



Geochemical signatures of waste rocks around Sarcheshmeh porphyry copper mine dumps, southeastern Iran: Implications for exploration, economic by-products and the environment



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ABSTRACT

The Sarcheshmeh porphyry copper deposit (1.7 Gt @ 0.65% Cu, 0.02% Mo, 1.22 ppm Ag, 0.06 ppm Au) is one of the giant Miocene continental arc porphyry ore systems in the Tethyan metallogenic copper belt. The supergene sulfide ore zone (6 Mt. @ 2.43% Cu, 0.022% Mo, 1.55 ppm Ag and 0.114 ppm Au) is mainly capped by a hematitic gossan. This hematitic gossan is a possible surficial exploration target for unexposed porphyry copper ores. The total tonnage of waste rocks is about 2.6 G tonnes of gossanized as well as sulfide-bearing waste rocks with an average modal content of 10% pyrite-chalcopyrite. The gossanized waste rocks show boxwork texture and are composed of hematite, goethite, jarosite, malachite, chalcantinite, brochantite and delafossite. In order to assess the exploration, economic and environmental aspects of chalcophile and precious elements in the waste rocks, a total of 86 waste rocks and 10 residual gossan samples were collected by a systematic random sampling method, analysed by XRF and ICP-MS methods for major oxides and 50 minor and trace elements at ALS Minerals Lab, Ireland. The highly anomalous elements in immature residual gossans are Au (0.775 ppm), Ag (13.4 ppm) and Mo (122 ppm). The gossanized waste rocks are also enriched in Au (0.608 ppm), Ag (87 ppm) and Mo (2960 ppm). These geochemical signatures could be used as possible exploration guides for concealed porphyry copper deposits. The enrichment of Au, Ag and Mo is caused by the lower mobility of these elements in the immature gossans and gossanized waste rocks. The elemental enrichment factors normalized to the Sarcheshmeh ore zone are Au (2.50), Pd (1.05), Ag (4.67), Pb (4.6), Zn (17.34), Sn (2.64), W (1.47), Re (22.22), Se (5.38), Te (5.75), Tl (4.1), Bi (3.29), Ga (1.15), In (11.5), La (1.2), Ce (1.2) and Y (4.1), respectively. The mean contents of the most valuable by-product elements in the gossanized waste rocks include Cu (3168.2 ppm), Mo (180.22 ppm), Au (0.085 ppm), Ag (5.7 ppm), W (42.76 ppm), Re (0.01 ppm), Bi (10.87 ppm) and Se (13.45 ppm). The S-NNP diagram highlights that the sulfide-bearing waste rocks have also a negative impact on the environment, are prone to generate acid mine drainage (AMD) and release the potentially harmful metal (loids): Pb (107 ppm), Zn (365.3 ppm), As (83.53 ppm), Sb (10.24 ppm), In (0.44 ppm), and Se (13.45 ppm) into the surrounding area. These elemental values occurred at concentrations about 4–269 times greater than the crustal abundances and natural background of fresh granodiorite. As such, the heavy metal-rich gossans and sulfide-bearing waste rocks around the Sarcheshmeh mining areas may be considered as an exploration guide for valuable by-product elements as well as environmental concern.

1. Introduction

Rock mine wastes are commonly dumped around mine sites and contain concentration of elements and compounds that can have severe environmental effects on ecosystem as well as containing some valuable by-product metals (Hettler et al., 1997; Hudson-Edwards et al., 2011; Lottermoser, 2011). Although, yesterday's waste rocks can be

considered as today's resources (Lottermoser, 2011), mineralogy, geochemistry, recycling, reuse and rehabilitation of mine wastes have recently attracted new ideas on mineral resources appraisal and environmental concerns. In this regard, it is highly opportune to mention that the reuse of the waste rocks for future resources of economic minerals as well as extraction of metals from the mining-waste dumps have been suggested by some authors (Wu et al., 2009; Lottermoser,

