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MOLYBDENITE OCCURRENCES IN GREECE: MINERALOGY, GEOCHEMISTRY AND DEPOSITIONAL ENVIRONMENT

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Abstract: Molybdenite occurs mainly in three mineralization types in Greece: (a) porphyry Mo-Cu-(±Te-Ag-Au), (b) reduced intrusion-related Mo-W systems (skarn, intrusion-hosted) and (c) shear zone-related Cu-Au-Bi-Mo. In porphyry-Mo-Cu prospects the molybdenite is the main ore constituent together with pyrite in quartz stockworks crosscutting sericite±carbonate altered porphyry stocks (dacite at Pagoni Rachi/Kirki, Myli/Esymi, Konos/Sapes, Melitena/Rhodopi and Stypsi/Lesvos; microgranite at Ktismata/Maronia; monzonite at Sardes/Limnos, Fakos/Limnos and Skouries/Chalkidiki). Reduced intrusion-related systems are characterized by the presence of molybdenite, pyrite and wolframite-scheelite in intrusion-hosted sheeted quartz veins and/or dissemination (granodiorite at Kimmeria/Xanthi, Plaka/Lavrion and leucogranite at Pigi/Kilkis and Seriphos) and skarn-hosted ores (Kimmeria/Xanthi). Finally in the shear-zone Stanos prospect molybdenite accompanies chalcopyrite, native Bi, Bi-tellurides and sulfosalts. The studied molybdenites display a wide spectrum of their rhenium content ranging from almost Re-free molybdenites at Stanos, to very low-Re molybdenite in the intrusion-related systems (Lavrion, Serifos, Pigia and Kimmeria), and high to ultrahigh-Re molybdenites in the northern Greek porphyries. The rare mineral rheniite (ReS_2), occurs along with Fe-Cu sulfides, Pb oxides, and native Sn in Pagoni Rachi and Konos prospects. Rheniite and high-Re molybdenite precipitated under oxidizing conditions and from relatively acid hydrothermal solutions, whereas Re-poor molybdenites are indicative of reduced conditions mostly dominant in the intrusion-related systems. At the northern Greek porphyry-Mo prospects, magmas previously enriched from their mantle source rocks were responsible for extreme contents of rhenium in molybdenite.

Keywords: Molybdenite, rheniite, mantle-crust origin, oxidizing vs reducing fluids.

1. Introduction

The Rhodope-Serbomacedonian- and Attic-Cycladic metamorphic belts in Greece comprise a number of styles of mineralization (base- and precious-metal porphyry, skarn, intrusion-related, shear zone-related, epithermal), which are in part genetically associated to arc-related magmatic rocks, and in part controlled by exhumation structures of high-pressure units in a back-arc setting (Arvanitidis and Constantinides, 1989; Arikas and Voudouris, 1998; Melfos et al., 2002; Skarpelis, 2002; Arvanitidis, 2003; Marchev et al., 2005; Voudouris, 2006; Tombros et al., 2007; Voudouris et al., 2008). Molybdenite occurs in a wide range of deposits/prospects, mainly those related to magmatic activity (porphyry-type, reduced intrusion-related), as well as deposits related to metamorphic or deformation processes (shear zone-related).

Previous studies reported the presence of Re-rich and Re-free molybdenite in various deposits/prospects in Greece and discussed the relationships between polytypism and rhenium content (Filippidis et al., 1986; Michailidis et al., 1993; Melfos et al., 1991; 2001). Recently, the extremely rare mineral rheniite (ReS_2) has been discovered in the Pagoni Rachi porphyry prospect (Voudouris et al., 2009), and this is the first occurrence of this mineral in a magmatic-hydrothermal deposit and only the second occurrence in the world after its type locality in the fumarolic sublimates in

Kudryavy volcano, Kurile islands (Korzhinsky et al., 1994). The study of Voudouris et al. (2009) indicated that the Re content of molybdenites from Pagoni Rachi is the highest ever reported (up to 4.70 wt.%), whereas the structural analyses demonstrated that they crystallized as the 2H polytype and not the 3R polytype, as previously hypothesized by Newberry (1979a, b) and others, thus suggesting that Re concentration does not correlate with a specific polytype. In addition the almost perfect linear correlation between the Mo and Re content of molybdenites from three northern Greek prospects (Pagoni Rachi, Maronia, Melitena) supports the concept previously proposed (e.g. Fleischer, 1959; Stein et al., 2001) that Re substitutes for Mo in the structure of molybdenite (Voudouris et al., 2009).

