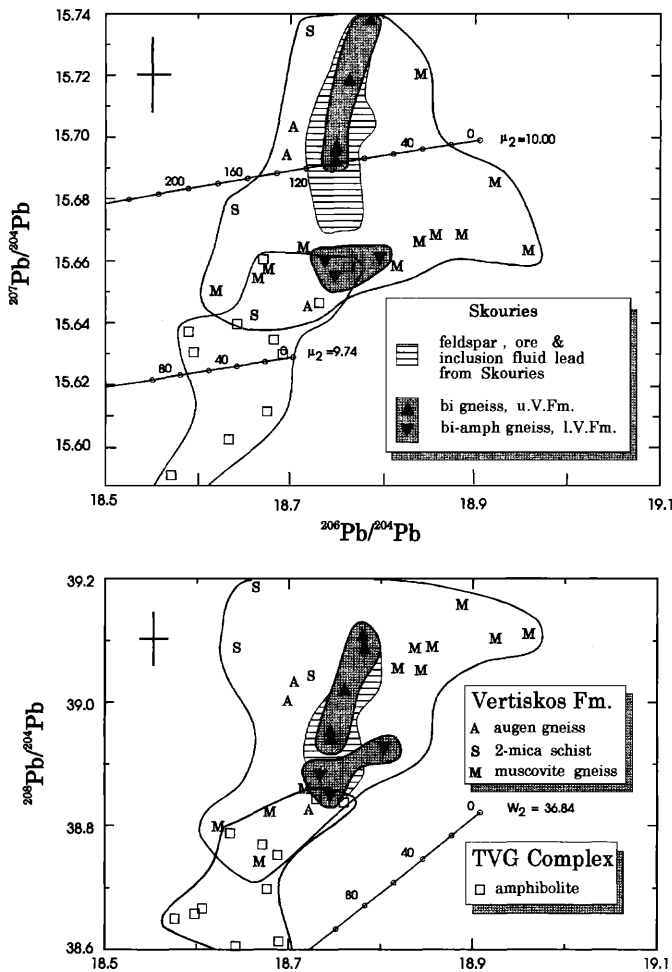


FIG. 9. Common lead isotope plot of whole-rock analyses from the Veriskos Formation and the Therna-Volvi-Gomati (TVG) Complex in northeast Chalkidiki (outlined data fields) and of lower and upper Veriskos rocks (l. V. Fm. and u. V. Fm.) from the Skouries area (shaded fields). Leads from the Skouries porphyry are plotted for comparison (hatched field). Crustal Pb growth curves for $\mu_2 = 9.74$ and 10.00 and $W_2 = 36.84$ (according to the model by Stacey and Kramers, 1975) are indicated for reference purposes.

potassically and propylitically altered porphyritic syenite (sample SK-G1) are listed in Table 7. Coexisting K feldspar and magnetite, which in the trachyte are considered primary magmatic, yield an equilibrium temperature of $636^\circ \pm 15^\circ\text{C}$, which is calculated from the experimental fractionation factors determined by Bottinga and Javoy (1973). A temperature of $589^\circ \pm 15^\circ\text{C}$ was derived for the quartz-magnetite pair of sample SK-G1, which represents phases coexisting in thin (<1.5 mm) hairline fractures formed during the potassic alteration.

One quartz sample each of an early (stage IIIA, sample SK-qtz-6) and a late (stage IIIB, sample SK-qtz-5) vein both within the porphyry and transecting the country rock were analyzed for their $\delta^{18}\text{O}$ values (Table 8). Using the temperatures deduced from the pyrite-chalcocopyrite sulfur isotope fractionation, the $\delta^{18}\text{O}$ value of the fluid was calculated from the relationship proposed by Bottinga and Javoy (1973). The range of $\delta^{18}\text{O}$ values from 3.5 to 7.6 per mil for the fluids in equilibrium with vein quartz is within the typical range of

magmatic fluids ($\delta^{18}\text{O}$ values between 5 and 13‰). Such values, however, can also be encompassed by exchanged meteoric water, exchanged seawaters, or metamorphic waters, so that no single source of the mineralizing fluids can be determined unequivocally from oxygen isotopes alone. There is no striking difference in the oxygen isotope compositions between fluids from veins within the stock and from veins transecting the country rocks, unlike the Pb and Sr isotope ratios of fluids from such veins.

Discussion

Lead isotopes

The lead isotopes from the trachyte, porphyry, and country rocks of the upper Veriskos Formation are characterized by high μ_2 (9.92–10.16) and W_2 values compared to the average crustal evolution defined by the model of Stacey and Kramers (1975). The Pb isotope pattern suggests that the lead in the ores developed in continental crustal environments with high μ_2 and W_2 values. However, the $^{207}\text{Pb}/^{206}\text{Pb}$ model ages of feldspars from the intrusion are too old (55–113 Ma) whereas the $^{208}\text{Pb}/^{206}\text{Pb}$ ages are too young. This suggests that the lead developed during a late stage of its evolution in a reservoir with high U/Pb and low Th/Pb.

The lead isotopes from biotite gneisses in the upper Veriskos pile, representing metamorphic equivalents of psammitic or graywacke-type precursors, furthermore imply that sometime in the past the rocks suffered U loss, although Th was not affected. U loss could have happened either during a metamorphic overprint or initially during sedimentation, whereas Th, remaining in more stable mineral phases, was less affected by leaching processes (during weathering, erosion, transportation, and sedimentation) than U. Biotite-amphibole gneisses in the lower Veriskos pile evolved in a similar Th/Pb system; the U/Pb ratio was distinctly lower than that of the biotite gneisses in the upper Veriskos pile.

