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Petrology and geochemistry of the shoshonite-hosted Skouries porphyry Cu–Au deposit, Chalkidiki, Greece

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Abstract The Skouries porphyry Cu–Au deposit, containing an indicated reserve of 206 Mt at 0.54% Cu and 0.80 g/t Au, is hosted by at least four hypabyssal monzonite–porphyry phases. In decreasing age, they are: (1) pink monzonite, (2) main monzonite, (3) intra-mineral monzonite, and (4) late-stage porphyry. High-grade ore is directly associated with the main and intra-mineral monzonite phases. All intrusive phases are cut by late-stage monzonite dykes that are barren. The monzonites have porphyritic textures with phenocrysts of plagioclase, alkali feldspar and amphibole as well as apatite and titanite microphenocrysts in a fine-grained feldspar-dominated groundmass. Mineralized samples are affected to varying degrees by potassic alteration, ranging from weak biotite–magnetite disseminations, through cross-cutting veinlets of hydrothermal orthoclase, to zones with pervasive orthoclase flooding. The high halogen contents of the Skouries intrusions are reflected in the high Cl and F concentrations of mica phases (up to 0.19 and 2.48 wt% respectively). The presence of magmatic magnetite in all intrusive phases implies high oxygen fugacities of the parental melts. All four monzonite phases have relatively evolved compositions, as reflected by their high SiO_2, low MgO and low mg#, and variable but low contents of mantle-compatible elements such as V, Ni and Co. However, their mg# suggests increasing degrees of fractionation of the parental melts with decreasing age. Their high K_2O (up to 5.8 wt%) and K_2O/Na_2O ratios (>1), as well as their high Ce/Yb and Th/Yb ratios (>34 and >21 respectively), which are believed to have been unaffected by alteration processes, are typical of alkaline rocks of the shoshonite association. Importantly, the Skouries intrusions are characterized by very high U and Th contents (up to 18.9 ppm and 62 ppm, respectively) that are consistent with accessory thorite and rare allanite in several samples. The high initial $^{87}Sr/^{86}Sr$ ratios (0.7082) for the Skouries intrusions suggest crustal contamination during emplacement. The use of geochemical discrimination diagrams assigns the rocks to a continental arc setting in accord with the interpretation of previous workers.

Keywords Skouries · Greece · Porphyry copper–gold · Shoshonite

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Introduction

The aim of this study is the documentation of the alkaline rocks that host porphyry Cu–Au mineralization at Skouries, Chalkidiki Peninsula, Greece. While previous workers have proposed a sub-alkaline character for the Skouries intrusions (e.g. Perantonis 1982; Tarkian and Stribrny 1999), our data clearly assign them to the shoshonite association as defined by Joplin (1968) and Morrison (1980).

Geological overview

The Skouries porphyry Cu–Au deposit is situated on the Chalkidiki Peninsula of northeastern Greece, approximately 90 km southeast of Thessalonica, and is part of the Kassandra mining district. This district lies within the Serbomacedonian metallogenic province, which, in turn, is part of the Serbomacedonian Massif (SMM). The SMM is a NW–SE-oriented tectono-magmatic belt perpendicular to the closing direction of the western Tethys, i.e. the NE-trending collision zone between Africa and Europe (Kockel et al. 1975; Frei 1995).

The SMM consists of crystalline series which have undergone almandine–amphibolite facies metamorphism during Paleozoic and Pre-Paleozoic times. The crystalline basement is unconformably overlain by late Paleozoic sedimentary rocks. During a Mesozoic orogeny, these sedimentary rocks were interfolded with the basement rocks and metamorphosed to the greenschist facies (Kockel et al. 1975).

The crystalline basement of the SMM comprises two lithostratigraphic–tectonic units, the lower Kerdyllia Formation and the upper Vertiskos Formation, separated by the NW-striking Stratoni–Varvara fault (Fig. 1). The Megali Panagia–Gomati fault, which also trends NW–SE, forms the southwestern border of the Vertiskos Formation. Both faults define the boundaries of a large synformal structure in which gneisses and schists of the Paleozoic or older Vertiskos Formation predominate (Frei 1995). The SMM mainly consists of gneisses of the Vertiskos Formation.

The Vertiskos Formation consists of muscovite–garnet–biotite–staurolite–tourmaline schists, amphibolite lenses and two-mica schists, and contains abundant quartz lenses and veins. It has suffered retrograde metamorphism to the greenschist facies. The Kerdyllia Formation is at higher metamorphic grade and comprises biotite, biotite–plagioclase and hornblende–biotite gneisses, amphibolite and several marble lenses. The precursor rocks of this formation were greywacke, limestone, calcareous marl and thin andesitic tuffaceous sedimentary layers. In the northeast of the Chalkidiki Peninsula of northern Greece a zone with mainly ultrabasic to basic rocks can be distinguished within the metasedimentary sequences of the Vertiskos and Kerdyllia Formations (Frei 1992). These ultrabasic rocks belong to the Therma–Golvi–Gomati (TVG) Complex, which is interpreted to represent ophiolites of the Kimmerian suture zone (cf. Frei 1992, and references therein).

The Serbomacedonian metallogenic province is a NW–SE-trending Alpine belt of Pb–Zn–(Cu–Mo–Sb) deposits mainly comprising Pb–Zn replacement, fracture-controlled Sb-vein-, Cu–Mo porphyry, and stratiform volcano-sedimentary deposits. All these deposits are interpreted to be related to Tertiary magmatic activity (Frei 1995).