Despite the above mentioned mineralogical studies of molybdenite mineralization in Greece, an integrated documentation of molybdenum bearing ores has yet to be undertaken. The aim of the present study is to review all mineralogical data concerning molybdenites from various deposits/prospects in Greece (Fig. 1), to present new information concerning recent molybdenite discoveries, to evaluate their rhenium content and finally to discuss their origin.

2. Methods

Seventy eight thin and polished thin sections of host rocks and sulfide assemblages were studied with an optical microscope and a JEOL JSM 5600 scanning electron microscope equipped with back-scattered imaging capabilities, at the Department of Mineralogy and Petrology, University of Athens, Greece. The chemical composition of molybdenite was determined with a Cameca SX 100 wavelength-dispersive electron microprobe at the Department of Mineralogy and Petrology, University of Hamburg, Germany. Operating conditions were: 20 kV and 20

Fig. 1. Location map of the studied molybdenite occurrences in Greece.

nA, beam diameter <1 μm. The following X-ray lines were used: Mo*L*β, Re*M*α, Cu*K*α, Fe*K*α and S*K*α. Pure elements (for Re), pyrite and chalcopyrite (for Fe and S) and molybdenite (for Mo), were used as standards. The chemical composition of molybdenite and rheniite was also determined using a JEOL JXA 8200 electron microprobe at Iowa State University. The concentrations of the major and minor elements were determined at Iowa State University at an accelerating voltage of 15 kV and a beam current of 15 nA, with 10 seconds as the counting time (5 seconds on each background). The standards employed were metallic rhenium and molybdenum for Re and Mo, chalcopyrite for Cu, and synthetic pyrite for S.

3. Description of the mineralizations

All granitoid rocks are considered as post-collisional and mainly of sub-alkaline character. It follows a brief description of the mineralization studied.

3.1. Porphyry Mo-Cu- and Cu-Au deposits

Pagoni Rachi/Kirki: The Pagoni Rachi Mo-Cu-Te-Ag-Au prospect is genetically related to an Oligocene dacite porphyry stock (Arikas, 1981; Voudouris et al., 2009). Molybdenite-rheniite-pyrite-bearing quartz stockworks are related to sericitic alteration of the intrusion.

Konos/Sapes: In the Sapes area two porphyry-type mineralizing events, which are genetically related to microdiorite and dacite porphyries are recognized (Voudouris et al., 2006; Ortelli et al., 2009). The Konos Cu-Mo porphyry is hosted in a subvolcanic dacite and contains molybdenite-pyrite veins in host rocks affected by sericitic alteration (Ortelli et al., 2009). Rheniite, lead oxides and native Sn accompany molybdenite in the veins (Fig. 2a to c), (Ortelli, 2009; present study).

Myli/Esymi: The Myli Cu-Mo prospect similarly to Pagoni Rachi and Konos, is related to a dacite porphyry stock (Arikas, 1985). Molybdenite-pyrite-bearing quartz stockworks are related to sericite-carbonate alteration of the dacite. Molybdenite occurs as laths surrounding pyrite (Fig. 2e).

Ktismata/Maronia: The porphyry-Cu-Mo mineralization at Ktismata is genetically related to a microgranite porphyry body intruding the Middle Oligocene shoshonitic intrusive complex of Maronia (Papadopoulou, 2002). Molybdenite occurs within quartz stockworks crosscutting sericitic altered microgranite and is associated with pyrite, chalcopyrite, base metal sulfides and sulfosalts (Melfos et al., 2002).

