

Rhenium abundance in molybdenites: a case study on vein-type Cu-Mo-Au mineralisation in the Qarachilar area, Sungun porphyry Cu and Siah Kamar porphyry Mo deposits, NW Iran

Vartan SIMMONDS^{1,*}, Ryan MATHUR² and David SELBY³

¹ University of Tabriz, Research Institute for Fundamental Sciences, Tabriz, 51666-16471, Iran

² Juniata Collage, Department of Geology, Huntingdon, 1700 Moore St, PA, 16652 USA

³ University of Durham, Department of Earth Sciences, Durham, DH1 3LE, UK

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The vein-type Cu-Mo-Au mineralisation in Qarachilar, the Sungun porphyry Cu deposit (PCD) and the Siah Kamar porphyry Mo deposit (PMD) are all located at the northwestern end of the Neo Tethys-related Urumieh–Dokhtar volcano-plutonic belt of Iran. Re contents of molybdenite samples from the Qarachilar, Sungun and Siah Kamar deposits are about 112.67–462 ppm, 53.24–252.29 ppm, and 10.44–41.05 ppm, respectively. Re contents of the first two deposits fall in the range of PCDs, while those of the latter are lower and correspond to PMDs. The relatively high Re content of the Qarachilar and Sungun molybdenites can be explained considering the low abundance of molybdenite, a mantle-dominated source for ore materials and the incorporation of oxidized and acidic hydrothermal fluids with high *f*Cl. The high abundance of molybdenite in the Siah Kamar PMD has resulted in volume dilution of Re. Furthermore, occurrence of the main ore within the potassic alteration zone and, hence, the alkaline nature of the responsible fluids in this zone have also affected the Re content of molybdenites. Variations of the Re content in different veins/veinlets showed a negative relationship with the formation temperature of these veins, and a positive/negative relationship with the acidity/alkalinity of the hydrothermal fluids, while the grain size of molybdenites showed a positive relationship.

Key words: Qarachilar, Sungun, Siah Kamar, Qaradagh Batholith, molybdenite, Re content.

INTRODUCTION

Rhenium is one of the most dispersed elements in the Earth's crust, with an average abundance of 0.7 ppb (Cardarelli, 2008). However, this is a chalcophile element and usually concentrated within Cu-Mo sulphides, and tends to be much more abundant in molybdenite than other coexisting sulphides (Berzina et al., 2005), which is due to the similar ionic radius and valence of Mo and Re (Sun et al., 2010).

It has been shown that molybdenite is the main host phase for Re in many hydrothermal deposits (McCandless et al., 1993). It incorporates considerable Re (tens to thousands of ppm) within its structure. This content is almost always in ppm

range and can reach several percent (Stein et al., 2001). However, Re contents of >1 wt.% in molybdenites are rare, although some processes in the porphyry and some epithermal systems associated with the porphyry mineralisation can lead to the extreme enrichment of Re in molybdenites or even formation of rheniite in such deposits. As a unique example, molybdenites in the Oligocene porphyry Cu-Mo-Au systems of the Pagoni Rachi and Sapes deposits of northeastern Greece are associated with pure rheniite, Mo-rich rheniite, as well as with intermediate (Mo,Re)S₂ and (Re,Mo)S₂ phases, with up to 46 wt.% Re, which occur as nanodomains and/or microinclusions in the intermediate molybdenite-rheniite phases (Voudouris et al., 2013). Rheniite appears either at the rims of molybdenite as a low-temperature exsolution product of high-Re molybdenite, or as separate grains.

Excluding the above-mentioned unique cases of extremely Re-rich molybdenites, which have been attributed to an anomalous mantle-wedge source with chemical inhomogeneities and local-scale processes, Voudouris et al. (2013) have shown that porphyry Cu-Au deposits contain the highest Re contents (case studies from Canada range from 3.858 to 8.170 ppm) and the

* Corresponding author, e-mail: simmonds_vartan@tabrizu.ac.ir
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porphyry Cu deposits take the second place (>4.000 ppm, with the highest content of 15.400 ppm from the Philippines). In addition, it is well-documented that molybdenites associated with porphyry Cu-Mo deposits exhibit relatively higher Re contents (with the mean of 1.830 ppm and the maximum content of 19.800 ppm, calculated based on the available data from 86 porphyry Cu-Mo deposits; [Berzina et al., 2005](#)) compared to those associated with porphyry Mo and Mo-Cu deposits ([Giles and Shilling, 1972](#); [Newberry, 1979b](#); [Stein et al., 1997](#)) with the mean of 42 ppm (obtained from 19 porphyry Mo-Cu and Mo deposits; [Berzina et al., 2005](#)). In general, molybdenites of deposits with higher Cu/Mo ratio typically have higher Re contents and there is a positive correlation between these two parameters ([Stein et al., 1997](#)), as the enormous quantities of molybdenite lead to volume dilution of Re concentration.

This contribution aims to determine and compare the Re abundances within the molybdenites of three different deposits in north-west Iran with each other: the vein-type Cu-Mo-Au mineralisation in Qarachilar (central part of the Qaradagh batholith), the Sungun porphyry Cu deposit (PCD) and the Siah Kamar porphyry Mo deposit (PMD) ([Fig. 1](#)), as well as with other molybdenite-bearing PCDs in Iran and in the adjacent Meghri-Ordubad pluton, north of the study area (southern Armenia). We also discuss potential controls on Re concentration in molybdenite, such as the source of parental magma and ore materials, contamination/assimilation extent and the physico-chemical conditions of the ore-bearing fluids.

The Qarachilar area is located 180 km north of Tabriz and ~6–7 km south of the Arax River, within the central part of the Qaradagh batholith. The Sungun porphyry Cu-Mo deposit is the largest known PCD in NW Iran and is located 130 km north of Tabriz, which is the second largest PCD in Iran and represents one of the numerous intrusive stocks in the Ahar-Jolfa metallogenic zone. The Siah Kamar porphyry Mo deposit (PMD) is the first reported deposit of this type in Iran, which is located 175 km south-east of Tabriz and 10 km west of Mianeh ([Fig. 2](#)).

All these deposits are located within the Alborz-Azərbayaj structural zone ([Nabavy, 1976](#)) of the Central Iranian domain ([Alavi, 1991](#); [Agha Nabaty, 2004](#)), in the Cenozoic Urumieh-Dokhtar magmatic arc (UDMA) ([Fig. 3](#)). This arc represents the subduction-stage to post-collisional magmatism resulted from closure of the Neo-Tethys Ocean between the central Iranian

and Arabian plates, which occurred in the Late Mesozoic–Early Cenozoic ([Berberian and King, 1981](#); [Alavi, 1991](#)). The porphyry copper metallogenic belt of Iran comprises three major metallogenic zones in its northwestern (Ahar-Jolfa), central and southeastern (Kerman) parts and hosts many major and small PCDs and prospects, which are associated mostly with Oligocene and Miocene intrusive bodies.

The ore-host stocks of the studied deposits have a high-K calc-alkaline to shoshonitic and metaluminous to peraluminous nature and belong to I-type active continental margin granitoids ([Mokhtari, 2008](#); [Zakeri et al., 2011](#) for Qarachilar; [Calagari, 2004a](#) for Sungun; [Khaleghi et al., 2013](#) for Siah Kamar). Moreover, based on the available age data, these stocks and/or their mineralisations represent the Middle Oligocene (including Qarachilar with the Re-Os age of 31.22 ± 0.28 to 25.19 ± 0.19 Ma, [Simmonds and Moazzen, 2015](#), and Siah Kamar with the U-Pb zircon age of 32.7 ± 0.4 to 30.9 ± 0.4 Ma and Re-Os age of 29.1 ± 0.2 to 28.1 ± 0.2 Ma, [Simmonds et al., 2019](#)) and the Early Miocene (Sungun PCD with U-Pb zircon age of 22.5 ± 0.4 to 20.5 ± 0.15 Ma, [Aghazadeh et al., 2015](#), and Re-Os age of 22.9 ± 0.2 to 21.7 ± 0.2 Ma, [Simmonds et al., 2017](#)), and hence are post-collisional.

GEOLOGIC BACKGROUND

QARACHILAR VEIN-TYPE Cu-Mo-Au MINERALISATION

The Qarachilar area is located in the central part of the Qaradagh batholith. This batholith was formed during several intrusive pulses of Eocene-Oligocene age. It intrudes the Upper Cretaceous and Cenozoic sedimentary and magmatic rocks ([Fig. 4](#)) and occupies an area of ~350 km². It includes granite, granodiorite, diorite, quartz-diorite, syenite, quartz-syenite, monzonite, quartz-monzonite, quartz monzodiorite and gabbro, although granodiorite is its dominant constituent ([Mokhtari et al., 2013](#)). Its northern extension beyond the Arax River is known as the Meghri-Ordubad pluton (southern Armenia), which also hosts several large porphyry Cu-Mo deposits, such as Agarak and world-class Kadjaran, along with other occurrences of Cu-Mo-Au-Ag mineralisation ([Fig. 2](#)).