During the Early Oligocene the SMM was intruded by a series of dioritic to andesitic porphyry stocks that have been derived in a continental arc setting and define a NE–SW-trending belt in the northeastern Chalkidiki Peninsula. Some of these intrusions are accompanied by characteristic phyllic alteration halos (Fig. 1). The Skouries porphyry intrusions were emplaced into the metamorphic basement of the SMM at 19 Ma (Frei 1995) and belong to a series of intrusions that were emplaced into the lower amphibolite facies mica schists and biotite gneisses of the Vertiskos Formation (Kockel et al. 1975; Kalogeropoulos 1986; Tobey et al. 1998).

The multiple hypabyssal pipe-like intrusions that host the Skouries deposit extend at surface over an area of approximately 200×200 m and have a vertical extent of 700 m (Tobey et al. 1998).

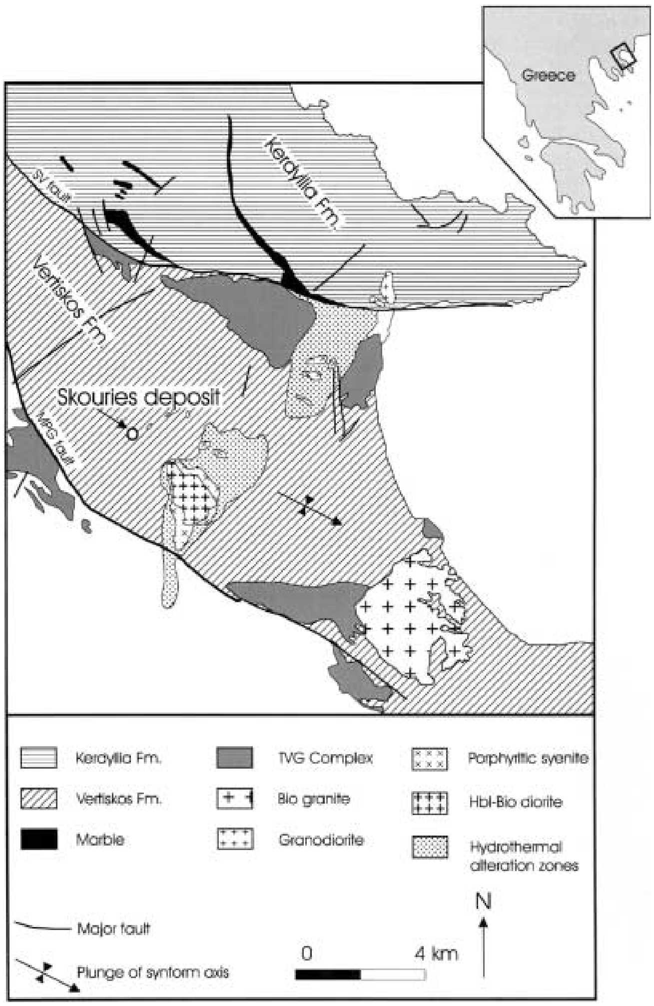

Fig. 1 Geological sketch map of northeast Chalkidiki Peninsula (Greece) showing location of the Skouries porphyry Cu–Au deposit (modified after Frei 1995). *SV fault* and *MPG fault* mark the locations of the Stratoni–Varvara and the Megali Panagia–Gomati faults, respectively

These hypabyssal intrusions were emplaced along a deep-seated NW–SE-striking fault system (Veranis 1994).

Porphyry Cu–Au mineralization

Systematic resource drilling by TVX Gold Inc. has defined an indicated reserve of 206 Mt at 0.54% Cu and 0.80 g/t Au (Magri et al. 1998; Tobey et al. 1998). Porphyry Cu–Au mineralization at Skouries is mainly of veinlet type, comprising pyrite, chalcopyrite and bornite. High-grade ore is characterized by intense potassic alteration, including secondary (hydrothermal) orthoclase and biotite–magnetite assemblages. In places, hydrothermal biotite crystals, as large as 1 cm in length, occur along small veins associated with hydrothermal magnetite. However, typically the hydrothermal biotite–magnetite assemblage occurs as fine-grained pervasive disseminated grains. Hydrothermal orthoclase ranges from patchy replacements of plagioclase phenocrysts, through cross-cutting veinlets, to zones with pervasive flooding.

Importantly, the large propylitic and phyllic alteration zones, that are common in many porphyry Cu deposits, are not present at Skouries (Tobey et al. 1998). In fact, the wall-rock gneisses have been overprinted by a moderate propylitic alteration that forms only a narrow (<50 m wide) contact halo around the intrusions (Frei 1995). The propylitic alteration mainly consists of chlorite and albite. Epidote is rare, probably due to the relatively aluminous composition of the wall-rock mica schists (cf. Kroll 2001).

Restricted phyllic alteration consisting of sericite and quartz with lesser amounts of calcite and dolomite post-dates both the potassic and propylitic alteration assemblages, and is mainly developed along structures. The phyllic alteration is commonly centred on late-stage barren dykes, and consists of sericite, quartz, dolomite and calcite.