Melitena: The Melitena porphyry-Mo prospect is hosted within a Tertiary intrusion of dacitic composition (Filippidis et al., 1986; Michailidis et al., 1993). Molybdenite forms disseminations and fissure fillings and is associated with quartz veinlets crosscutting the sericitic altered porphyry body together with pyrite, pyrrhotite, sericite, pyrophyllite, diaspore and aluminium-phosphate-sulfate minerals (Michailidis et al., 1993; Melfos et al., 2001).

Lesvos island: The Stypsi porphyry-Mo prospect (Voudouris and Alfieris, 2005) in the north-central part of the island is hosted by a high-K calc-alkaline dacite porphyry. A stockwork of grey to black silica veinlets crosscutting sericite-carbonate altered dacite, contain pyrite, chalcopyrite, bismuthinite, molybdenite and galena (Voudouris and Alfieris, 2005). Molybdenite occurs as laths surrounding pyrite (Fig. 2f).

Limnos island: Two bodies of quartz monzonite porphyry have intruded the volcanic and sedimentary rocks in the central part of Fakos peninsula, as well as near Sardes in the northwestern part of the island (Voudouris and Alfieris, 2005). The Fakos and Sardes prospects are telescoped porphyry-epithermal systems, where molybdenite occurs within a stockwork of quartz + pyrite veinlets crosscutting sericite-tourmaline altered monzonite and sedimentary rocks and overprinting earlier K-silicate alteration.

Skouries/Chalkidiki: The Skouries porphyry Cu-Au-Pd deposit is hosted by at least four monzonite porphyry phases (Eliopoulos and Economou-Eliopoulos, 1991; Kroll et al., 2002). Molybdenite occurs in late pyrite veinlets related to sericite-carbonate alteration of the porphyry stocks (Frei, 1995).

3.2. Reduced intrusion-related Mo-W deposits

Kimmeria/Xanthi: The Kimmeria ore district is characterized by an intrusion-related polymetallic system that includes intrusion-hosted sheeted quartz veins and stockworks crosscutting sericite-carbonate altered granodiorite, rich in pyrite, molybdenite, scheelite, wolframite, chalcopyrite as well as skarn ores enriched in chalcopyrite, magnetite, pyrrhotite and minor molybdenite (Fig. 2g) (Walenta and Pantzartzis, 1969; Vavelidis et al., 1990; present study).