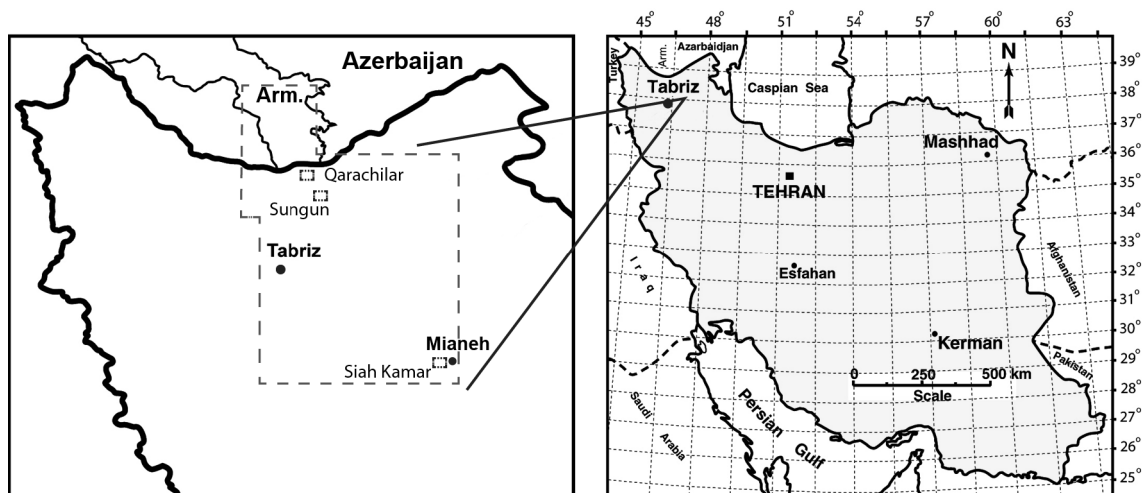


Fig. 1. Location of the studied Qarachilar, Sungun and Siah Kamar deposits in NW Iran

Outline of [Figure 3](#) is shown by dotted line

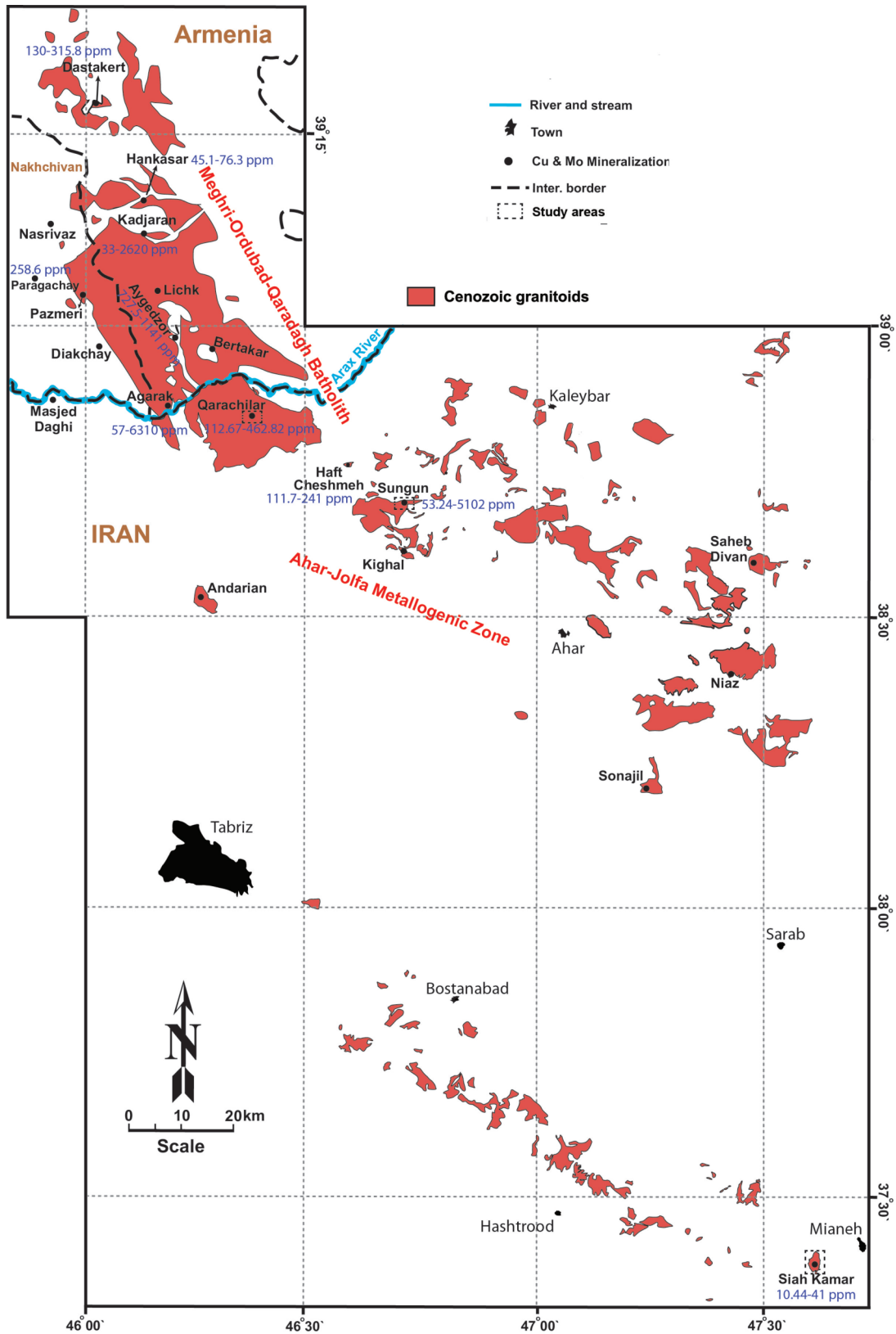


Fig. 2. Distribution of Cenozoic (mainly Oligo-Miocene) granitoids in NW Iran and southern Armenia, including the major Meghri-Ordubad and Qaradagh plutons and other smaller intrusive bodies, as well as the main porphyry Cu-Mo, base and precious metal deposits in the region, along with the available Re contents of molybdenites from these deposits

The rhenium contents for the south Armenian deposits are from [Magakian et al. \(1984\)](#) and [Moritz et al. \(2016\)](#), and those of the Haft Cheshmeh PCD are from [Aghazadeh et al. \(2015\)](#)

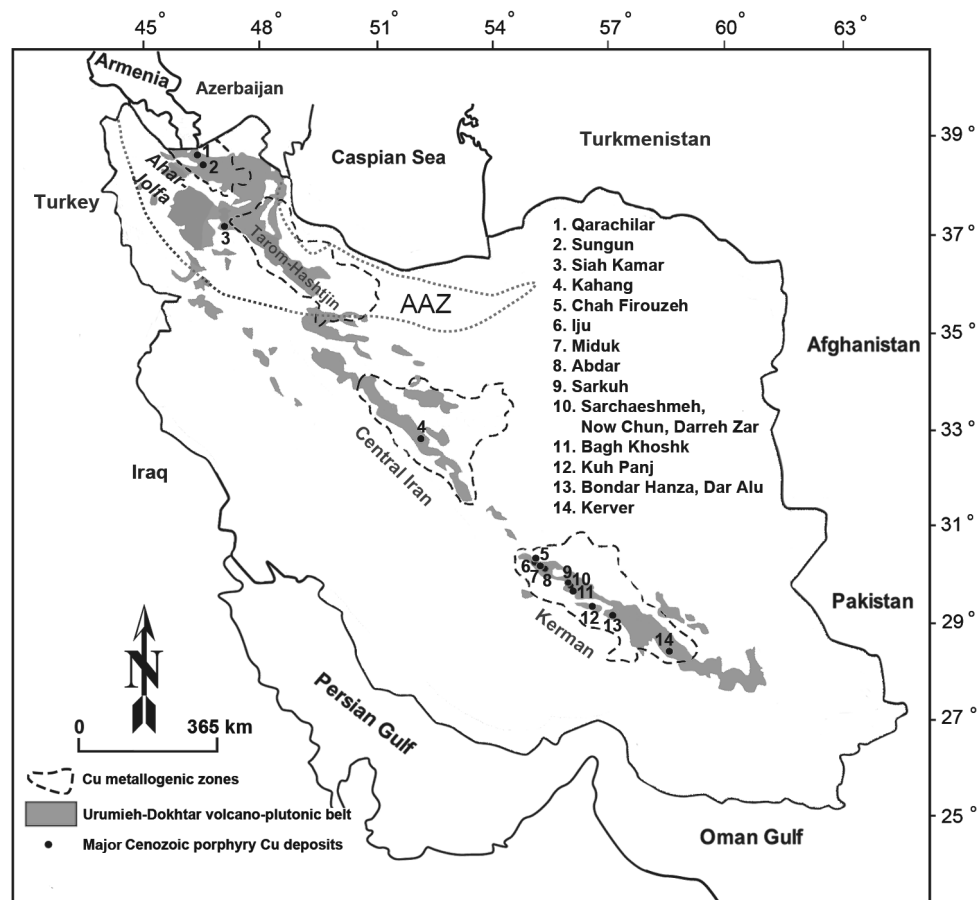


Fig. 3. The Urumieh-Dokhtar magmatic arc (Agha Nabaty, 2004), which also coincides with the Cu metallogenetic belt of Iran, comprised of the Ahar-Jolfa, Taron-Hashjtjin, Central Iran and Kerman zones