Perantonis (1982) described a vertical zoning of metal mineralogy and overall metal content in the orebody. The upper part consists of an oxidized zone with azurite–malachite assemblages that is underlain by a supergene enrichment zone comprising mainly covellite. Hypogene ore mainly consists of quartz–chalcopyrite–pyrite–bornite stockwork veinlets with sulfide contents of about 2–3 vol% (Perantonis 1982). However, chalcopyrite can also occur as fine-grained disseminations and, in places, replaces mafic phenocrysts or hydrothermal magnetite. The characterization of veinlet types at Skouries is directly derived from the definitions given by Gustafson and Hunt (1975). Early-stage A-type quartz veinlets (1–2 mm in thickness) can be distinguished from B-type veins. The discontinuous and curvilinear A-type veinlets contain embayments of plagioclase phenocrysts and are interpreted to have formed under semiductile conditions within the main monzonite intrusion. They contain disseminated chalcopyrite–bornite assemblages. In contrast, B-type veinlets are characteristically regular and continuous with variable thicknesses, from 0.5 to 8.0 mm. They typically have continuous planar structures with internal banding consisting of quartz with fine trails of chalcopyrite. The B-type veins commonly have orthoclase selvages. Both vein types are cut by late-stage pyrite veins (<2 mm in thickness) with sericitic halos. These D-type veins normally occupy continuous, though locally irregular, systematically oriented fractures.

The Skouries porphyry Cu–Au deposit has important Pd credits of up to 480 ppb that are interpreted to be intrinsic to the system (Tarkian and Stribrny 1999).

Mineralogy and petrography of the alkaline porphyries

Petrographically, four main intrusive phases can be distinguished (Fig. 2): (1) pink monzonite porphyry, (2) main porphyry, (3) intramineral porphyry, and (4) barren porphyry (Tobey et al. 1998). Characteristic samples are shown in Fig. 3.

The *pink monzonite porphyry* is coarse-grained with crowded porphyritic texture and normally contains up to 60 vol% phenocrysts, comprising alkali feldspar (< 40 mm), plagioclase (< 8 mm), amphibole (< 3 mm) and apatite microphenocrysts set in a fine-grained feldspar-dominated groundmass (Fig. 3b). In places, the pink monzonite porphyry contains anhydrite veinlets and patches (< 2 mm). The rock was affected by a weak, selectively pervasive potassic alteration, resulting in partial replacement of plagioclase phenocrysts by hydrothermal orthoclase and of amphibole by hydrothermal biotite. The fine-grained hydrothermal biotite–magnetite assemblage commonly occurs in clusters up to 3 mm in diameter that are distributed throughout the rock (Kroll 2001). The pink monzonite is only weakly mineralized by B-type quartz–pyrite–chalcopyrite veinlets (0.5–4.0 mm) with orthoclase selvages. In places, the pink monzonite is cut by quartz–chalcopyrite–molybdenite veinlets.

The *main porphyry* is intimately associated with high-grade ore and stockwork mineralization (Fig. 3e, f). The rock consists of medium-grained, pinkish-grey monzonite with up to 60 vol% phenocrysts of plagioclase (< 10 mm), alkali feldspar (< 8 mm), amphibole (< 5 mm) and apatite (< 0.5 mm) set in a very fine-grained feldspar-dominated groundmass. The main porphyry is affected by strong potassic alteration which may be subdivided into hydrothermal orthoclase (Fig. 3d) and hydrothermal biotite–magnetite assemblages (Fig. 3c). Hydrothermal orthoclase typically occurs as veinlets (2–5 mm) and, less commonly, forms pink zones of pervasive, texturally destructive flooding. The hydrothermal biotite–magnetite assemblage normally occurs as pervasive disseminations and, less commonly, as narrow (0.1–10 mm) veinlets with quartz. The main monzonite porphyry is strongly mineralized, with high-grade ore normally characterized by abundant quartz–chalcopyrite-bornite stockwork veinlets (3.0–8.0 mm). The sulfides either occur as trails (i.e. B-type veinlets) or as disseminations within quartz stockwork veinlets. In places, hydrothermal magnetite is replaced by disseminated chalcopyrite. The stockwork veinlets are discontinuous and vary in thickness from 1 to 10 mm.

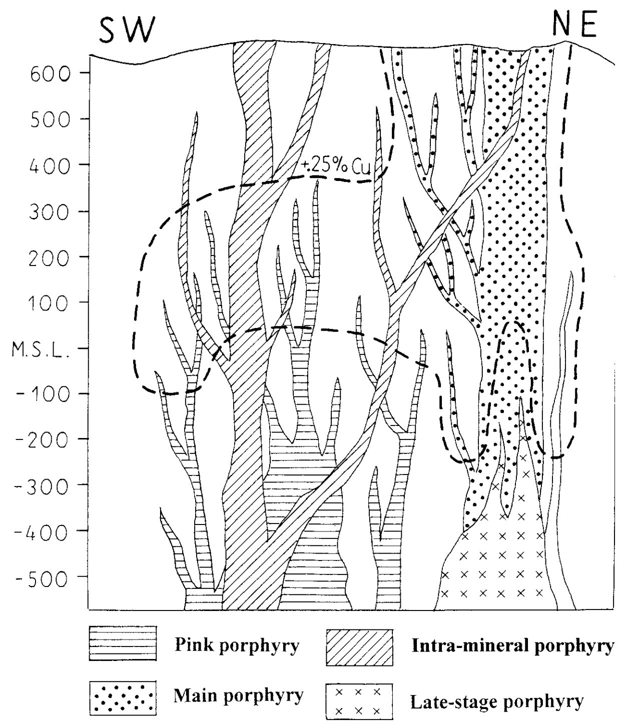

Fig. 2 Geological cross section of the Skouries intrusions showing the cross-cutting relationships between the four phases: pink monzonite, main monzonite, intra-mineral monzonite and barren monzonite porphyries. Copper contents > 0.25% are shown by the *dashed line*. Horizontal scale equals vertical scale, the latter of which is shown on the figure. Taken from Tobey et al. (1998)

Late-stage veinlets are normally surrounded by alteration halos in which sericite has replaced biotite; they are inferred to have formed during waning stages of orthomagmatic activity.