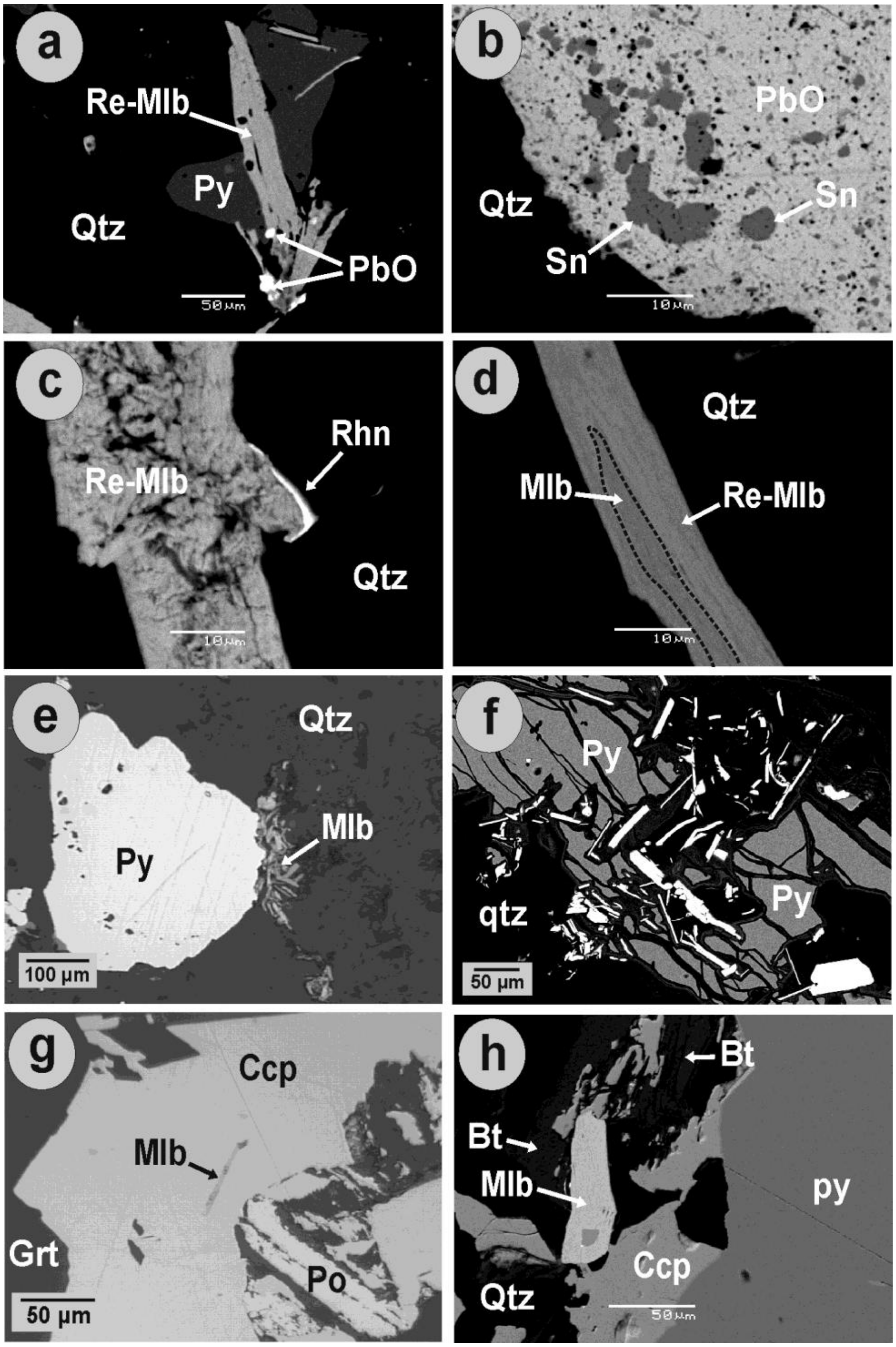

Fig. 2. Photomicrographs of molybdenite- and rheniite-bearing assemblages from various mineralization in Greece. (a) Rhenium-rich molybdenite (Re-Mlb) associated with pyrite (Py) and lead oxides (PbO) in quartz (Qtz) veinlet from the Konos/Sapes porphyry-Mo prospect (SEM–BSE image); (b) Native Tin (Sn) and lead oxide (PbO) from the Konos/Sapes porphyry-Mo prospect (SEM–BSE image); (c) Re-rich molybdenite (Mlb) and rheniite (Rhn) in quartz (Qtz) veinlet from the Konos/Sapes porphyry-Mo prospect (SEM–BSE image); (d) Rhenium-rich molybdenite (Re-Mlb) interfingered with Re-poor molybdenite (Mlb) in quartz (Qtz) veinlet from the Konos/Sapes porphyry-Mo prospect (SEM–BSE image); (e) Re-poor molybdenite (Mlb) surrounding pyrite (Py) in quartz (Qtz) veinlet from the Myli/Esymi porphyry-Cu-Mo prospect (SEM–BSE image); (f) Re-rich molybdenite (white flakes) surrounding pyrite (Py) in quartz (Qtz) veinlet from the Stypsi/Lesvos porphyry-Mo prospect (SEM–BSE image); (g) Chalcopyrite (Ccp) including Re-poor molybdenite (Mlb) and surrounded by pyrrhotite (Po) and garnet (Grt) in the intrusion-related Mo-W-Cu skarn prospect at Kimmeria/Xanthi (reflected light image); (h) Re-depleted molybdenite (Mlb) associated with chalcopyrite (Ccp) and biotite (Bt) postdating pyrite (Py) from shear-zone related Au-Bi-Cu-Te mineralization at Stanos/Chalkidiki.