A comparison of Figures 8 and 9 shows that the upper part of the porphyry data field, i.e., disseminated late propylitic sulfides (stage IV), coincides with the data field of the upper Veriskos gneisses. The lower part of the porphyry data field extends toward the data field defined by the biotite-amphibole gneisses of the lower Veriskos pile and toward the amphibolite data field enclosing the leads from Therna-Volvi-Gomati Complex rocks. The leads of the potassically altered porphyritic syenite and also the unaltered trachyte are best explained, therefore, as mixtures of leads from the lower and upper parts of the Veriskos Formation and possibly also of lead from the Therna-Volvi-Gomati Complex. The feldspar leads from Skouries imply that large masses of Veriskos country rock (preferentially from the lower part of the metamorphic pile) was probably assimilated by the magma during its residence at upper crustal levels prior to emplacement into shallower levels. Xenoliths of country rock within the porphyry and the occurrence of larger xenoliths at the border zone of the stock strengthen the assumption of a possible interaction of the magma with the biotite-amphibole gneisses at deeper levels. During the early propylitic stage (stage IIIA and B) Pb in vein sulfides from veins within the porphyry was dominated by a magmatic component.

The Pb isotope composition of inclusion fluids in quartz from a mineralized quartz sulfide vein (stage IIIA) transecting

TABLE 4. Rubidium and Strontium Isotope Analyses of Whole Rocks, Minerals, and Vein Fluids from the Skouries Porphyry Copper Deposit

Sample no.	Phase	Type	Alteration	Location	$^{87}\text{Sr}/^{86}\text{Sr}$	$2\sigma_{(\text{mean})}$	$^{87}\text{Rb}/^{86}\text{Sr}$	Sr (ppm)	Rb (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}_{t=19 \text{ Ma}}$
Porphyritic syenite										
TS-12	wr	Trachyte	Stage I	Skouries-Asprolakkos	0.70667	4	0.406	1,255.80	176.30	0.70656
TS-12	apa	Trachyte	Stage I	Skouries-Asprolakkos	0.70669	1				
SK-1	apa	Porphyritic syenite	Stage II	Skouries, drill core	0.70804	2				
SK-1	kfs	Porphyritic syenite	Stage II	Skouries, drill core	0.70810	3				
SK-1	kfs	Porphyritic syenite	Stage II	Skouries, drill core	0.70815	2	0.365	1,492.25	188.43	0.70805
SK-G1	wr	Porphyritic syenite	Stage IV	Skouries, old adit, dump	0.70846	3	0.862	599.38	178.53	0.70793
SK-G1	plag	Porphyritic syenite	Stage IV	Skouries, old adit, dump	0.70796	6	0.114	2,329.79	92.19	0.70796
SK-G1	kfs	Porphyritic syenite	Stage IV	Skouries, old adit, dump	0.70828	1	0.608	1,201.35	252.40	0.70812
Veins, transecting porphyritic syenite										
SK-qtz-2	Incl. fluid	Porphyritic syenite	Stage IIIB	Skouries, drill core	0.70732	22	4.119	0.180	0.256	0.70621
SK-qtz-2	Cal f. seam	Porphyritic syenite	Stage IIIB	Skouries, drill core	0.70658	18				
SK-qtz-3	Incl. fluid	Porphyritic syenite	Stage IIIB	Skouries, drill core	0.70879	24	5.512	0.138	0.262	0.70730
SK-qtz-3a	Incl. fluid	Porphyritic syenite	Stage IIIB	Skouries, drill core	0.70759	24	5.669	0.135	0.265	0.70606
SK-qtz-4	Incl. fluid	Porphyritic syenite	Stage IIIB	Skouries, drill core	0.70856	10	4.187	0.161	0.233	0.70743
SK-qtz-5	Incl. fluid	Porphyritic syenite	Stage IIIB	Skouries, drill core	0.70912	11	4.169	0.210	0.303	0.70799
Veins, transecting country rocks										
SK-qtz-6	Incl. fluid	Bi gneiss	Stage IIIA	Skouries, drill core	0.71125	18	5.255	0.112	0.203	0.70983
SK-qtz-7	Incl. fluid	Bi gneiss	Stage IIIB	Skouries, drill core	0.70977	31	4.263	0.180	0.265	0.70862
SK-qtz-8	Incl. fluid	Bi gneiss	Stage IIIA	Skouries, drill core	0.71046	30	1.943	0.170	0.114	0.70993
Country rocks										
SK-G5	wr	Bi gneiss	Unaltered	Skouries, profile	0.73514	8	3.891	98.49	132.09	0.73420
SK-G6	wr	Bi gneiss	Unaltered	Skouries, profile	0.71439	2	3.644	108.94	137.11	0.71351
SK-G7	wr	Bi gneiss	Unaltered	Skouries, profile	0.71623	4	2.668	214.58	197.74	0.71558

$2\sigma_{(\text{mean})}$ values correspond to the last digits of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios; error on the $^{87}\text{Rb}/^{86}\text{Sr}$ ratios are $<1\%$ (2σ)
 apa = apatite, bi = biotite, cal = calcite, incl. fluid = inclusion fluid, kfs = K feldspar, plag = plagioclase, wr = whole rock

the country rock (sample SK-qtz-6) differs from that in veins hosted by the porphyry (sample SK-qtz-4) by its elevated $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratio. The fluid in the vein within the porphyry is characterized by a magmatic lead, whereas fluid in the vein transecting the country rock is mainly domi-

nated by Pb from the upper Vertiskos Formation. This suggests that the lead isotope composition of the propylitic fluids is very sensitive to contamination by lead from the vein host rocks. The $^{207}\text{Pb}/^{204}\text{Pb}$ -dominant component in the vein transecting the biotite gneiss most probably was leached from narrow alteration zones around these veins, as suggested from thin section examination (see also Fig. 4). During the late stage of propylitic alteration (stage IV) Pb was derived mainly from the upper Vertiskos Formation.