The *intra-mineral porphyry* cuts both the pink monzonite and main porphyries (Fig. 2) and consists of porphyritic, medium- to coarse-grained grey monzonite with about 45 vol% alkali feldspar phenocrysts (< 15 mm), plagioclase (< 8 mm), amphibole (< 5 mm) and apatite (< 0.5 mm) in a fine-grained feldspar-dominated groundmass. The intra-mineral porphyry is weakly to moderately mineralized by chalcopyrite–bornite S-type veinlets (1 mm) and affected by intense potassic alteration. The potassic alteration typically consists of hydrothermal biotite and magnetite forming pervasive and texturally destructive clusters or interstitial disseminations in the groundmass. In places, both mafic phenocrysts and hydrothermal magnetite grains are partly replaced by chalcopyrite.

The final stage of mineralization was accompanied by intense chlorite–pyrite–specularite alteration accompanied by removal and remobilization of Cu and Au to higher levels where the metals were redeposited in almost pure sulfide 'S-type' veinlets (1 mm to 15 cm) consisting of chalcopyrite–bornite ± quartz (Tobey et al. 1998). These S-type veinlets are defined by high sulphide contents, comprising chalcopyrite and bornite with common, but lesser, digenite ± covellite and by minor contents of quartz and alkali feldspar (E. Tobey, personal communication, 2001). The S-type veins normally have weak chlorite–Fe oxide alteration halos. Due to this alteration effects, it has not been possible to decide which was the causative intrusion, although the presence of abundant aplite and vein dykes and cross-cutting barren monzonite dykes are suggestive of a deep, late-stage intrusion, which has been termed the *late oxidized porphyry* (Tobey et al. 1998). This hypothetical intrusion, as well as the related cross-cutting monzonite dykes, probably represent a barren late-stage melt portion from the fractionating magma chamber at depth. The pinkish-grey monzonite dykes are characterized by medium- to coarse-grained porphyritic texture and contain about 55 vol% phenocrysts of alkali feldspar (< 20 mm), plagioclase (< 15 mm), amphibole (< 5 mm) and biotite (< 2 mm), as well as apatite and titanite microphenocrysts in a fine-grained feldspar-dominated groundmass (Fig. 3a). In places, the dykes contain disseminated anhydrite patches. The titanite microphenocrysts are unusually large (up to 0.5 mm in length) and are interpreted to host the elevated Th concentrations characteristic of the Skouries intrusions. In places, the dykes underwent weak potassic alteration with interstitial disseminations of hydrothermal biotite and magnetite. Mafic minerals are partly replaced by hydrothermal chlorite and carbonate.

Biotite phenocrysts in the porphyries have high halogen contents (Table 1). Magmatic biotites contain slightly elevated Cl (about 0.08 wt%), but low F contents (< 0.22 wt%). In contrast, hydrothermal phlogopites from rocks displaying potassic alteration have high F (up to 2.48 wt%) and very high Cl concentrations (up to 0.19 wt%). In contrast to the hydrothermal phlogopites, magmatic biotite phenocrysts contain elevated BaO contents of up to 0.78 wt% (Table 1). The high Cl contents of the micas are consistent with those from other porphyry Cu–Au deposits such as Grasberg, Indonesia, and Northparkes (Goonumbla), Australia (cf. Müller and Groves 2000).

Geochemistry of the alkaline porphyries

Major elements were determined by XRF and trace elements by ICP and NAA methods and representative data are given in Table 2.

The rocks have relatively evolved compositions, as reflected by high SiO_2 (62.0–68.0 wt%) and low MgO (1.1–2.2 wt%) contents, and by variable, but low concentrations of mantle-compatible elements (< 92 ppm V, < 103 ppm Ni, < 18 ppm Co). The relatively high degrees of fractionation are consistent with the relatively low mg# of the rocks (36–52), calculated using a molecular $Fe^2/(Fe^2 + Fe^3)$ set at 0.15, a common ratio in potassic igneous