Plaka/Lavrion: An intrusion-related polymetallic mineralization consisting of pyrite, molybdenite, chalcopyrite, pyrrhotite and minor scheelite, occurs within sheeted quartz veins and stockworks cross-cutting the granodiorite pluton of Plaka (Bonsall et al., 2007; Voudouris et al., 2008).

Pigi/Axiopolis: The Pigi Mo-deposit is related to the Upper Jurassic Fanos pluton, which is composed of high silica peraluminous leucogranites intruded the Mesozoic ophiolites of the Vardar zone (Christofides et al., 1990). Molybdenite is found within the leucogranites as disseminations and filling veinlets. Associated minerals are wolframite, pyrite, galena, quartz, sericite, chlorite, fluorite and kaolinite (Paraskevopoulos, 1958; Marakis and Skounakis, 1972; Michailidis et al., 1993).

Seriphos island: This study demonstrates the presence of an undeformed leucogranite at the southern part of Seriphos, composed of K-feldspar, quartz, minor plagioclase and biotite. Molybdenite occurs together with pyrite as disseminations and fracture fillings within fresh leucogranite.

3.3. Shear zone-related Cu-Au-Bi-Mo mineralization

Stanos/Chalkidiki: The Stanos mineralization is emplaced within a shear zone hosted in two-mica gneisses of the Serbomacedonian massif that records strong mylonitization and iron-potassic alteration with muscovite, biotite, chlorite and siderite (Voudouris and Sakellaris, 2008). The mineralization was formed in two stages: early pyrite, pyrrhotite and arsenopyrite deposition followed by a polymetallic assemblage including chalcopyrite, molybdenite (Fig. 2h), galena and Bi-Au-Te-bearing minerals contemporaneous with lower amphibolite/greenschist metamorphism (Voudouris and Sakellaris, 2008).

4. Composition of Re-bearing molybdenite

Representative electron-microprobe data of the molybdenites studied are presented in Table 1 and all data are plotted in the binary Re vs. Mo diagram (Fig. 3). Four groups of molybdenites are distinguished on the basis of their rhenium content: (a) Re-free molybdenites at Stanos/Chalkidiki, (b) very low-Re molybdenites (Re-content from 10 to 1310 ppm, average 206ppm) in the intrusion-related systems of Lavrion, Serifos, Pigi and Kimmeria, (c) intermediate- to high-Re molybdenites (Re-content from 300 to 10600 ppm, average 2302 ppm) in the porphyry-systems of Stypsi, Sardes, Fakos, Skouries and Myli, and (d) ultrahigh-Re