Some of the main porphyry Cu-Mo deposits with available Re contents are also shown;
AAZ – Alborz-Azarbaidjan structural zone (Nabavy, 1976)

The granodioritic host rock in Qarachilar is made of plagioclase (euhedral to subhedral, 40–60 vol.%), K-feldspar (anhedral, 5–15 vol.%) and quartz (anhedral and interstitial, 15–25 vol.%), with subordinate amounts of biotite (euhedral, 5–15 vol.%), amphibole (euhedral to subhedral, 0–10 vol.%), pyroxene (subhedral, 0–5 vol.%) and opaque minerals (0–5 vol.%). It displays hetero-granular texture. Accessory minerals are apatite, zircon and titanite.

The main hydrothermal alteration zones observed in the Qarachilar area are phyllic and potassic. The phyllic alteration is recognized by the sericitization of feldspars and replacement of ferro-magnesian minerals by sericite and chlorite, accompanied by the formation of quartz and pyrite, while the potassic alteration zone is characterized by the formation of shreddy biotite and fine-grained anhedral and intergranular orthoclase, along with opaque minerals (magnetite, chalcocopyrite and pyrite). This alteration zone is found in the walls of the deeply eroded Qarachilar Valley. Some dark-coloured veins of less than 5 cm in thickness are also found in the lower topographic levels, which contain secondary K-feldspar, quartz and shreddy biotite, further manifesting the occurrence of potassic alteration (Mokhtari et al., 2013). The boundary between potassic and phyllic alteration zones is transitional.

These alterations within the Qaradagh batholith are accompanied by Cu, Mo and Au mineralisation, especially in the Qarachilar area and its environs in Qaradareh, Zarlidareh and Anigh (Fig. 4). Mineralisation in this area occurs mainly as parallel swarms of mono-mineralic and quartz-sulphide veins and veinlets and silicified zones, as well as disseminations within the host rock, while stockwork-type mineralisation is also evident in the environs of the Qarachilar area. Two major sulphide-bearing quartz veins (GV1 and GV2) with the general NW–SE trend occur in the area. Their length is about 700 and 400 m, respectively, and their thickness ranges between 0.5 and 1 m. Furthermore, many other parallel veins and veinlets (less than 2 cm thick) are also present around the main quartz veins. These veins are surrounded by intense phyllic alteration.

The main sulphide minerals are pyrite, chalcocopyrite and molybdenite with lesser amounts of bornite and digenite. Pyrite is the most abundant sulphide mineral, while chalcocopyrite is the main hypogene Cu sulphide. Molybdenite is present as flakes (2–3 mm) or aggregates of anhedral and tiny crystals (>2 mm), disseminated within the quartz veins-veinlets, silicified zones and/or host rock.

Based on the analysed surficial samples, the Mo grade ranges from 20 ppm up to 3.6 wt.% and the Cu grade is be-

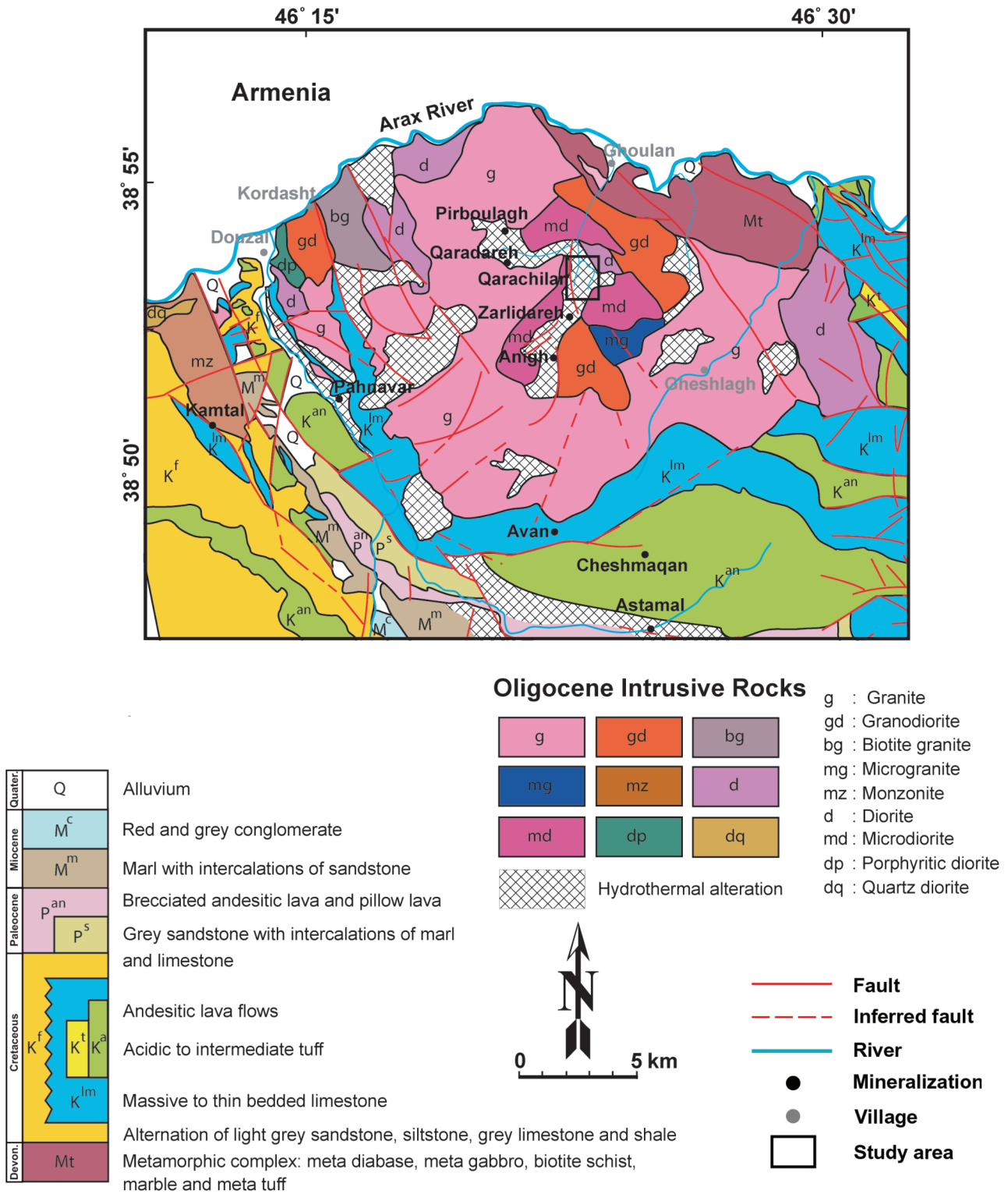


Fig. 4. Geologic map of the Qaradagh batholith and the studied Qarachilar area (simplified and modified after Mehrpartou et al., 1997)

tween 0.7 and 5 wt.% (Rezai Aghdam and Sohrabi, 2010; Zakeri, 2013). Moreover, based on the geochemical analysis of 16 altered and fresh rock samples from the mineralized zone in the Qarachilar area by Rezai Aghdam and Soharbi (2010), the Cu and Mo contents range from 50 to 33.594 and from 6 to 529 ppm, respectively, where both the highest contents belong

to a single sample. The Cu/Mo ratio for these data ranges from 4.5 to 96.6, with an average of 19.8, and most of the data cluster between 5 and 20. On the other hand, 68 samples taken from two main quartz-sulphide veins in the Qarachilar area yielded the average Cu/Mo ratios of 2.87 and 14.94, respectively, with the mean Cu contents of 0.8 and 1.8 wt.%, average Mo concen-

trations of 2.910 and 1.261 ppm, and mean Au contents of 5.76 and 3.9 ppb, respectively (Mokhtari, 2008).

The genesis of mineralisation hosted by the Qaradagh batholith is controversial, being presented as intrusion-related gold (Mokhtari, 2008; Mokhtari et al., 2013) and vein-type Cu-Mo-Au (Rezai Aghdam and Sohrabi, 2010), as well as porphyry type Cu-Mo mineralisation (e.g., Amini Fazl, 1994; Zakeri et al., 2011; Zakeri, 2013).