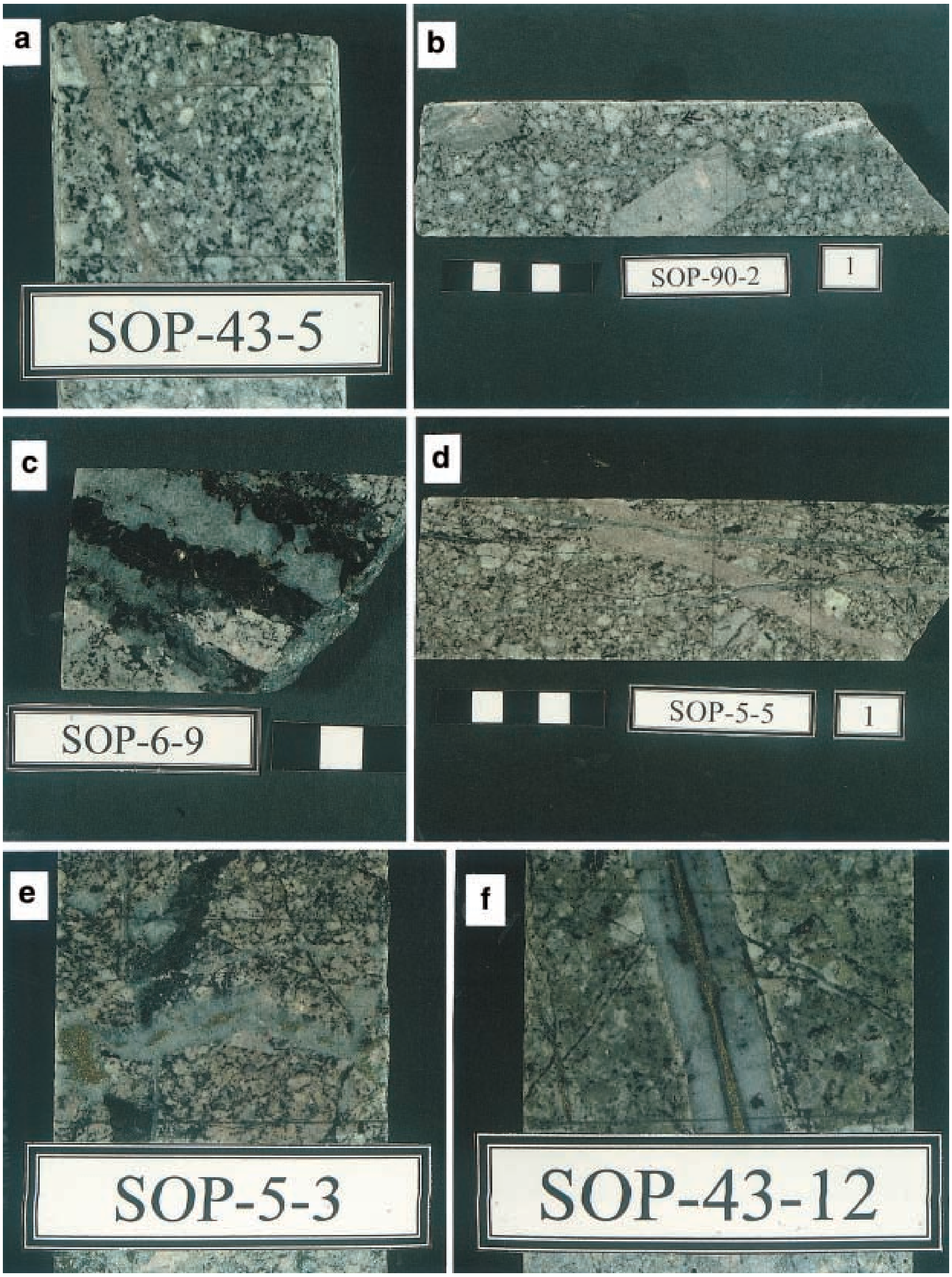

Fig. 3 Selected drill core samples from Skouries (core width is about 4 cm): **a** late-stage monzonite porphyry with hydrothermal orthoclase veinlet; **b** pink monzonite porphyry with large (up to 4 cm) alkali feldspar phenocrysts; **c** main monzonite porphyry with quartz–chalcopyrite vein containing large (1 cm) crystals of hydrothermal biotite; **d** main monzonite porphyry with hydrothermal orthoclase veinlet and cross-cutting quartz veinlets; **e** main monzonite porphyry with A-type quartz–chalcopyrite–bornite stockwork veining cross-cutting a black biotite–magnetite veinlet; **f** main mineral porphyry with B-type quartz–chalcopyrite–biotite vein

rocks (Müller et al. 1992). Importantly, the pink monzonite porphyry, the oldest of the Skouries intrusions, has the highest mg# (52), whereas the mineralized main quartz-monzonite porphyry has relatively low mg# (36–39) implying higher degrees of fractionation. This is consistent with other alkaline rock-hosted porphyry Cu–Au systems, such as Phu-Phu, Laos (B. Burke, personal communication, 1998; D. Müller, unpublished data), and Northparkes (Goonumbla), Australia (Müller et al. 1994), that each consist of a series of interconnected intrusions ranging from mafic to increasingly more fractionated compositions. Typically, the stockwork mineralization is directly associated with the relatively evolved quartz-monzonite phase. The high K_2O contents (4.2–5.8 wt%) and high K_2O/Na_2O ratios (>1) of the least altered samples are typical of alkaline rocks of the shoshonite association (cf. Joplin 1968; Morrison 1980; Müller et al. 1992). This relationship is consistent with the high Ce/Yb (>34) and Th/Yb (>21) ratios of the Skouries intrusions. The REE are widely considered to remain immobile even during alteration processes (Pearce 1982). Importantly, all investigated samples unequivocally plot in the 'shoshonite' field on the K_2O versus SiO_2 diagram (Fig. 4) of Peccerillo and Taylor (1976). The Skouries intrusions have very high U and Th concentrations (up to 18.9 and 62 ppm respectively), consistent with accessory allanite and thorite in several samples (Tobey et al. 1998). Consequently, all samples have high Th/Yb ratios (>20) and plot in the shoshonite field on the biaxial Th/Yb versus Ta/Yb discrimination diagram (Fig. 5) after Pearce (1982). This contradicts some previous workers who propose a subalkaline character for the Skouries intrusions (e.g. Perantonis 1982; Tarkian and Stribrny 1999).