Inferences for the source of Cu from Pb isotope data generally are complicated by the different behavior of these elements during the generation of magmas, by their different enrichment factors during subsequent evolution of an aqueous volatile phase, and also by their often very different con-

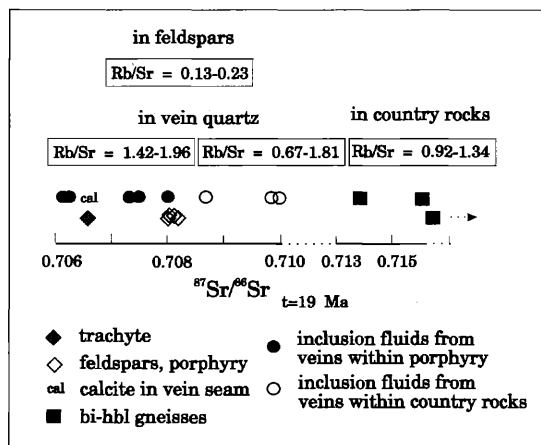


FIG. 10. Summary of the rubidium-strontium isotope results of feldspars from the trachyte dike (sample TS-12) and the porphyritic syenite and of inclusion fluids from veins transecting both the porphyry and the country rocks and from country rocks of the upper Vertiskos pile. The $^{87}\text{Sr}/^{86}\text{Sr}$ values are in situ corrected for 19 Ma.

TABLE 5. Sulfur Isotope Results of Vein Type and Disseminated Pyrite and Chalcopyrite

Sample no.	Stage	Phase	$\delta^{34}\text{S}_{\text{CDT}}$ (‰)	2σ
SK-3	IIIA	Pyrite	0.16	0.01
SK-3	IIIA	Chalcopyrite	-0.62	0.01
SK-qtz-3	IIIB	Pyrite	0.30	0.01
SK-qtz-3	IIIB	Chalcopyrite	-0.75	0.01
SK-G1	IV	Pyrite	-0.23	0.01
SK-G1	IV	Chalcopyrite	-2.14	0.01

TABLE 6. Pyrite-Chalcopyrite Sulfur Isotope Fractionation Temperatures

Sample no.	Stage	Ore type	Δ_{py-cpy} (‰)	T (°C)
SK-3	IIIA	Quartz sulfide vein	0.78	484 ± 45
SK-qtz-3	IIIB	Quartz sulfide-calcite vein	1.05	380 ± 40
SK-G1	IV	Disseminated	1.90	213 ± 30

centrations in the source rocks. Conclusions are generally based on the assumption of a common source for Pb and Cu. Under this assumption, Pb isotope data indicate a magmatic affinity of Cu during the first stage of propylitization (veining stages IIIA and B) and, similarly, that the more basic rocks from the lower Vertiskos Formation and the underlying Therma-Volvi-Gomati Complex amphibolites were a possible source for Cu during both vein stages. However, this is speculative, because Pb isotope data in the Skouries porphyry system have shown that Pb was very sensitive to contamination by country-rock lead. This could have masked preexisting lead isotope signatures pointing to other possible sources for Cu. According to Burnham and Ohmoto (1980), mafic amphibolites of the lower continental crust tend to yield partial melts that are enriched in base and precious metals and thus are appropriate source rocks for porphyry copper-type magmas. The possibility of a primary deep-seated magma generation involving lower continental crustal rocks with elevated Cu and low Pb concentrations has to be evaluated. Considering the idea of a possible connection of the two mafic bodies of Gomati and Straton (Therma-Volvi-Gomati Complex) in the synclinal structure (Fig. 2), Therma-Volvi-Gomati Complex rocks could represent potential Cu and Pb sources, because they could have been assimilated by the magma that generated the porphyries. However, lead isotope data of representative amphibolites from the Therma-Volvi-Gomati Complex ($^{206}\text{Pb}/^{204}\text{Pb}$ from 18.57–18.76, $^{207}\text{Pb}/^{204}\text{Pb}$ from 15.59–15.66, and $^{208}\text{Pb}/^{204}\text{Pb}$ from 38.61–38.85) differ from the lead in the ore minerals from Skouries and therefore contradict models involving a major contribution of Therma-Volvi-Gomati Complex Pb to the Skouries magmatic system (Frei, 1992). In view of the small alteration halo in the upper Vertiskos gneisses, it is doubtful that Cu deposited during the late propylitization (stage IV) was principally derived from the upper Vertiskos Formation. A redistribution of Cu during the change from early to late propylitic alteration, as proposed by Eliopoulos and Economou-Eliopoulos (1991), is more likely but cannot be established from the lead isotope data.