SUNGUN PORPHYRY Cu DEPOSIT (PCD)

A monzonite to quartz-monzonite porphyry stock (Qm – abbreviation in Fig. 5) of Early Miocene age intruded the Upper Cretaceous pelagic limestone sequence (K^m), Paleocene sandstone (P^s), and Eocene andesitic and dacitic-trachytic rocks (E^a and E^{dt}) in the Sungun area (Fig. 5). The porphyry stock was later intruded by two barren porphyry monzonite (Mz) and diorite (Di) stocks, as well as four generations of post-mineralisation dykes, ranging in composition from quartz diorite-quartz monzodiorite through gabbro diorite, microdiorite-microtonalite, and latite to trachyandesite and dacite. Finally, it is overlain by Plio-Quaternary dacitic (PIQ^{da}) and trachyandesitic (PIQ^t) rocks (Fig. 5; Pars Olang, 2004).

The porphyritic quartz-monzonite stock has produced vast hydrothermal alterations and porphyry-type Cu-Mo mineralisation. It comprises euhedral to subhedral plagioclase (30–45 vol.%; <5 mm), biotite (5–10 vol.%) and amphibole (0–5 vol.%; <2 mm), fine- to medium-grained quartz (10–20 vol.%), K-feldspar (30–40 vol.%; <0.2 mm) and opaque minerals (0–10 vol.%). It displays a porphyritic texture with microgranular to fine-grained groundmass.

The central part of the quartz-monzonite porphyry stock experienced hydro-fracturing and hydrothermal alteration. The dominant alterations are phyllic and potassic. The potassic alteration zone is characterized by the formation of secondary K-feldspar (2–5 vol.%; disseminated within the groundmass or occurring as replacing plagioclase and/or overgrowths on primary orthoclase phenocrysts) and shreddy biotite (2–10 vol.%; replacing the primary ferro-magnesian phenocrysts or occurring as disseminations within the groundmass). The phyllic alteration zone is recognized by the formation of sericite (40–50 vol.%), quartz (30–50 vol.%) and sulphides (5–15 vol.%). At the boundary zone between potassic and phyllic alterations, the phyllic assemblage is superimposed on the potassic assemblage, creating a potassic-phyllic transitional alteration zone.

Hypogene sulphide mineralisation includes pyrite, chalcopyrite and molybdenite, which have mainly occurred within the potassic and phyllic alteration zones as stock-work veinlets and disseminations. Supergene processes have also produced covellite, chalcocite, and minor amounts of bornite, native copper and cuprite.

According to the data published by Ghodrati (2009, 2010), the average contents of Cu, Mo and Au in the Sungun PCD are 0.6 wt.%, 0.02 wt.% and 0.04 ppm, respectively, and the highest concentration of molybdenite occurred in the potassic zone. Based on 174 samples taken from the hypogene zone (Ghodrati, 2009), the average grades of Cu and Mo are 6.094 and 276.7 ppm, respectively, yielding a Cu/Mo ratio of 3.15. These values for the supergene enriched zone ($n = 53$) are 6.492 and 120.4 ppm, respectively, with a mean Cu/Mo ratio of 53.92. Based on the same samples, the average Cu, Mo and Cu/Mo values for the oxidized-leached zone ($n = 7$) are 2.832 ppm, 46.4 ppm and 61.03, respectively. Additionally, the average Cu contents in the potassic ($n = 77$), transitional

potassic-phyllic ($n = 33$) and phyllic ($n = 64$) alteration zones are 6.568, 7.942 and 6.753 ppm, respectively, while the average Mo contents are 330, 187 and 245 ppm, respectively, which yield Cu/Mo ratios of 19.9, 42.47 and 27.56, respectively.

SIAH KAMAR PORPHYRY Mo DEPOSIT (PMD)

According to field investigations and the previous researches (e.g., Khaleghi et al., 2013), a quartz-monzonite porphyry stock was emplaced within the porphyritic trachybasalt, basaltic andesite and trachyandesite (E^t), tuffs, agglomerates and volcanic ashes (E^i) of Eocene age during the Oligocene (Fig. 6; Zarnab Ekteshaf, 2009), which hosts the Mo mineralisation and the related hydrothermal alterations. The southern and southeastern parts of the area are covered by Pliocene sedimentary rocks.

The porphyry stock contains plagioclase (20–40 vol.%, both as euhedral to subhedral phenocrysts and microlites), anhedral fine- to medium-grained K-feldspar (20–35 vol.%) and quartz (5–15 vol.%), and anhedral to subhedral opaque minerals (<5 vol.%). It shows a porphyritic texture with fine-grained to microlitic groundmass.

Potassic, phyllic, argillic, propylitic and silicic hydrothermal alterations are observed within this stock. They show rather regular zonation from the centre of the porphyry stock towards the wall rocks. The potassic alteration is developed mainly within the central part of the stock and has affected the adjacent volcanic rocks. This alteration zone is characterized by the formation of shreddy biotite (sometimes up to 40 vol.%), as well as disseminated magnetite within the groundmass. The phyllic alteration occurred both within the porphyry stock and the adjacent volcanic and pyroclastic rocks. It is recognized by the formation of quartz, sericite (up to 50 vol.%), pyrite and chlorite.

The main ore minerals are pyrite, molybdenite and magnetite. Molybdenite mineralisation occurs mainly within the potassic and transitional potassic-phyllic alteration zones (the latter produced by the superimposition of phyllic alteration assemblage on the potassic zone) of the porphyry stock in the form of stockwork-type quartz-sulphide and/or mono-mineralic molybdenite veinlets, as well as disseminations. The ore reserve of the Siah Kamar PMD is about 105.6 Mt, of which 39.2 Mt is the proved reserve at 539 ppm Mo, and 66.4 Mt is the probable resource at 266 ppm Mo.

Based on the results of 87 surficial samples taken from the porphyry stock and the altered country rocks (analysed by the AAS method in the laboratory of the Sarcheshmeh Cu Complex; Khaleghi et al., 2013), the average Mo grade is above 0.02 wt.%, with a maximum value of 0.27 wt.%. However, subsurface core samples reveal grades up to 0.54 wt.%, with an average of 0.25 wt.%. The Cu content in these samples ranges from 50 to an abnormally high value of 406 ppm, while most of the samples show Cu grades of 50–<100 ppm. The average Cu/Mo ratio of these samples is about 0.44, with values even as low as 0.02.

MATERIALS AND METHODS

Field studies and sampling of molybdenite-bearing quartz veins-veinlets and the host rocks in the Qarachilar area, Sungun and Siah Kamar deposits were carried out during 2012–2016. Subsequently, petrographic and mineralographic studies were completed at the Research Institute for Fundamental Sciences, University of Tabriz (Iran). In the Qarachilar area, in addition to two main quartz-sulphide veins, three other