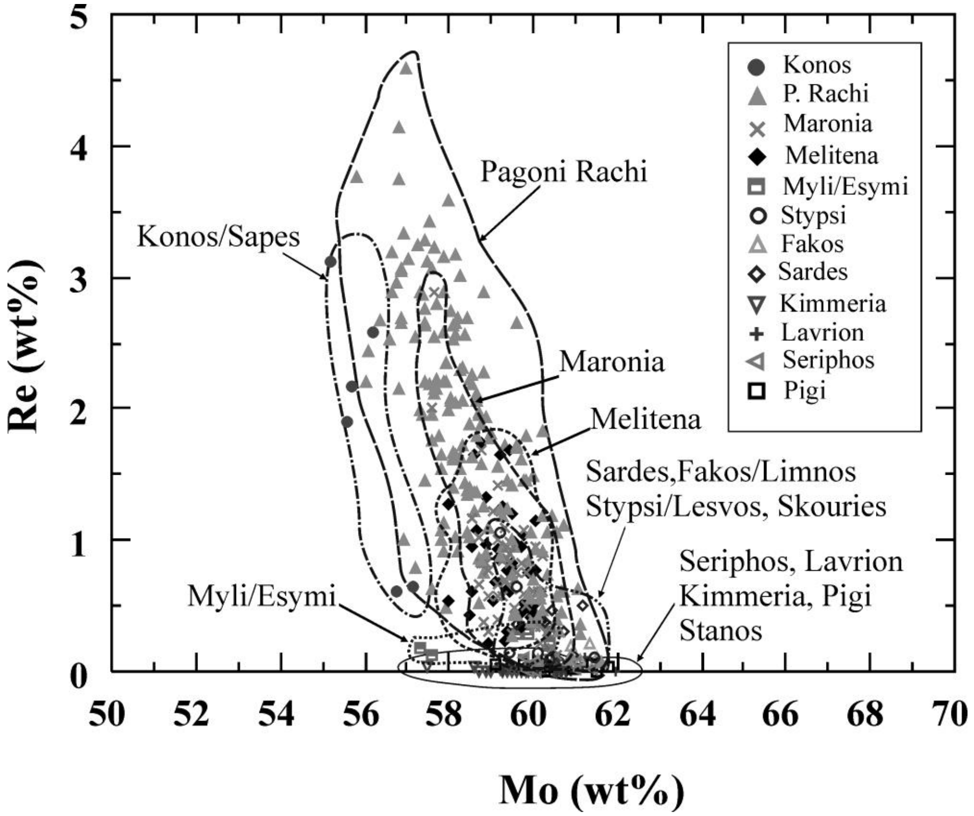

Fig. 3. Correlation diagram of rhenium (Re) and molybdenum (Mo) contents from the molybdenites from Greek occurences.

molybdenites in the northeastern Greek porphyries at Pagoni Rachi, Konos/Sapes, Melitena and Maronia (Re-content from 379 to 46900 ppm, average 13182 ppm). There is a correlation between the Mo and Re content of molybdenite supporting the concept that Re substitutes for Mo in the structure of molybdenite (Fig. 3). The Re content of molybdenite varies by more than 1 wt.% Re even within the same crystal (Fig. 2d) and it is highly likely that this heterogeneity is from the inhomogeneous distribution of rheniite (ReS_2) throughout the crystal. Rheniite was described recently from the Pagoni Rachi prospect (Voudouris et al. 2009). Rheniite also occurs in the Konos/Sapes deposit on grain boundaries of Re-rich molybdenite (Fig. 2c). Although Stein et al. (2001), Kosler et al. (2003) and Selby and Creaser (2001, 2004) suggested that Re must have redistributed or separated (decoupled) within molybdenite after formation, our study indicates that rheniite is not an exsolution-derived mineral from high-Re molybdenite (Voudouris et al., 2009).

5. Discussion

The Re content of molybdenite is controlled by several factors, including the composition of ore-forming solutions and host rocks, the nature and source of the host rock, the total amount of molybdenite in a given deposit, and the physicochemical conditions of ore formation (Berzina et al., 2005). Stein et al. (2001) related the Mo contents to mass balance considerations in which the Re content of molybdenite in Cu-Mo deposits was higher because of the restricted volume of molybdenite compared to that in Mo deposits. However, our study indicates that there is no clear relationship between Re content and molybdenite abundance, since molybdenite from the northern Greek porphyry Mo or Mo-Cu deposits (e.g. Pagoni Rachi, Konos/Sapes, Maronia, Melitena) is extremely enriched in Re. Relatively high Re concentrations, up to 0.35 wt.%, in the Majdanpek/Serbia and Elatsite/Bulgaria Cu-Mo porphyry deposits support a melt-metal source in fertile mantle and/or juvenile lower crust (Zimmerman et al., 2008). Mao et al. (1999) proposed that the rhenium contents in mo-

Table 1. Representative electron microprobe analyses (in wt. %) and atomic proportions of molybdenite from various known and new mineralization bd: below detection.