Rubidium-strontium isotopes

The initial $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.70656 for the unaltered trachyte lies within the range of 0.70547 to 0.70707 defined by

various unmineralized Tertiary intrusions in northeast Chalkidiki (Frei, 1992). The range is compatible with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios typical of magmas that have been generated in the lower crust or uppermost mantle. The markedly higher initial Sr values for the porphyry, as characterized by feldspars from potassically and propylitically altered rocks and by whole-rock analyses from a propylitized sample, which lie in the range of 0.70793 to 0.70812 (avg 0.70802 ± 8), suggest crustal contamination during either the generation and emplacement of the magma or the subsequent alteration stages. $^{87}\text{Sr}/^{86}\text{Sr}$ values from the apatites of sample TS-12 (0.70669) and sample SK-1 (0.70804) exhibit the same discrepancy, i.e., a higher initial Sr value for the porphyritic syenite than for the barren trachyte. Because the apatites have perfect idiomorphic shapes, they are considered to have remained resistant to hydrothermal alteration processes, and the shift toward higher $^{87}\text{Sr}/^{86}\text{Sr}$ values in the porphyry must have resulted from magmatic assimilation of more radiogenic crustal components in shallow levels rather than from a subsequent alteration process, during which Sr was leached from the country rocks. The analyses of Sr isotopes from lower Vertiskos rocks would help to place more constraints on the source(s) of Sr in the porphyry and the trachyte prior to the onset of the hydrothermal alteration. The present data do not allow confirmation or contradiction of the conclusion, based on Pb isotope data, that rocks of both lower and upper Vertiskos Formation were involved in the generation of the magma.

The results depicted in Figure 10 agree well with those from the Pb isotopes. Stage III vein fluids are characterized by typical magmatic Sr isotope characteristics. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the fluids are in agreement with the whole-rock Sr isotope result of 0.70656 from the unmineralized trachyte and indicate that the fluids of the first stage of propylitization were of relatively deep seated, magmatic origin. As overpressures developed and the roof began to rupture, deeper seated magmatic fluids rich in Cl, S, metals, and alkalis could ascend along fracture pathways. These fluids deposited ore minerals and led to the typical vein-type mineralizations as stockworks. The spread of the Sr isotope data of these fluids together with the observation of narrow vein-host rock alteration zones, suggesting the effectiveness of variable lead contamination of the vein fluids, both argue against a unique source of Sr. Pb and Sr isotope data rather suggest a mixture of leached components from the potassically altered porphyry and a component of deeper seated origin, characterized by $^{87}\text{Sr}/^{86}\text{Sr}$ values < ~0.706 and $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios < ~15.67 and ~38.85, respectively. Such a deep-seated fluid could have been formed by interaction of the magmatic fluid with country rocks underlying the Vertiskos Formation, for example, with amphibolites of the Therma-Volvi-Gomati Complex.

TABLE 7. Oxygen Isotope Results from Magnetite, Quartz, and K Feldspar from Trachyte and Porphyritic Syenite and Calculated Equilibrium Temperatures

Sample no.	Rock type	Stage	Phase	$\delta^{18}\text{O}_{\text{SMOW}}$	2σ	$\Delta^{18}\text{O}$ (‰)	T (°C)
TS-12	Trachyte	I	K feldspar	9.38	0.08	5.71	636 ± 15
TS-15	Trachyte	I	Magnetite	3.67	0.03		
SK-G1	Porphyry	II	Quartz	9.29	0.04	7.24	589 ± 15
SK-G1	Porphyry	II	Magnetite	2.05	0.02		

TABLE 8. Oxygen Isotope Composition of the Vein Fluids

Sample no.	Vein type	Phase	$\delta^{18}\text{O}$ (‰)	σ	T (°C)	$\delta^{18}\text{O}_{\text{fluid}}$ (‰)
SK-qtz-5	Within porphyry	Quartz	9.71	0.03	340–420	3.5–5.5
SK-qtz-6	Transecting country rock	Quartz	9.92	0.03	440–530	6.1–7.6

The distinctly higher initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in fluids from veins transecting the country rocks relative to values from fluids in veins within the porphyry suggest a contribution of Sr from the biotite gneisses of the upper Vertiskos Formation. This result is in agreement with the Pb isotope data from both vein types. The shift toward more radiogenic, appropriately in situ corrected $^{87}\text{Sr}/^{86}\text{Sr}$ values in the veins transecting the country rocks, despite the similarity of the Rb/Sr concentration ratios of primary fluid inclusions from both veins, indicates an initial isotope difference between both vein fluids, which therefore cannot have been caused by in situ decay of Rb.

Sulfur isotopes

A magmatic origin for the sulfur is indicated by the $\delta^{34}\text{S}$ values of disseminated and vein-related pyrite and chalcopyrite, which range from -2.14 to $+0.3$ per mil. Sulfur isotopes are depleted in ^{34}S in both disseminated pyrite and chalcopyrite relative to the same minerals in the veins. This could be explained either by contamination from the Vertiskos Formation or by increasing fractionation effects due to decreasing temperature. Biotite solid solution data indicate decreasing f_{O_2} during the potassic and propylitic alteration (Frei, 1992); therefore, increasing f_{O_2} cannot be responsible for the observed shift in $\delta^{34}\text{S}$ values.

Equilibrium temperatures of chalcopyrite-pyrite pairs are in accordance with the paragenetic sequence of two early propylitic vein stages at 380° to 480°C followed by the propylitic patchy alteration with disseminated pyrite and minor amounts of chalcopyrite at about 210°C . The obtained temperature range for the early propylitic vein formation is consistent with a maximum of T_{h} (temperature of homogenization into the liquid phase) data of highly saline (~ 50 – 65 wt % NaCl equiv) multiphase inclusions in vein quartz at $\sim 380^\circ \pm 65^\circ\text{C}$ (1σ) (samples L234 and L226; Tompouloglou, 1981). These inclusions are characterized by T_{s} (dissolution temperature of the last salt, i.e., halite) ranging from 450° to 600°C . The very few T_{h} data of moderately saline two-phase (liquid-vapor) inclusions in paragenetically late matrix quartz (sample L214; Tompouloglou, 1981) in the range of 270° to 300°C confirm the existence of a cooler, late propylitic alteration fluid in the Skouries porphyry copper system.