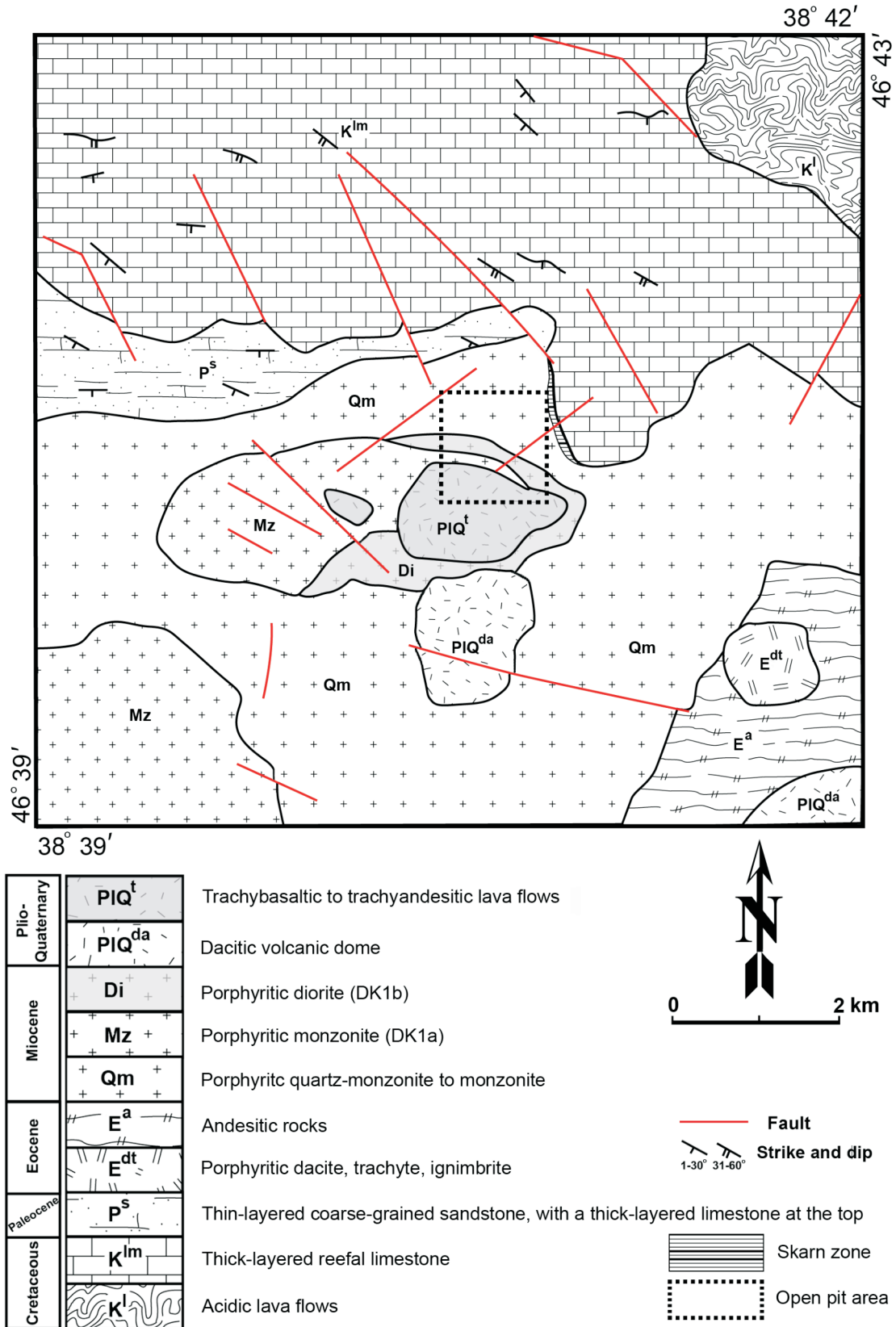


Fig. 5. Geologic map of the Sungun area (modified after Pars Olang, 2004)

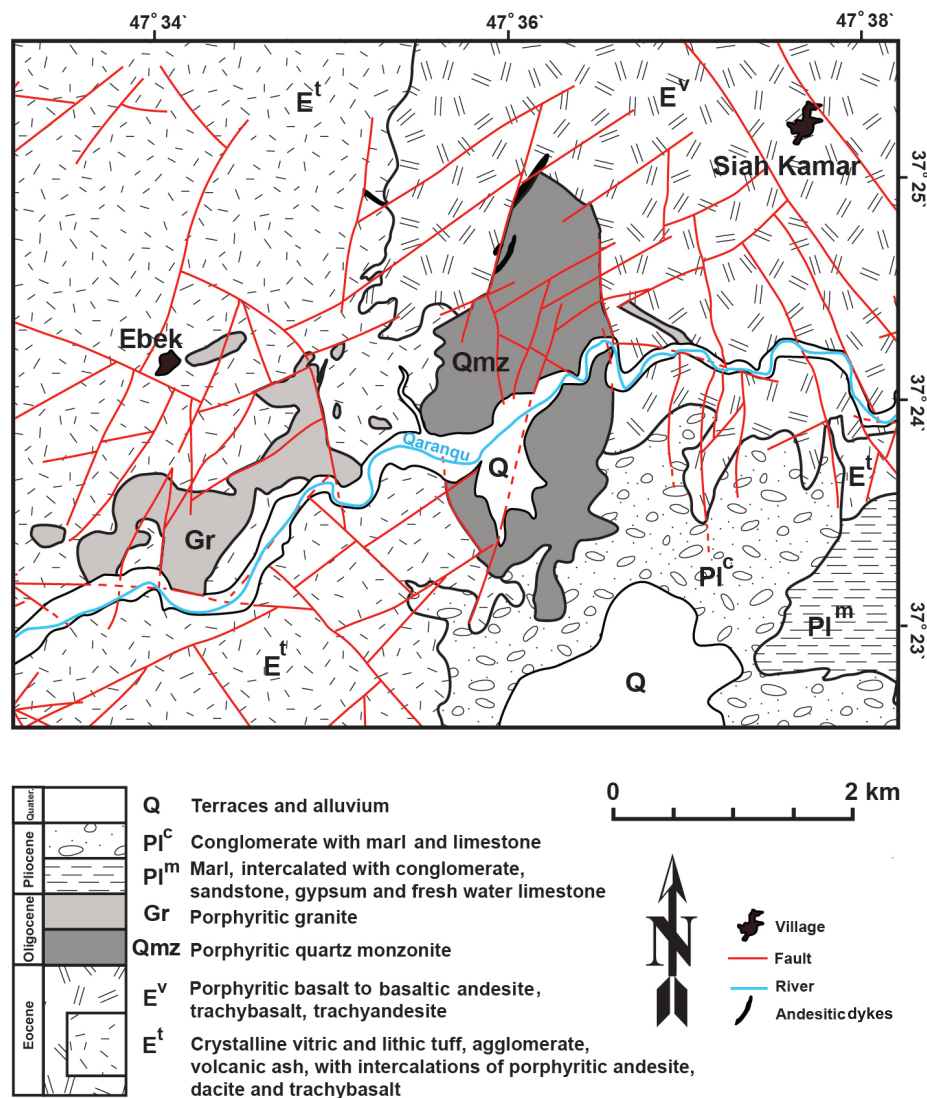


Fig. 6. Geologic map of the Siah Kamar area (1:25 000; simplified and modified after Zarnab Ekteshaf, 2009)

silicic veinlets with various wall-rock alterations were also sampled for Re content analysis. In the Sungun PCD and the Siah Kamar PMD, molybdenite-bearing samples were selected from diamond-drilled cores within the quartz-monzonite stocks.

In order to separate molybdenite from accompanying minerals, the fine- to medium-grained (<2 mm) molybdenite-bearing samples were crushed and the separation was done under a binocular microscope. For large aggregates of molybdenite flakes from the Qarachilar area, they were scraped from the vein sample using a stainless steel blade and then checked under the binocular microscope. Finally, the molybdenite separates with 99% purity were powdered using an agate mill.

To determine the purity of the Qarachilar molybdenite separates and its polytype, two representative samples were analysed by a *Siemens D500 X-Ray* powder diffractometer with a Ni-filtered Cu- α source and a graphite diffracted beam monochromator in the X-Ray laboratory of the Faculty of Physics, University of Tabriz.

The Re content of five representative molybdenite separates from the Qarachilar area was determined at the Key Labo-

ratory of Isotope Geochronology and Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, using *XSeries-7 quadrupole ICP-MS* (Thermo Scientific, USA) with a glass spray chamber and a concentric glass nebulizer. Each sample was digested by means of the Carius tube method using concentrated HNO_3 , which leads to precipitation of Mo as insoluble MoO_3 and, therefore, effectively removes the Mo matrix, resulting in much simple separation of Re from the molybdenite sample. Details of the analytical procedure are described in Sun et al. (2010). Accuracy and precision of the results were validated using the *GBW04435 (HLP-5)* molybdenite reference sample from the carbonatite vein-type Mo-U deposit in the Jinduicheng-Huanglongpu region of the Shaanxi province, China. In general, the precision for isotopic measurements is better than 0.2% and the correction of mass fractionation has been applied for all results.

Four molybdenite separates of the Sungun PCD were analysed at the University of Arizona (USA), using negative thermal ionization mass spectrometry (NTIMS; Creaser et al., 1991) by a *VG 54* mass spectrometer. Each 30–50 mg sample was dis-

solved in heated (180–220°C) Carius tubes loaded with 4ml of re-aqua-regia (3:1 mixture of ultrapure 16N HNO₃:12N HCl) and 2ml of hydrogen peroxide (added to enhance the oxidation of Os) for >14 hours. Re was separated by a solvent extraction method using carbon tetrachloride, as described in Cohen and Waters (1996) and Pearson and Woodland (2000). Re was further purified by ion exchange chromatography, as described in Mathur (2000), and measured using a Faraday collector. An internal NIST Os standard was measured throughout the study (n = 3) and the ¹⁸⁷Os/¹⁸⁸Os of the standard remained constant at 0.1492 ± 0.0002. A Henderson molybdenite standard was also measured to check the accuracy of the data.

Four molybdenites separates from the Siah Kamar PMD were analysed at the University of Durham (UK), using a Thermo Scientific TRITON mass spectrometer. 10–50 mg aliquots of the molybdenite separates and tracer solution (¹⁸⁵Re + isotopically normal Os) were loaded into a Carius tube with 11N HCl (1 ml) and 15.5N HNO₃ (3 ml), sealed and digested at 220°C for ~24 h. Re was isolated using standard NaOH-acetone solvent extraction and anion column chromatography and measured using a static Faraday collector. The reproducibility of the isotopic measurements was checked using the RM8599 NIST molybdenite standard, which was analysed during the same period as that of Li et al. (2017).

RESULTS

Based on the XRD analysis data, the Qarachilar molybdenite samples are of 2H polytype with hexagonal structure. The most intense picks for the two analysed samples appear at 14.42 and 14.39, 39.65 and 39.59, 49.90 and 49.92, 32.79 and 39.84, respectively. This polytype is common in porphyry copper deposits (Newberry, 1979a, b).