	Mo	Re	Fe	S	Total	Chemical formula (based on 3 apfu)
1	59.59	0.64	0.01	40.54	100.78	$Mo_{0.986}Re_{0.005}S_{2.008}$
2	59.23	1.06	bd	40.35	100.64	$Mo_{0.984}Re_{0.009}S_{2.007}$
3	60.13	0.14	0.02	40.11	100.40	$Mo_{1.001}Re_{0.001}Fe_{0.001}S_{1.997}$
4	60.26	0.38	0.34	39.87	100.85	$Mo_{1.002}Re_{0.003}Fe_{0.010}S_{1.985}$
5	61.20	0.52	0.17	39.66	101.55	$Mo_{1.017}Re_{0.004}Fe_{0.005}S_{1.973}$
6	56.81	3.75	0.12	38.85	99.53	$Mo_{0.973}Re_{0.033}Fe_{0.004}S_{1.991}$
7	58.80	0.76	0.10	39.32	98.98	$Mo_{0.997}Re_{0.007}Fe_{0.003}S_{1.994}$
8	59.21	1.65	bd	39.42	100.28	$Mo_{0.998}Re_{0.014}S_{1.988}$
9	60.20	0.39	0.01	39.86	100.46	$Mo_{1.005}Re_{0.003}S_{1.991}$
10	59.16	1.42	0.03	40.05	100.66	$Mo_{0.987}Re_{0.012}Fe_{0.001}S_{1.999}$
11	60.33	0.31	bd	39.60	100.24	$Mo_{1.011}Re_{0.003}S_{1.986}$
12	60.45	0.13	bd	40.35	100.93	$Mo_{1.000}Re_{0.001}S_{1.998}$
13	61.01	0.06	bd	38.86	99.93	$Mo_{1.032}Re_{0.000}S_{1.967}$
14	60.55	0.01	0.03	40.03	100.61	$Mo_{1.007}Re_{0.000}Fe_{0.001}S_{1.992}$
15	60.08	bd	0.02	39.63	99.73	$Mo_{1.009}Re_{0.000}Fe_{0.001}S_{1.991}$
16	60.92	0.03	0.04	40.06	101.05	$Mo_{1.010}Re_{0.000}Fe_{0.001}S_{1.988}$
17	61.77	0.04	0.02	39.81	101.63	$Mo_{1.024}Re_{0.000}Fe_{0.001}S_{1.975}$
18	60.92	0.19	nd	40.64	101.75	$Mo_{1.001}Re_{0.002}S_{1.998}$
19	61.50	0.11	nd	40.23	101.84	$Mo_{1.014}Re_{0.001}S_{1.985}$
20	59.75	0.10	nd	40.93	100.79	$Mo_{0.983}Re_{0.001}S_{2.016}$
21	60.70	0.02	nd	39.99	100.72	$Mo_{1.009}Re_{0.000}S_{1.990}$
22	59.84	0.33	nd	40.92	101.09	$Mo_{0.984}Re_{0.003}S_{2.013}$
23	60.08	0.04	nd	40.56	100.69	$Mo_{0.993}Re_{0.000}S_{2.006}$
24	56.18	2.59	bd	40.43	99.20	$Mo_{0.944}Re_{0.022}S_{2.034}$
25	57.17	0.65	bd	41.26	99.08	$Mo_{0.948}Re_{0.006}S_{2.047}$

1-3: Stypsi/Lesvos; 4,5: Sardes/Limnos; 6,7: Pagoni Rachi ; 8,9: Melitena; 10,11: Ktismata/Maronia; 12,13: Plaka/Lavrion; 14,15: Kimmeria/Xanthi; 16,17: Axioupolis/Kilkis; 18,19: Fakos/Limnos; 20,21: Seriphos; 22,23: Myli/Esymi; 24,25: Konos/Sapes lybdenite decrease gradually from mantle sources, to mixtures between mantle and crust, and then to crust source. Furthermore, Stein et al. (2001) suggested that molybdenite in porphyry style deposits possess high Re contents if they are genetically related to the melting of mafic or ultramafic rocks, or if the source rocks involve mantle underplating or metasomatism. Deposits that are derived from intermediate crustal rocks generally contain molybdenite with lower Re concentrations (Stein et al., 2001). Molybdenite can occur with very low Re abundance (very low ppm and even ppb): Low ppb Re bearing molybdenites are quite common from intrusion-related systems like Mactung and Pogo deposits, as well as from highly evolved granite systems, especially in pegmatites (D. Selby, written commun. 2010). Low Re concentrations in molybdenite are also highly diagnostic of a metamorphic derivation (Stein, 2006).