Oxygen isotopes

The temperature of $636^\circ \pm 15^\circ\text{C}$ obtained from the oxygen isotope fractionation between primary potassium feldspar and magnetite in the unaltered trachyte is at the lower end of the temperature range encountered during the emplacement of shallow intrusions. Barren porphyries are commonly emplaced at temperatures of about 600° to 900°C (Hunt, 1991). It is therefore assumed that the obtained temperature may represent the temperature at which the isotope system ceased

to equilibrate. This in turn would imply that the oxygen isotope system may have remained open during the early stages of cooling of the porphyry, i.e., at temperatures between 400° and 600°C which typically prevail during potassic alteration (Hunt, 1991). The same might be true in the case of the quartz-magnetite pair in the potassically and propylitically altered sample SK-G1. The temperature of $585^\circ \pm 15^\circ\text{C}$ is significantly lower than the temperatures deduced from secondary biotite (biotite II) solid solutions from potassically altered samples that are in the range of 670° to 810°C (Frei, 1992). Chiba et al. (1989) assume that the quartz-magnetite thermometer is very susceptible to reequilibration and generally gives erroneously low temperatures. Such effects could have played a role in sample SK-G1, because a later propylitic alteration has affected this sample. The overprint of low-temperature propylitic fluids caused redistribution of $\text{Fe}^{2+}/\text{Fe}^{3+}$ in primary and secondary biotite that in turn lowered the apparent equilibrium temperatures from values of 670° to 810°C to values varying from 481° to 505°C (Frei, 1992).

From the isotope composition of quartz, it can be concluded that the syenite porphyry of Skouries is most probably characterized by whole-rock $\delta^{18}\text{O}$ values below approximately 9.3 per mil and therefore might be classified as an I type or magnetite series intrusion (Takahashi et al., 1980). This would be in agreement with other discrimination criteria (Sasaki and Ishihara, 1979; Ishihara, 1981), i.e., an $^{87}\text{Sr}/^{86}\text{Sr}$ whole-rock value of 0.7066, a whole-rock sulfur isotope value of 4.6 per mil (Frei, 1992) and f_{O_2} values reaching the hematite-magnetite redox buffer (Frei, 1992) in the barren trachyte (sample TS-12). Also, the associated Cu (Au) \pm Mo mineralization and the occurrence of hornblende as a diagnostic mineral can be taken as a further indication for a magnetite series intrusion.

The oxygen isotope composition of the fluid that coexisted with quartz in the early propylitic veins was in the range 3.5 to 7.3 per mil, which indicates a fluid in equilibrium with the magma. The analyses of D/H isotopes would further help to elucidate whether or not meteoric water was involved at some stage during hydrothermal alteration at Skouries.

Summary and Conclusions

The results of this study of the porphyritic syenite of Skouries and its associated porphyry copper-type mineralization are summarized in Table 9. They can be described as follows.

Lead isotopes from the Skouries deposit indicate a crustal affinity and correspond to the isotopic characteristics of other basic to intermediate porphyric intrusions in the area, some of which (Fisoka, Alatina) are related in space and time to economically important Pb-Zn (Au, Ag) replacement deposits (Madem Lakkos, Mavres Petres) with similar lead isotope characteristics (Frei, 1992; Gilg, 1993; Frei and Gilg, in prep.). The lead isotope similarity between intruded country

TABLE 9. Summary of the Pb, Sr, O, and S Isotope Results from the Skouries Porphyry Cu System

Stage	Pb	Sr	O	S
Magmatic (I)	Barren trachyte; $^{206}\text{Pb}/^{204}\text{Pb} = 18.752 \pm 13$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.677 \pm 7$, $^{208}\text{Pb}/^{204}\text{Pb} = 38.869 \pm 25$; contribution of Pb from the upper and lower Vertiskos Fm.	Barren trachyte; $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.70656$; contribution of Sr from the lower Veriskos Fm., deeper seated origin of Sr (TVG Complex, upper mantle to lower crust?)	$T_{\Delta\text{kfs-mgt}} \sim 640^\circ\text{C}$	
Potassic (II)	Porphyritic syenite; $^{206}\text{Pb}/^{204}\text{Pb} = 18.749 \pm 6$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.685 \pm 8$, $^{208}\text{Pb}/^{204}\text{Pb} = 38.919 \pm 25$; contribution of Pb from the upper and lower Vertiskos Fm.	Porphyritic syenite; $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.70805$ (potassically altered samples); additional contribution of Sr from the upper Vertiskos Fm.	$T_{\Delta\text{qtz-mgt}} \sim 590^\circ\text{C}$	
Early propylitic (IIIA and B)	Ore minerals from veins in the porphyry; $^{206}\text{Pb}/^{204}\text{Pb} = 18.739 \pm 12$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.685 \pm 10$, $^{208}\text{Pb}/^{204}\text{Pb} = 38.915 \pm 16$; ore deposition in veins is characterized by magmatic Pb, vein fluids have Pb characteristics of their hosts, i.e., the porphyry and biotite gneisses	$^{87}\text{Sr}/^{86}\text{Sr}_{\text{fluid}} = 0.70700 \pm 83$, veins in the porphyry $^{87}\text{Sr}/^{86}\text{Sr}_{\text{fluid}} = 0.70946 \pm 73$; veins in biotite gneisses, deeper seated source of Sr in vein fluids from veins within the porphyry, contamination of the vein fluid by radiogenic Sr from the biotite gneisses in veins within the country rocks	$\delta^{18}\text{O}_{\text{fluid}} \sim 3.5\text{--}7.6$ per mil (fluids in equilibrium with the magma)	Substage IIIA: $T_{\Delta\text{pv-cpy}} \sim 440^\circ\text{--}530^\circ\text{C}$ Substage IIIB: $T_{\Delta\text{py-cpy}} \sim 340^\circ\text{--}420^\circ\text{C}$
Late propylitic (IV)	Disseminated ore minerals; $^{206}\text{Pb}/^{204}\text{Pb} = 18.758 \pm 13$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.706 \pm 12$, $^{208}\text{Pb}/^{204}\text{Pb} = 39.000 \pm 43$; major contribution of Pb from the biotite gneisses of the upper Vertiskos Fm.	$^{87}\text{Sr}/^{86}\text{Sr} = 0.70800 \pm 10$ (propylitically altered porphyry); magmatic origin of Sr plus additional radiogenic Sr contribution from the biotite gneisses		$T_{\Delta\text{py-cpy}} \sim 210^\circ\text{C}$