Initial $^{87}Sr/^{86}Sr$ ratios of eight monzonite samples from Skouries are given in Table 3. The samples have relatively high average initial $^{87}Sr/^{86}Sr$ ratios of 0.7082 suggesting crustal

Table 1 Representative microanalyses of phlogopite phases from the Skouries porphyry intrusions. The analyses were conducted at the Institute for Metallurgy, TU Bergakademie Freiberg. Note that magmatic mica phenocrysts are biotite, while hydrothermal mica derived from potassic alteration is phlogopite

Sample Intrusion Mineral	SOP5-2-5/1 Late porphyry Phlogopite	SOP5-6-2/5 Main porphyry Phlogopite	SOP6-6/1-1 Main porphyry Phlogopite	PP-1/2-6/2 Late porphyry Biotite	SOP5-3/1-7 Main porphyry Phlogopite	SOP6-9-4/1 Main porphyry Phlogopite
SiO_2	40.93	39.43	40.15	35.45	42.11	39.97
TiO_2	2.19	2.69	2.04	2.81	0.96	2.11
Al_2O_3	11.92	12.31	12.04	15.19	10.92	11.84
Cr_2O_3	0.00	0.00	0.02	0.03	0.01	0.06
FeO	10.65	11.82	10.54	17.53	8.74	10.93
MgO	20.01	18.82	20.03	13.65	22.10	19.70
CaO	0.00	0.00	0.02	0.02	0.00	0.00
MnO	0.04	0.10	0.14	0.30	0.06	0.13
BaO	0.00	0.00	0.00	0.78	0.00	0.00
Na_2O	0.25	0.27	0.11	0.48	0.20	0.18
K_2O	9.82	10.11	10.27	9.66	9.61	10.12
H_2O^-	3.16	3.23	3.21	3.95	2.99	3.18
F^-	2.14	1.87	1.95	0.22	2.48	1.98
Cl^-	0.14	0.19	0.15	0.08	0.14	0.16
Total	100.34	100.03	99.84	100.04	99.27	99.51
mg#	81	79	81	64	85	81
Cations (O = 12)						
Si	2.912	2.837	2.882	2.611	3.005	2.882
Ti	0.117	0.146	0.110	0.156	0.052	0.114
Al	0.999	1.044	1.019	1.318	0.918	1.006
Cr	0.000	0.000	0.001	0.002	0.001	0.003
Mg	2.122	2.019	2.144	1.499	2.351	2.117
Ca	0.000	0.000	0.002	0.002	0.000	0.000
Mn	0.002	0.006	0.009	0.019	0.004	0.008
Fe	0.570	0.640	0.569	0.972	0.469	0.593
Ba	0.000	0.000	0.000	0.023	0.000	0.000
Na	0.034	0.038	0.015	0.069	0.028	0.025
K	0.891	0.928	0.941	0.908	0.875	0.931
Total	7.649	7.658	7.691	7.576	7.701	7.680

contamination of their parental melts during emplacement (Fig. 6). The data are in close agreement with previous results reported by Frei (1995).

Discussion

Features that Skouries has in common with other porphyry Cu–Au deposits (Sillitoe 1979):

1. Occurrence of potassic and propylitic alteration zones.
2. Association of Cu–Au with little Zn (E. Tobey, personal communication, 2001).
3. Highest Au concentrations in the potassic alteration zone.
4. Presence of magnetite and anhydrite in addition to sulfides, suggesting relatively high oxygen fugacities of the parental melts.

The Skouries porphyry Cu–Au deposit is another example of alkaline rock-hosted porphyry Cu–Au mineralization, others being Bajo de la Alumbrera, Bingham, Grasberg, Goonumbla and Ok Tedi (cf. Müller and Groves 2000). All these porphyry systems are interpreted to represent pulses of volatile-rich, moderately fractionated melt derived from an underlying magma chamber. Commonly, the intrusive stocks occur in clusters and consist of finger-like, interconnected intrusions that range from diorite through monzodiorite and monzonite to quartz-monzonite, the last intimately associated with stockwork mineralization. The high bornite contents in the Skouries ore may be compared with several other alkaline rock-hosted porphyry Cu–Au deposits such as Bingham, Grasberg and Goonumbla (Keith et al. 1997; MacDonald and Arnold 1994; Müller et al. 1994). Typically, the high-grade ore is characterized by high bornite contents, with gold occurring preferentially as micro-inclusions in bornite (Simon et al. 2000).

Skouries has many similarities to the Northparkes deposits in the Goonumbla district (Müller et al. 1994; Heithersay and Walshe 1995). Both systems are characterized by small, interconnected, finger-like monzonite intrusions that are inferred to have formed as late-stage differentiates of andesitic parental melts with shoshonitic compositions. These intrusions host bornite–chalcopyrite-dominated stockwork mineralization. In both systems, the hypogene mineralization includes high-grade zones containing >0.7% Cu and >0.7 g/t Au.

The monzonitic porphyries at Skouries are characterized by pink colour probably due to the presence of Fe in the orthoclase structure that has been documented at Goonumbla (P. Heithersay, personal communication, 1996). In most porphyry Cu–Au systems where the mineralization is hosted by monzonite or monzodiorite intrusions the rocks normally have buff or grey colours in hand specimen (e.g. Bingham, USA; Grasberg, Indonesia; Ok Tedi, Papua New Guinea). Pink monzonites have only been documented previously at the Cadia and Northparkes porphyry Cu–Au deposits, NSW, Australia (Müller and Groves 2000).