Re contents of the molybdenite separates prepared from the Qarachilar quartz-sulphide veins-veinlets, and the Sungun and Siah Kamar porphyry stocks are presented in Table 1. The uncertainties for Re concentration are given as absolute amounts at the 2σ level. The Re concentration in molybdenites of the Qarachilar area and the Sungun PCD are in the range of several hundred ppm (112.67–462.82 ppm for Qarachilar with

an average of 262.28 ppm, and 53.24 to 252.29 ppm for Sungun with a mean of 123.82 ppm; Table 1). Ghodrati (2010) also reported Re contents of four molybdenite samples from the Sungun PCD ranging from 1.251 to 5.102 ppm, with the average of 2.202 ppm. Altogether, these values are in good agreement with the range reported from porphyry Cu-Mo deposits and comparable with similar mineralisations across the world (e.g., Berzina et al., 2005).

Based on the data published to date, the Re values obtained for the Qarachilar share a similar range with the Re contents of most of the Cu-Mo deposits in China (except Tangshan), Mongolia, Kazakhstan (except Kounrad), Armenia (except Elpin and Dzhindara), Chile (except Los Pelambres) and North America (except Castle Dome, Copper Creek, and San Manuel in USA) (Berzina et al., 2005 and references therein). PCDs in Greece, Bulgaria and Serbia have higher ranges compared to Qarachilar. Among the Cu and Cu-Mo mineralisations in the Meghri-Ordubad pluton with available rhenium data (Fig. 2), the Re content of the Qarachilar molybdenites is in the range of those from the porphyry Cu-Mo deposits of Dastakert, Paragachay, Agarak and world-class Kadjaran (Table 2), although the Re ranges for the latter two deposits are much more wider. Such a narrow range for the studied samples may result from the limited number of analyses and the small sampling area in the Qaradagh batholith. In the Iranian territory, data reported from the Haft Cheshmeh, Sarcheshmeh, Sarkuh, Kerver and Now Chun PCDs (Table 2) have similar and/or overlapping Re ranges, while in the Re versus Cu/Mo plot of Figure 7, Qarachilar is plotted near the Now Chun, Sarcheshmeh, Haft Cheshmeh and Bagh Khoshk deposits of Iran and the Dastakert and Kadjaran PCDs of Armenia. All of them fall within the fields of Cu-dominated porphyry deposits.

The total range of the Re content in the Sungun molybdenites (53.24–5.102 ppm) is comparable with all the PCDs across the world and the region, especially the Agarak and Kadjaran PCDs in southern Armenia (Table 2), which have such a wide range, as well as with El Teniente in Chile, Toquepala in Peru, Bingham, Esperanza and Morenci in the USA and other PCDs in Kazakhstan and Uzbekistan (based on the data published by Berzina et al., 2005). The Re range is also comparable with the molybdenites of Kahang, Sarcheshmeh,

Table 1

Re content of the molybdenite separated from the Qarachilar area (Mo1–5), Sungun PCD (S1–4) and Siah Kamar PMD (K1–4)

Sample	Borehole no. and depth	Re [µg/g]	
		Measured	2σ
Mo1	Surficial	288.46	0.93
Mo2	Surficial	462.82	2.34
Mo3	Surficial	244.71	1.24
Mo4	Surficial	202.76	0.96
Mo5	Surficial	112.67	0.50
S1	SUS62-649 m	252.29	
S2	SUS61-381 m	53.24	
S3	SUS70-183 m	65.95	
S4	SUS62-605 m	158.08	
K1	10–97 m	41.05	0.22
K2	10–99 m	21.69	0.14
K3	17–33 m	30.17	0.17
K4	17–36 m	10.44	0.05

Table 2

Re contents of molybdenites in porphyry Cu deposits of the southern Armenia and the Cu metallogenic zones across the UDMA (Iran); locations of these deposits are shown in Figure 3

PCDs and prospects	Location	Re [ppm]	Sample number	References
Agarak	SAB	538.8	1	Moritz et al. (2016)
		57–6310 (mean = 820)	820	Magakian et al. (1984)
Aygedzor	SAB	727.5–1141	2	Moritz et al. (2016)
Kadjaran	SAB	104.3–368.3 (mean = 229.3)	6	Moritz et al. (2016)
		33–2620 (mean = 245)	237	Magakian et al. (1984)
Dastakert	SAB	207.9–315.8 (mean = 242.8)	4	Moritz et al. (2016)
		130–300 (mean = 220)	8	Magakian et al. (1984)
Hankasar	SAB	45.1–76.3	2	Moritz et al. (2016)
Paragachay	SAB	258.6	1	Moritz et al. (2016)
Haft Chashmeh	Ahar–Jolfa	111.7–241	2	Aghazadeh et al. (2015)
Kahang	Central Iran	1332	1	Aghazadeh et al. (2015)
Sarcheshmeh	Kerman	10.8–631 (mean = 292.8)	20	Aminzadeh et al. (2011)
		418–987 (mean = 607.5)	6	Aghazadeh et al. (2015)
Bagh Khoshk	Kerman	451–657 (mean = 545.5)	6	Aghazadeh et al. (2015)
Sarkuh	Kerman	302.21	1	Mirnejad et al. (2013)
		164.6–1904 (mean = 832.1)	4	Aghazadeh et al. (2015)
Iju	Kerman	1715.4	1	Mirnejad et al. (2013)
		938–945	2	Aghazadeh et al. (2015)
Miduk	Kerman	1221.8–1229.9	2	Taghipour et al. (2008)
Kerver	Kerman	304–1490	2	Aghazadeh et al. (2015)
Abdar	Kerman	4247–4467	2	Aghazadeh et al. (2015)
Bondar Hanza	Kerman	527–690	2	Aghazadeh et al. (2015)
Now Chun	Kerman	200.5	1	Aghazadeh et al. (2015)
Darreh Zar	Kerman	944.4	1	Aghazadeh et al. (2015)
Dar Alu	Kerman	817	1	Aghazadeh et al. (2015)
Chah Firouzeh	Kerman	3273	1	Aghazadeh et al. (2015)
Kuh Panj	Kerman	1699	1	Aghazadeh et al. (2015)

Miduk, Sarkuh, Iju, Kerver, Abdar, Chah Firouzeh and Kuh Panj in Central Iran and Kerman metallogenic zones (Table 2), which show relatively higher Re contents in the range of thousands of ppm. Furthermore, in the Re versus Cu/Mo plot of Figure 7, the Sungun PCD is plotted near the Kahang and Agarak PCDs, showing very high similarity regarding the averages of Re content and Cu/Mo ratio, while these averages are higher than those of the Qarachilar mineralisation. These deposits are also falling within the fields of Cu-dominated porphyry deposits.

The Re contents of both the Qarachilar mineralisation and the Sungun PCD are higher than those reported from Mo and Mo-Cu deposits, as well as the Siah Kamar PMD, in which it varies between 10.44 and 41.05 ppm with an average of 25.84 ppm. Considering the concentration of several tens of ppm, the Siah Kamar data are comparable with those of PMDs, such as the typical deposits of Endako and Max in Canada (Fig. 7), and Climax and Urad Henderson in the USA, as well as most of the

measured PMDs in Russia (except Amudzhikan and Davenda) and Central Asia. However, the Siah Kamar values are a little lower than those reported from Boss Mountain and Lime Creek in Canada and Questa in the USA (Berzina et al., 2005 and references therein). The average Re content of the Siah Kamar samples is also slightly lower than the average of 42 ppm calculated based on 19 PMDs and porphyry Mo-Cu deposits across the world (Berzina et al., 2005). As shown in Figure 7, the Siah Kamar data point plot in the field of PMDs, having very low Cu/Mo ratio and Re content in comparison with the studied and plotted porphyry Cu-Mo deposits of Iran and Armenia.

On a regional scale of north-west and central Iran and southern Armenia (mineralisations of the latter are studied in detail by Moritz et al., 2016), the Siah Kamar deposit is the only PMD discovered to date and therefore, there is no other counterpart to make comparison. When comparing it with porphyry Cu-Mo deposits across the region, it is clearly seen that the

measured values of the Siah Kamar PMD are much lower than those of the PCDs (Fig. 7). The exceptions are two samples from the Sarcheshmeh PCD with values of 10.85 and 21.30 ppm reported by Aminzadeh et al. (2011), and a few samples from the Kadjaran PCD (Magakian et al., 1984), which show an overlap with the Siah Kamar values.