rocks of the Vertiskos Formation and the overall lead isotope pattern outlined by whole rock, feldspar, and ore minerals from Skouries suggests a major contribution, possibly by assimilation, of country rocks from the Vertiskos Formation at depth prior to the final emplacement. This in turn suggests the existence of a magma plume that resided for some time at crustal levels before giving rise to individual, shallow-level porphyritic intrusions. Dominantly northeast-southwest-trending, steep faults (Voidomatis et al., 1990) in the Serbomacedonian zone seem to have triggered the final emplacement by creating pathways for the deeper seated magma.

Cu deposition mainly occurred during two subsequent vein stages (stage IIIA and B) at temperatures of 340° to 420°C and 440° to 530°C , respectively. The depositional temperatures calculated from the sulfur isotope fractionation are in agreement with the T_{hy} -temperature range of $\sim 300^\circ$ to 600°C of highly saline multiphase fluid inclusions in vein quartz (Tompouloglou, 1981). A rough estimate of the proportion of Cu deposited in veins relative to Cu deposited as disseminations in the stockwork indicates a ratio of about 3/1 to 5/1. Combined Pb and Sr isotope data allow speculation on the source of Cu in the porphyry. They both suggest that most of the Cu in the Skouries deposit was derived from the magma, which was contaminated by country-rock lead farther down in the lithologic pile, most probably from the lower Vertiskos Formation or the Therma-Volvi-Gomati Complex. Rocks from the upper Vertiskos Formation are unlikely to have been a major source for Cu deposited during propylitization. The lack of a wide alteration halo around the porphyry can be taken as further evidence that significant Cu was not leached from the upper Vertiskos Formation. The oxygen isotope composition of the fluid in equilibrium with vein quartz is in the range of typical magmatic fluids. The $\delta^{34}\text{S}$ values of vein pyrite (0.2‰) and chalcopyrite (-0.7‰) indicate a magmatic source for the sulfur as well.

The onset of a more localized, patchy, and late propylitic alteration (stage IV) affecting the host as well as the country rocks in a narrow alteration halo has led to disseminated mineralization consisting of pyrite and minor chalcopyrite. This alteration took place at about 210°C as calculated from the sulfur isotope fractionation between pyrite and chalcopyrite. This temperature is consistent with fluid inclusion homogenization temperatures obtained on matrix quartz formed during the late propylitic stage (Tompouloglou, 1981). During this stage, the upper part of the Vertiskos Formation was the main contributor of lead.

From the results of the combined strontium and lead isotope investigation of vein-related ore minerals and vein fluids, it can be further concluded that ore hosted in early propylitic quartz sulfide-(calcite) veins mainly contains a magmatic lead (identical to the feldspar lead) plus a lead component probably derived from the intruded country rock (biotite gneisses) of the upper Vertiskos metamorphic pile. The lead isotope analyses of fluids from inclusions within veins correspond to those of their host rocks. Therefore, the lead in fluids is a very sensitive isotope tracer. Strontium isotopes from vein fluids are an equally sensitive tracer for elucidating the hypogene leaching processes in this porphyry system. From the Sr isotope study of vein fluids it can be concluded that the mineralizing fluid, from which the Cu was deposited, is of magmatic origin and that Sr isotope contamination has taken place where these veins crosscut the country rocks. Surprisingly, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from vein fluids from within the porphyry (0.7062–0.7079) are even lower than those of feldspars (0.7079–0.7082), indicating that these fluids could ascend rapidly from deeper seated levels without reacting with the porphyry. Magmatic fluids from Skouries show the same Sr isotope characteristics as the barren trachyte ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7066$) and are very similar to initial $^{87}\text{Sr}/^{86}\text{Sr}$ values from other barren porphyritic intrusions in the area, such as those at Tsikara, Vathilakkos, Asprolakkos, and Stratonis (Frei, 1992).