Available geochemical and stable isotope data suggest that the Oligocene to Miocene plutonic rocks in northern Greece and associated porphyry mineralizations with high- and ultrahigh Re-molybdenites, have geochemical compositions indicative of a derivation from sub-continental lithospheric mantle and/or the lower crust, with a minimal contribution from the crust (Christofides et al., 1998, Pe-Piper and Piper, 2002). Slab break-off resulted in the local ascent of asthenospheric mantle into mantle lithosphere and magma generation from a subcontinental lithospheric mantle, heterogeneously enriched by fluids and melts derived from previous subduction events (De Boorder et al., 1998; Pe-Piper and Piper, 2002). More precisely (a) a LILE- and LREE-enriched subcontinental mantle as the magma source of the Pagoni Rachi and Konos dacite magmas (Del Moro et al., 1988); (b) a lower crustal origin for the Maronia porphyritic microgranite (Papadopoulou, 2002); (c) a mantle source for the high-K calc-alkaline dacite porphyry at Stypsi (Pe-Piper and Piper, 2002); (d) dehydration melting of enriched metabasaltic amphibolite at the base of crust, triggered by rising mantle melts from both the asthenosphere and the enriched subcontinental lithosphere for the Limnos igneous rocks (Pe-Piper et al., 2009); and (e) a magma genesis in the upper mantle and subsequent crustal contamintation of the parental melts during emplacement for the Skouries deposit (Kroll et al., 2002). On the other hand, although Re-poor molybdenites (as present in the Kimmeria, Lavrion, Seriphos and Pigi prospects/deposits) should be indicative of magmas derived from crustal sources, available data are controversial: both a dehydration melting of lower crust without any contribution from mantle components, and a mantle origin with an important felsic component of crustal origin have been proposed for the formation of Xanthi granodiorite by Jones et al. (1992) and Christofides et al. (1998), and Lavrion granodiorite by Altherr and Siebel (2002) and Skarpelis et al. (2008). The source materials for the leucocratic granites of Fanos and Seriphos are suggested to be of crustal origin (Christofides et al., 1990; Iglseder et al., 2008). The lower Re-content in the intrusion-related systems of Lavrion, Kimmeria, Pigi and Seriphos is consistent with the reducing nature of mineralizing fluids as proposed by the experimental work of Xiong and Wood (2002) who suggested that reducing fluids containing sulfur have a lower capacity for transporting rhenium and, therefore, are not favorable for the formation of rhenium-enriched sulfide deposits. To form rhenium deposits, oxidizing fluids must be operative at some stage(s) of ore formation and this was the case for the ultrahigh Re deposits in northern Greece.

The coexistence of native Sn, lead-, lead-tin oxides and rheniite at Pagoni Rachi and Konos prospects is evidence that these phases formed directly from gas transport and precipitation as sublimates in a manner similar to that in the Kudryavy volcano, Kurile islands (Yudovskaya et al., 2006). According to Yudovskaya et al. (2006) the gas transport mechanism and the nano-scale phase formation allow coexistence of the reduced and oxidized phases of the transition metals. In the Kudryavy case, formation of native metals does not necessarily involve highly reduced fluids. Such nonequilibrium associations with coexisting various valence states are characteristic of high-temperature stages where the hydrothermal fluids exist as a gas phase, and mineral assemblages are precipitated as a result of gas transport reactions.

A rhenium release from the asthenospheric mantle wedge by subduction-related fluids and melts similarly to Kudryavy volcano, Kurile islands (Tessalina et al., 2008) could explain the enrichment of Re in the northern Greek magmatic systems.

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