DISCUSSION

Investigations carried out on molybdenites of porphyry Cu and Mo deposits show that Re content variations may be related to the composition of parental magmas and/or fractionation, reactions between crustal rocks and magmas (contamination), depth of the sub-volcanic stocks, sources of the ore materials, variations in physical and chemical conditions of crystallisation (fO_2 , activity of Cl, P, T), total amount of molybdenite in a given deposit, and the polytype of molybdenite (2H or 3R) (Giles and Shilling, 1972; Newberry, 1979b; Todorov and Staikov, 1985; Ishihara, 1988; Economou-Eliopoulos and Eliopoulos, 1996; Melfos et al., 2001; Xiong and Wood, 2001, 2002; Berzina et al., 2005).

In recent years, Re content of molybdenites is used to detect the source of ore materials (e.g., Mao et al., 1999, 2003, 2006; Stein et al., 2001; Delibaş and Genc, 2012). Mao et al. (1999) suggested that the metal source may affect the Re content, so that it gradually decreases from the mantle source (several hundred ppm) through a mixed source of mantle and crustal materials (tens of ppm) towards the crustal source (several ppm) (Mao et al., 1999, 2003, 2006; Stein et al., 2001; Selby and Creaser, 2001; Berzina et al., 2005; Dai et al., 2009; Delibaş and Genc, 2012). In other words, Re concentration decreases from the mantle towards the deposits related to I-type and then to S-type granites (Berzina et al., 2005). In this regard, for the ultrahigh- and high-Re molybdenites in the Pagoni Rachi and Konos deposits (Greece), a LILE- and LREE-enriched sub-continental mantle is proposed as a magma source with minimal contribution of the continental crust (Del Moro et al., 1988), where the mantle wedge had some chemical inhomogeneities, which triggered post-subduction metasomatism (Voudouris et al., 2013). It is while porphyry Mo and Mo-W deposits with either crustal origin or a major contribution of crustal materials in Greece contain Re-poor molybdenites (Voudouris et al., 2013).

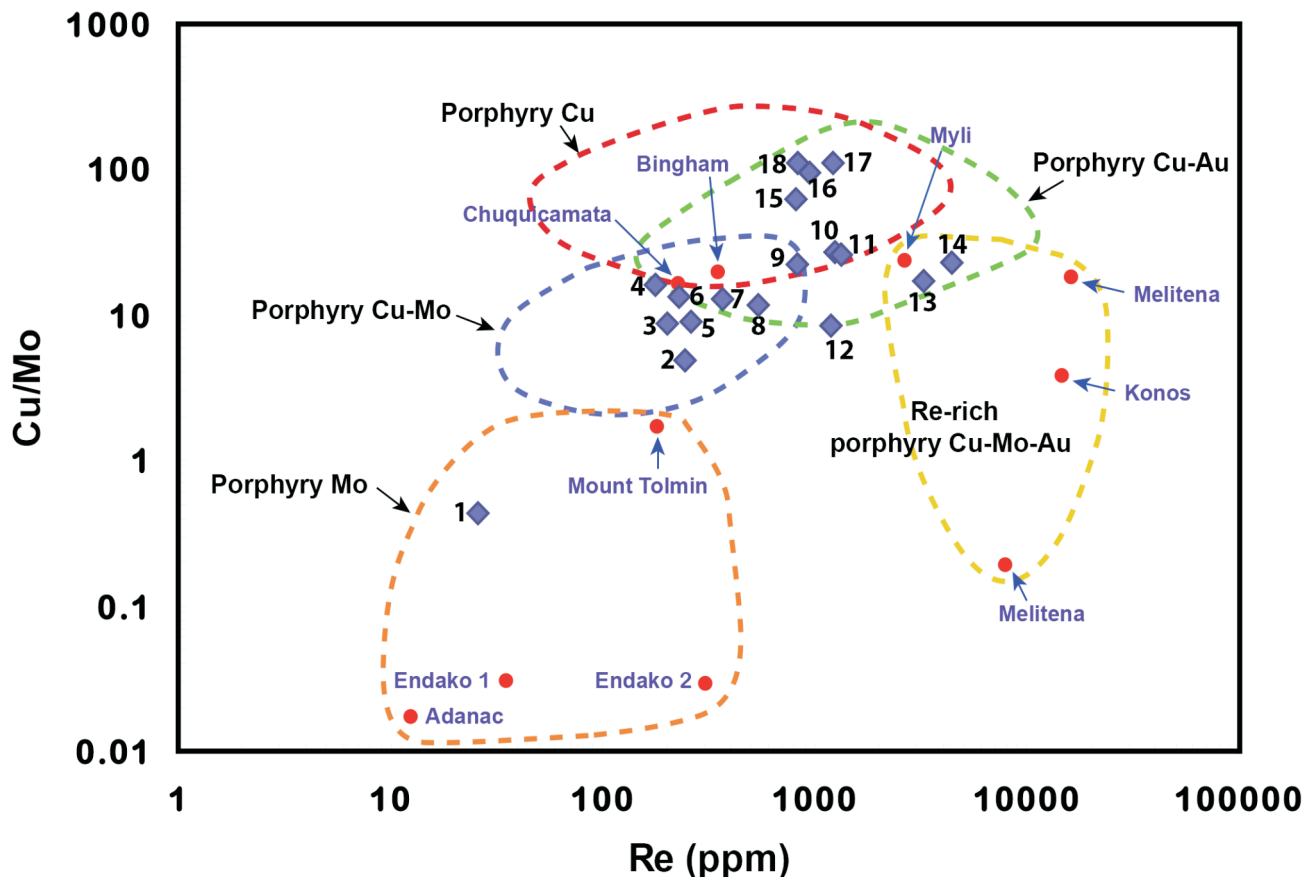


Fig. 7. Re content of molybdenites versus Cu/Mo ratios of the porphyry deposits in Iran and southern Armenia, with fields defined by Voudouris et al. (2013) for porphyry Cu, Cu-Mo, Cu-Au, Mo and Re-rich deposits worldwide and some well-known examples

1 – Siah Kamar (Khaleghi et al., 2013), 2 – Kadjaran (U.S. Geological Survey, 2019), 3 – Now Chun (Daneshvar Saein, 2017), 4 – Haft Cheshmeh (Hassanpour et al., 2010), 5 – Qarachilar (Mokhtari, 2008; Rezaei Aghdam and Soharbi, 2010), 6 – Dastakert (U.S. Geological Survey, 2019), 7 – Sarcheshmeh (Shafiei and Shahabpour, 2008), 8 – Bagh Khoshk (Khakzad and Shaban, 2006), 9 – Agarak (U.S. Geological Survey, 2019), 10 – Sungun (Ghodrat, 2009), 11 – Kahang (Komeili et al., 2016), 12 – Iju (Mirnejad et al., 2013), 13 – Chah Firouzeh (Karimi et al., 2011), 14 – Abdar, 15 – Daralu, 16 – Darreh Zar, 17 – Miduk, 18 – Sarkuh (14–18 – Shafiei and Shahabpour, 2008)

The Re contents of the Qarachilar and Sungun molybdenites, as well as those of the Siah Kamar PMD, are relatively high within the ranges defined for PCDs and PMDs, respectively, which most likely indicate a mixed (mantle+crustal) source for ore materials with the more predominant role of the mantle source compared to the crustal component. The I-type characteristics of the granitoid host rocks and the other intrusive rocks in the studied areas and generally in NW Iran also prove a mantle-derived source for these rocks and consequently for the mineralisation related to them. Moreover, Zakeri (2013) has reported very low initial $^{87}\text{Sr}/^{86}\text{Sr}$ values for samples taken from the Qaradagh intrusive complex, ranging between 0.7037 and 0.7041, which are very close to the mantle values and indicate a magma source with the high contribution of mantle component and insignificant contribution or assimilation by upper crustal rocks. This feature can be generalized to two other deposits studied, especially the Sungun PCD which is about 30 km south-east of it and shares many petrogenetic and geodynamic features with the Qaradagh batholith.

Furthermore, U-Pb and Re-Os age reports of the studied deposits show a Middle Oligocene-Early Miocene time span. It confirms that magmatism and mineralisation in these areas were post-collisional, post-dating the closure of the Neo-Tethyan basin (e.g., Berberian and King, 1981; Alavi, 1991; Agard et al., 2006). Owing to the emergence of extensional tectonics after the previously prevailing compressional conditions, they can be responsible for the low incorporation of continental crust in supplying the ore materials and the dominance of mantle source for them. On the other hand, in post-subduction and post-collisional environments, partial melting of the previously metasomatized mantle by the fluids released from the subducted slab and the associated sediments could be the key to metal enrichment, leading to the formation of Re- and/or Te-enriched porphyry Cu-Mo-Au deposits (Voudouris, 2006; Voudouris et al., 2009). Both these conditions will lead to a relatively higher Re content of molybdenites in the resulting ores.

On the other hand, by taking into account the I-type and oxidizing nature of the studied granitoid host rocks, it can be conceived that the magmatic-hydrothermal fluids derived from these intrusives were also oxidizing in nature. They had favourable conditions for Re transportation and subsequent deposition within the molybdenite structure (Xiong and Wood, 1999, 2001, 2002), whereas sulphur-containing reducing fluids have a lower capacity for transporting rhenium and are not favourable for the formation of Re-rich molybdenites.