The high contents of hydrothermal magnetite (up to 6 vol%) at both Skouries and Goonumbla imply high oxygen fugacities (f_{O2}) of their parental melts. At high values of f_{O2}, iron is partially transformed into Fe^{3+} and oxide minerals such as magnetite crystallize in preference to Fe^{2+}-bearing silicate minerals (Haggerty 1990). A high oxygen fugacity of the melt, as indicated by significant concentrations of hydrothermal magnetite, is characteristic of Au-rich porphyry Cu deposits (Sillitoe 1979).

Table 2 Representative whole-rock major and trace element compositions of the Skouries porphyry intrusions. Major elements determined by XRF facilities at the Institute for Mineralogy, TU Bergakademie Freiberg (T.K., analyst), and trace elements assayed by ICP and NAA methods at Actlabs Laboratories, Ancaster, Ontario. *b.d.l.* = below detection limit

Sample Rock type	SOP6-7/3 Main porphyry	SK18-5 Main porphyry	SOP-5-6 Main porphyry	SOP5-2 Late porphyry	SOP6-BD5 Late porphyry	LPS1/1 Late porphyry	A-P2/1 Late porphyry	SOP43-3 Intra-mineral	SOP90-2 Pink porphyry
SiO_2	64.80	64.79	64.40	63.50	65.05	63.15	65.50	63.60	63.15
Al_2O_3	16.90	17.20	17.30	17.40	16.90	17.90	17.60	17.60	16.30
Fe_2O_3	4.90	4.89	4.70	4.91	4.45	5.28	3.55	4.90	2.95
MnO	0.16	0.05	0.08	0.47	0.07	0.05	0.07	0.05	0.03
MgO	1.28	1.37	1.13	1.67	1.72	1.85	1.45	1.80	1.35
CaO	1.60	1.69	1.36	1.83	2.48	1.51	3.73	2.08	2.89
Na_2O	3.62	3.88	3.92	4.23	3.73	3.54	2.60	3.74	3.46
K_2O	5.20	4.80	5.80	4.40	4.28	4.93	4.25	4.50	5.45
TiO_2	0.35	0.35	0.35	0.43	0.34	0.48	0.41	0.43	0.34
P_2O_5	0.24	0.28	0.28	0.32	0.30	0.31	0.24	0.26	0.23
SO_3	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.02	b.d.l.	b.d.l.	2.98
S	0.13	0.03	0.04	0.20	0.03	0.01	0.04	0.22	n.a.
Total	99.18	99.35	99.36	99.35	99.33	98.99	99.44	99.18	99.11
mg#	38	39	36	44	47	45	49	46	52
V	71	75	52	80	83	92	64	86	68
Co	7	7	6	18	7	8	5	10	6
Ni	19	18	22	103	3	12	5	13	8
Rb	155	94	147	120	110	99	123	106	123
Sr	1,173	1,155	1,155	1,160	1,203	1,170	962	1,440	1,245
Ba	2,300	2,100	2,100	2,000	1,900	2,300	1,800	2,000	2,050
Zr	320	320	320	330	320	313	190	310	320
Hf	8	9	8	9	9	8	4	8	9
Cu	1,424	328	318	495	264	1,439	54	2,293	2,120
Pb	57	62	95	103	83	45	53	43	51
Zn	28	36	53	32	29	39	52	21	14
La	38.0	56.1	19.7	32.7	83.7	84.8	52.1	39.8	53.7
Ce	69.0	106.0	41.0	70.0	151.0	162.0	92.0	83.0	100.0
Yb	1.3	1.7	1.2	1.4	1.9	2.2	1.4	1.5	1.6
Ta	1.2	<0.5	1.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Th	61.7	62.0	59.0	61.1	57.4	50.8	29.4	55.3	57.5
U	18.9	16.1	12.7	11.0	18.3	14.0	13.1	11.8	17.0
Ce/Yb	53	62	34	50	79	74	66	55	62
Th/Yb	47	36	49	44	30	23	21	37	36
K_2O/Na_2O	1.4	1.2	1.5	1.0	1.1	1.4	1.6	1.2	1.6

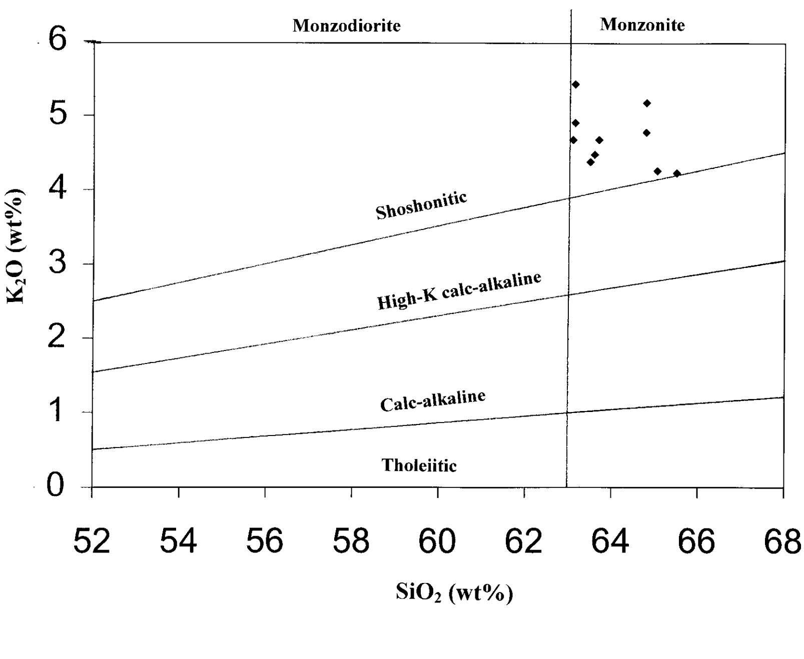

Fig. 4 Representative samples plotted on the K_2O versus SiO_2 diagram of Peccerillo and Taylor (1976) showing the potassic compositions of the Skouries intrusions