The lack of an extensive alteration around the stock and the oxygen isotope composition of the mineralizing fluid ($\delta^{18}\text{O} = 3.5\text{--}7.6\text{‰}$), which is compatible with magmatically derived oxygen, show that the porphyry copper at Skouries remained a self-sustaining and unaffected magmatic system throughout its life. It appears likely that meteoric hydrothermal circulation outside the potassic zone as proposed by the model of Lowell and Guilbert (1970) did not exist, because external phyllic, argillic, and propylitic zones are not established. Thus, Skouries differs from the many examples where external hydrothermal convection cells produced extensive alteration halos. The lack of such a halo, therefore, should not be misinterpreted as indicating the absence of mineralization in the central, mainly potassic alteration zone of a porphyry.

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REFERENCES

- Amov, B.G., Bogdanov, B., and Baldzieva, C., 1974, Izotopni sostav suinca i nekotore voprosi genezisa i vozrasta orudneniy yuzhnoy Bolgarii: International Association on the Genesis of Ore Deposits (IAGOD) Quadrennial Symposium, 4th, Proceedings, v. 2, p. 13-25.
- Bottinga, Y., and Javoy, M., 1973, Comments on oxygen isotope geothermometry: *Earth and Planetary Science Letters*, v. 20, p. 250-265.
- Burnham, C.W., and Ohmoto, H., 1980, Late-stage processes of felsic magmatism: *Society of Mining Geologists of Japan Special Issue* 8, p. 1-11.
- Channell, J.E.T., and Horvath, F., 1976, The African/Adriatic promontory as a paleogeographical premise for Alpine orogeny and plate movements in the Carpatho-Balkan region: *Tectonophysics*, v. 35, p. 71-101.
- Chiba, H., Chacko, T., Clayton, R.N., and Goldsmith, J.R., 1989, Oxygen isotope fractionations involving diopside, forsterite, magnetite, and calcite: Application to geothermometry: *Geochimica et Cosmochimica Acta*, v. 53, p. 2985-2995.
- Clayton, R.N., and Mayeda, T.K., 1963, The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis: *Geochimica et Cosmochimica Acta*, v. 27, p. 43-52.
- Dewey, J.E., Pitman, W.C., Ryan, W.B.F., and Bonnin, J., 1973, Plate tectonics and the evolution of the Alpine system: *Geological Society of America Bulletin*, v. 84, p. 3137-3180.
- Dixon, J.E., and Dimitriadis, S., 1984, Metamorphosed ophiolitic rocks from the Serbo-Macedonian Massif near Lake Volvi, north-east Greece, in Dixon, J.E., and Robertson, A.H.F., eds., *The geological evolution of the eastern Mediterranean*: Geological Society of London Special Publication 17, p. 603-618.
- Eliopoulos, D.G., and Economou-Eliopoulos, M., 1991, Platinum-group element and gold contents in the Skouries porphyry copper deposit, Chalkidiki peninsula, northern Greece: *Economic Geology*, v. 86, p. 740-749.
- Fytikas, M., Giullani, O., Innocenti, F., Mannetti, P., Mazzuoli, R., Peccerillo, A., and Villari, L., 1980, Neogene volcanism of the northern and central Aegean region: *Annales Géologiques des Pays Helleniques*, v. 30, p. 106-129.
- Frei, R., 1992, Isotope (Pb,Rb-Sr,S,O,C,U-Pb) geochemical investigations on Tertiary intrusives and related mineralizations in the Serbomacedonian Pb-Zn, Sb + Cu-Mo metallogenetic province in northern Greece: Unpublished Ph.D. dissertation, Zürich, Switzerland, Eidgenössische Technische Hochschule (ETH), 231 p.
- Gilg, H.A., 1993, Geochronology (K-Ar), fluid inclusion, and stable isotope (C,H,O) studies of skarn, porphyry copper, and carbonate hosted Pb-Zn (Ag,Au) replacement deposits in the Kassandra mining district (eastern Chalkidiki, Greece): Unpublished Ph.D. dissertation, Zürich, Switzerland, Eidgenössische Technische Hochschule (ETH), 153 p.
- Gilg, H.A., and Frei, R., 1994, Chronology of magmatism and mineralization in the Kassandra mining area: Implications for the potentials and limitations of dating hydrothermal illites: *Geochimica et Cosmochimica Acta*, v. 58, p. 2107-2122.
- Hunt, J.P., 1991, Porphyry copper deposits: *Economic Geology Monograph* 8, p. 192-206.
- Institute of Geology and Mining Research, 1978, Stratoniki sheet: Athens, Publication Department of Geological Maps.
- Irvine, N.T., and Baragar, A.R.W., 1971, A guide to the chemical classification to the common volcanic rocks: *Canadian Journal of Earth Sciences*, v. 8, p. 523-548.
- Ishihara, S., 1981, The granitoid series and mineralization: *Economic Geology 75th Anniversary Volume*, p. 458-484.
- Jankovic, S., 1977, Metallogeny and plate tectonics in the northeastern Mediterranean, in Dimitrijevic, M., and Grubic, A., eds., *Models of geotectonic development of the northeastern Mediterranean*: Belgrade, Faculty of Mining and Geology, p. 59-103.
- 1978, The isotopic composition of lead in some Tertiary lead-zinc deposits within the Serbo-Macedonian metallogenetic province (Yugoslavia): *Geoloski Anali Balkanskoga Paluostrova (Annales géologiques de la péninsule balkanique)*, v. 42, p. 507-525.
- Kajiwaru, Y., and Krouse, H.R., 1971, Sulfur isotope partitioning in metallic sulfide systems: *Canadian Journal of Earth Sciences*, v. 8, p. 1397-1408.
- Kalogeropoulos, S.I., Kiliass, S.P., Bitzios, D.C., Nicolau, M., and Both, R.A., 1989, Genesis of the Olympias carbonate-hosted Pb-Zn(Au,Ag) sulfide ore deposit, eastern Chalkidiki peninsula, northern Greece: *Economic Geology*, v. 84, p. 1210-1234.
- Kalogeropoulos, S.I., Economou, G.S., Gerouki, F., Karamonou, E., Kougoulis, C., and Perlikos, P., 1991, The mineralogy and geochemistry of the Stratoniki granodiorite and its metallogenetic significance: *Geological Society of Greece Bulletin*, v. 25, p. 225-243.
- Kockel, F., Mollat, H., and Gundlach, H., 1975, Hydrothermally altered and (copper) mineralized porphyritic intrusions in the Serbomacedonian Massif (Greece): *Mineralium Deposita*, v. 10, p. 195-204.
- Kockel, F., Mollat, H., and Walther, H.W., 1977, Erläuterungen zur geologischen Karte der Chalkidiki und angrenzender Gebiete 1:100000 (Nord-Griechenland): Hannover, Bundesanstalt für Geowissenschaften und Rohstoffe, 119 p.
- Lowell, J.D., and Guilbert, J.M., 1970, Lateral and vertical alteration mineralization zoning in porphyry ore deposits: *Economic Geology*, v. 65, p. 538-550.
- Nebel, M.L., Hutchinson, R.W., and Zartman, R.E., 1991, Metamorphism and polygenesis of the Madem Lakkos polymetallic sulfide deposit, Chalkidiki, Greece: *Economic Geology*, v. 86, p. 81-105.
- Nesbitt, R.W., Billett, M.F., Ashworth, K.L., Deniel, C., Constantinides, A., Demetriades, A., Katirtzoglou, C., Michael, C., Mproskos, E., Zachos, S., and Sanderson, D., 1988, The geological setting of base metal mineralisation in the Rhodope region, northern Greece, in Boissonnas, J., and Omenetto, P., eds., *Mineral deposits within the European Community*: Berlin, Heidelberg, Springer Verlag, p. 499-514.
- Neubauer, W.H., 1957, Geologie der blei-zinkreichen Kieslagerstätten von Kassandra (Chalkidiki, Griechenland): *Berg und Hüttenmännische Monatshefte*, v. 102, p. 1-16.
- Nicolau, M.N., 1960, L'intrusion granitique dans la région de Stratoniki-Olympiade et sa relation avec la metallogenèse: *Annales Géologiques des Pays Helleniques*, v. 11, p. 214-265.
- 1964, The mineralogy and micrography of the sulphide ores of Kassandra mines, Greece: *Annales Géologiques des Pays Helleniques*, v. 16, p. 111-139.
- 1969, Recent research on the composition of the Kassandra Mines orebodies: *Praktika tes Akademias Athenon*, v. 44, p. 82-93 (in Greek with English abstract).
- Papadakis, A., 1971, On the age of the granitic intrusion near Stratonion