Evidence like vein-type and disseminated mineralisation of pyrite and chalcopyrite in addition to molybdenite in the Qarachilar and Sungun deposits, as well as the presence of abundant multi-phase fluid inclusions containing halite and sylvite daughter minerals within the sulphide-bearing quartz veins-veinlets in these deposits (up to 65 wt.% $\text{NaCl}_{\text{equiv}}$; Simmonds and Moazzen, 2016 for Qarachilar; Calagari, 2004b, for Sungun) testify to the high activity of Cl and its role as a metal transporting complex in the magmatic-hydrothermal fluids. On this basis, the relatively high Re contents of the studied molybdenite samples may also be attributed to the high fugacity of rhenium chloride within these fluids (Berzina et al., 2005). This is in a good agreement with the experimental data obtained by Xiong and Wood (2001, 2002), which showed that chloride complexes can have an important role in hydrothermal transportation of Re at temperatures between 400 and 500°C. For the Siah Kamar PMD, such multi-phase inclusions are scarce and the overall salinity, and thus the f_{Cl} in the ore-bearing fluids, was relatively low (2.63–26.2 wt.% $\text{NaCl}_{\text{equiv}}$; Khaleghi et al., 2013), which may have affected the Re content of the resulting molybdenites.

In each porphyry Cu-Mo deposit, the Re content of molybdenites precipitated from acidic hydrothermal fluids (i.e. in the phyllic alteration zone) is higher than those precipitated from alkali fluids (i.e. in the potassic alteration zone) (Filimonova et al., 1984; Ivanov and Yushko-Zakharova, 1989; Berzina et al., 2005). In this regard, in the potassic alteration zones formed by dominantly alkali solutions, which have high capacity for Re dissolution and transportation, the Re content of molybdenites will be low, whereas it increases towards the phyllic alteration zone. Samples No. 4 and No. 5 of the Qarachilar area, as well as the analysed samples of the Siah Kamar PMD, were taken from veinlets with potassic alteration in their wall rocks and therefore, they show relatively low Re concentration, while other Qarachilar samples were collected from veinlets surrounded by dominant phyllic alteration and have higher values. Similarly, all the samples from the Sungun PCD are collected from the potassic-phyllic alteration zone, where acidic fluids of the later-stage phyllic alteration have left their fingerprint by precipitating molybdenites with a relatively higher Re content. In this regard, sample No. S2, which has the lowest Re, shows moderate to intense potassic and weak later-stage phyllic alteration. In the other samples, the phyllic alteration is more intense, justifying their relatively higher Re contents. Therefore, the acidity-alkalinity of the ore-forming fluids can be used, together with other factors, to explain the Re variations in these samples.

The Re content of molybdenites can also be affected by fluid temperature or the deposition stage (Giles and Shilling, 1972; Newberry, 1979b; Filimonova et al., 1984; Todorov and Staikov, 1985). Experimental studies show that there is a negative correlation between the temperature of molybdenite deposition and its Re content (Giles and Shilling, 1972; Newberry, 1979b; Filimonova et al., 1984; Todorov and Staikov, 1985), although Popov (1977) suggested that this relationship is not applicable for all Cu-Mo deposits across the world.

Microthermometry of 2-phase (L–V) and multiphase fluid inclusions within the ore-bearing quartz veins-veinlets yielded temperature ranges of 220–540°C for Qarachilar, with most of the data clustering between 240 and 420°C and showing boiling evidence (Simmonds and Moazzen, 2016), 160–600°C for Sungun, where the evolved magmatic fluids involved at the onset of phyllic alteration and sulphide mineralisation had temperatures ~560–580°C and experienced continuous boiling (Calagari, 2004b), and 211–300°C for Siah Kamar (Khaleghi et al., 2013), which reveals that at least some of these veins-veinlets are formed at a relatively high temperature and this factor may influence the Re content of the sampled molybdenites. For example, samples No. 4 and No. 5 from the Qarachilar area are taken from high temperature quartz-sulphide veins-veinlets and their lower Re content may also result from their higher formation temperature. For the Siah Kamar PMD, the resulting molybdenites have low Re content due to their alkali nature and the dilution effect, although the ore-forming fluids were relatively low-temperature.

Faramazian (1961) suggested that molybdenites of the same generation show a direct relationship between their grain size and the Re content. Among the samples analysed in this study, sample No. 2 from Qarachilar, with the highest Re value, was extracted through scraping by a stainless steel blade from relatively coarse-grained assemblages, while other samples of the studied deposits were collected from veinlets containing fine-grained molybdenite (<2 mm). Meanwhile, the extremely high Re values of up to 5.102 ppm reported by Ghodrati (2010) were measured on molybdenite separates extracted using a hand drill from large-grained aggregates. Therefore, the positive relationship between the molybdenite grain size and its Re

content, as well as the cause of such high contents in the latter samples, is clearly perceivable from the data presented herein.

To conclude, the Re abundances in the molybdenites are affected by the mutual and complex interaction of several factors, as was earlier postulated by [Berzina et al. \(2005\)](#) and references therein). The factors include the source of parental magma and ore materials, the total molybdenite abundance, Eh–pH, fCl and temperature of ore-forming fluids, although the volume dilution effect seems to have the dominant control on the global distribution of Re between Mo-dominated and Cu-dominated deposits. However, [Stein et al. \(2005\)](#) have presented another explanation for low-moderate Re contents in molybdenites of the Myszków Mo-Cu-W deposit in Poland, although it is not the case for the studied deposits. Molybdenite in Myszków is generally associated with quartz veins and patches in granodiorite, although these ill-defined and scattered veins do not constitute stockwork in the classical sense. Moreover, while the potassic alteration is prevalent, secondary biotite, magnetite and significant pyrite are conspicuously sparse ([Stein et al., 2005](#)). The low-moderate and fairly consistent Re contents of molybdenites ranging from 40 to 75 ppm in Myszków do not support a subduction-related porphyry-style origin ([Stein et al., 2001](#)), and a better alternative would be a moderately local derivation from a crustal reservoir rather than origination of the materials from different reservoirs, mixing and system-wide fluid separation (porphyry model). In other words, development of veins likely depended on local separation and volatile enhancement of hydrothermal fluids that were not far-travelled. On this basis, authors suggest that the Myszków Mo-Cu-W deposit is the product of rapid orogenic uplift and exhumation melting, which have limited the development of a classic porphyry-style mineralisation.

CONCLUSIONS

The Re contents of five molybdenite separates extracted from quartz-sulphide veins-veinlets in the Qarachilar area and four molybdenite separates from the Sungun deposit are in the range of PCDs across the world, while those of the Siah Kamar deposit ($n = 4$) are obviously distinguishable from porphyry Cu deposits with their lower values and correspond to the range defined for porphyry molybdenum deposits. This difference can be related predominantly to the volume dilution of Re with the presence of large volumes of molybdenite in PMDs, while in the Cu-dominated mineralisations, the low molybdenite abundance leads to the concentration of Re within it as its main host (e.g., [Berzina et al., 2005](#) and references therein).

The relatively high Re contents in the studied deposits compared to the ranges proposed for each type can be explained by considering a mixed mantle + crust source for the ore materials with a more dominant role of the mantle source compared to the crustal component. The I-type characteristics of the host rocks and the post-collisional setting of the magmatism and mineralisation under the extensional tectonic regime confirm this assumption.

Meanwhile, variations of Re content in different samples taken from these areas and from different veins can be explained by taking into account the formation temperature of these veins, acidity/alkalinity of hydrothermal fluids or, in other words, the type of alteration accompanying the mineralisation, as well as the grain size of molybdenites. Thus, molybdenites formed in higher temperatures or within the potassic alteration zone were found to have lower Re contents compared to those formed in lower temperatures or within the phyllic alteration zone. Additionally, it is clearly evident that a positive correlation exists between the grain size of molybdenites and their Re content in the studied samples.

On the regional scale and based on the Re contents, the Qarachilar and Sungun molybdenites are comparable with the Dastakert, Agarak and world-class Kadjaran porphyry Cu-Mo deposits in the Meghri-Ordubad pluton (southern Armenia), which is considered as the northern extension of the Qaradagh batholith. These similar Re ranges further confirm similarities regarding the tectonic setting and mineralisation conditions between both batholiths. Additionally, the Re contents of molybdenites in these two deposits are in the range of those from the Haft Cheshmeh (NW Iran), Sarcheshmeh, Sarkuh and other PCDs and prospects in the Kerman Cu metallogenic zone, which are also located on the UDMA and share similar tectonic and petrogenetic features with the studied deposits. However, as the Siah Kamar deposit is the first porphyry Mo mineralisation discovered in Iran and the southern Lesser Caucasus, it has no counterpart to compare with, while its Re content is lower than all the PCDs in these regions.

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