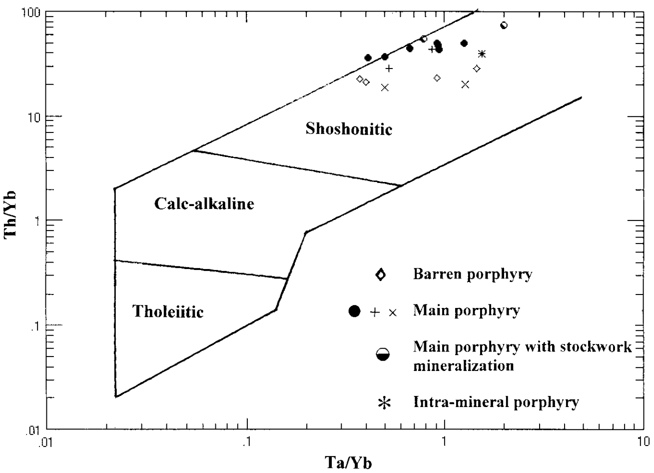

Fig. 5 Complete data set from Kroll (2001) plotted on the Th/Yb versus Ta/Yb discrimination diagram of Pearce (1982). Note that these data also contain potassic altered porphyries. Due to high Th/Yb ratios (>20), all samples plot in the 'shoshonite' field

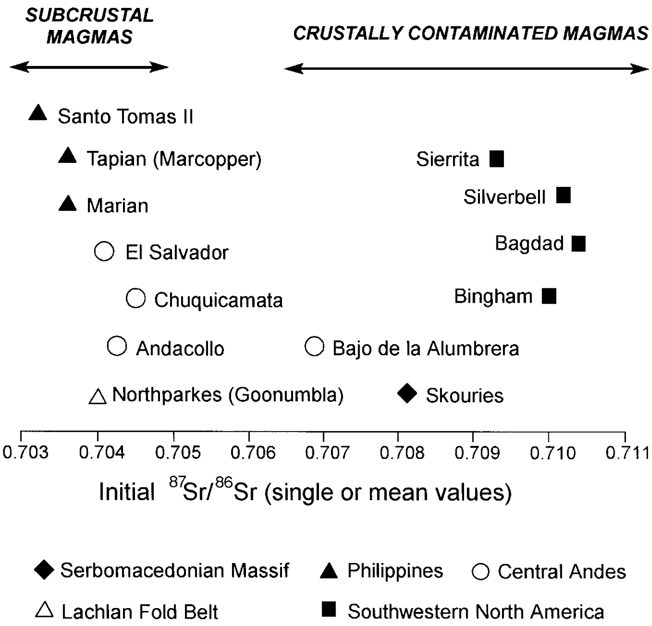

Fig. 6 The high initial $^{87}Sr/^{86}Sr$ ratios of the samples are suggestive of crustal contamination of their parental melts during emplacement. The data are consistent with those from other porphyry Cu deposits from continental arc settings (Heithersay and Walshe 1995; Sillitoe 1987 and references therein)

Table 3 Initial $^{87}Sr/^{86}Sr$ ratios of the Skouries intrusions. Data obtained at the Institute for Mineralogy, TU Bergakademie Freiberg

Sample	$^{87}Sr/^{86}Sr$	2σ
PP-1-b	0.707269	0.000042
SOP-5-2	0.708314	0.000028
SOP-5-2	0.708265	0.000017
SOP-43-5	0.708058	0.000020
SOP-5-6	0.708312	0.000028
SOP-6-7/3	0.708321	0.000026
SK-18-5	0.708180	0.000033
SOP-90-2	0.708203	0.000025

Previous workers have shown that subduction-derived melts normally have elevated concentrations in the large radius cations U and Th when compared to MORB and OIB (Brenan et al. 1995). It is widely interpreted that these elements are metasomatically added to the mantle wedge above subduction zones by fluids derived from dehydration of the subducted slab (Gill and Williams 1990). However, the distinctly high Th concentrations of up to 62 ppm of the Skouries porphyries are unusual even in alkaline rocks and appear to have only been documented from shoshonitic lamprophyres associated with Au-bearing base-metal veins in the Marienberg district of the central Erzgebirge, Germany (Seifert 1999).

Both the high F concentrations of micas and the high whole-rock LILE concentrations of the Skouries intrusions could reflect a mainly fluid-derived component during magma genesis in the upper mantle (Bailey et al. 1989). During uprise, the melts underwent moderate degrees of olivine–clinopyroxene ± amphibole fractionation and crustal contamination, as suggested by their relatively high initial $^{87}Sr/^{86}Sr$ ratios.

Plotting the analysed samples on the geochemical discrimination diagrams of Müller et al. (1992) unequivocally assigns them to a continental arc-setting, an interpretation that agrees with studies by Veranis (1994).

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