- Chalkidiki, Greece: *Annales Géologiques des Pays Helléniques*, v. 23, p. 297–300.
- Pavrides, S.B., and Tranos, M.D., 1991, Structural characteristics of two strong earthquakes in the North Aegean: Ierissos (1932) and Agios Efstratios (1968): *Journal of Structural Geology*, v. 13/2, p. 205–214.
- Sakai, H., 1968, Isotopic properties of sulfur compounds in hydrothermal processes: *Geochemical Journal*, v. 2, p. 29–49.
- Sakellariou, D., 1989, *Geologie des Serbomazedonischen Massivs in der nordöstlichen Chalkidiki, N-Griechenland—Deformation und Metamorphose*: Unpublished Ph.D. dissertation, Athens, Greece, National and Kapodistrian University, 177 p.
- Sasaki, A., and Ishihara, S., 1979, Sulfur isotopic composition of the magnetite-series and ilmenite-series granitoids in Japan: *Contributions to Mineralogy and Petrology*, v. 68, p. 107–115.
- Stacey, J.S., and Kramers, J.D., 1975, Approximation of terrestrial lead isotope evolution by a two-stage model: *Earth and Planetary Science Letters*, v. 26, p. 207–221.
- Takahashi, M., Aramaki, S., and Ishihara, S., 1980, Magnetite-series/ilmenite-series vs. I-type/S-type granitoids: *Society of Mining Geologists Special Issue 8*, p. 13–28.
- Tompouloglou, C., 1981, *Les minéralisations Tertiaires, type cuivre porphyrique, du Massif Serbo-Macédonien (Macédoine Grèce) dans leur contexte magmatique (avec un traitement géostatistique pour les données due prospect d'Alexia)*: Unpublished Ph.D. dissertation, Paris, France, Ecole Nationale Supérieure des Mines de Paris, 204 p.
- Voidomatis, P.S., Pavrides, S.B., and Papadopoulos, G.A., 1990, Active deformation and seismic potential in the Serbomacedonian zone, northern Greece: *Tectonophysics*, v. 179, p. 1–9.
- Yanagisawa, F., and Sakai, H., 1983, Thermal decomposition of barium-sulfate-vanadium pentoxide-silica glass mixtures for preparation of sulfur dioxide in sulfur isotope ratio measurements: *Analytical Chemistry*, v. 55, p. 985–987.
- Zachos, K., 1963, Discovery of a copper deposit in Chalkidiki peninsula, N-Greece: *Geological and Geophysical Research*, v. 8, p. 1–26.