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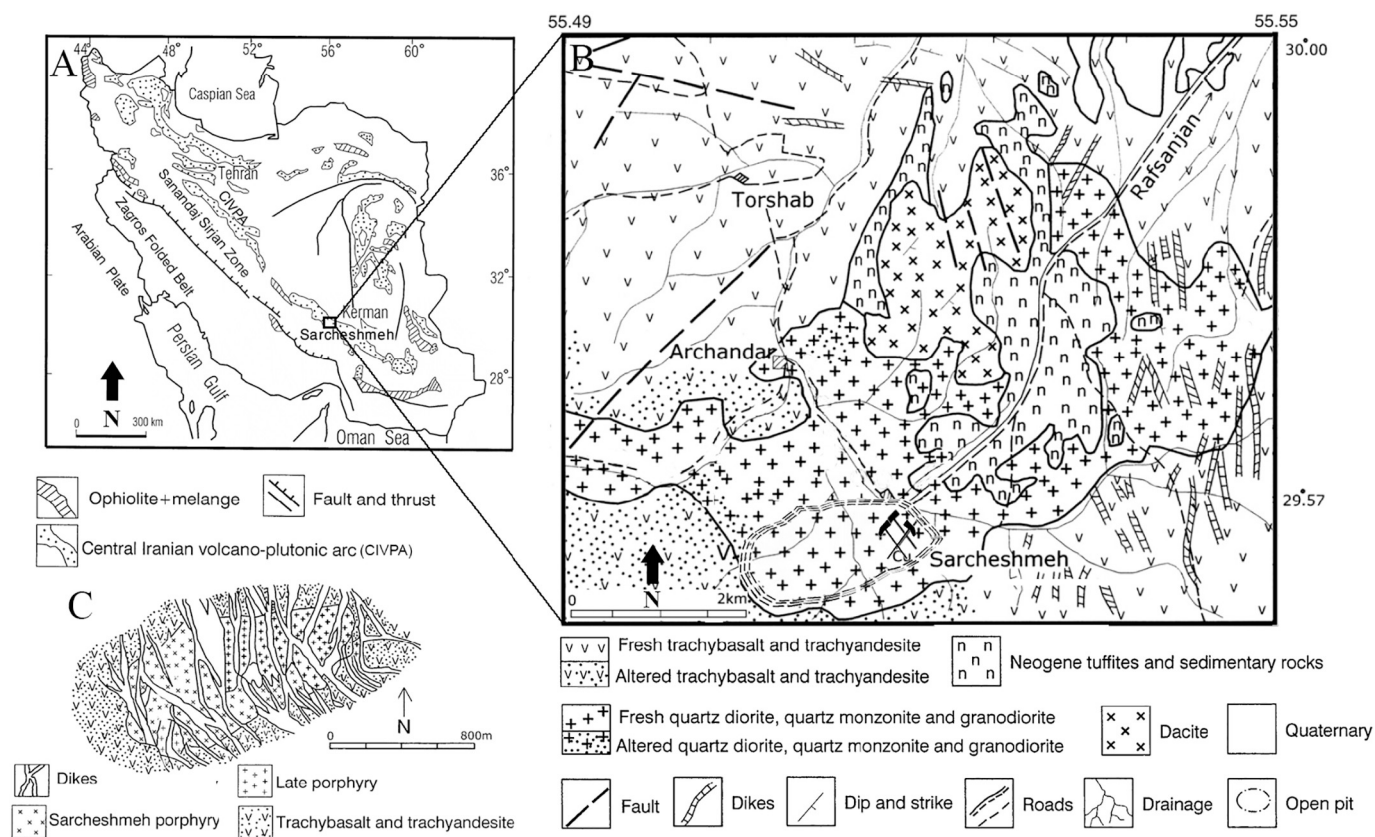


Fig. 1. Map of structural zones of Iran (A), geological map around Sarcheshmeh porphyry copper mine (B) and of Sarcheshmeh porphyry copper mine, rock units and alteration zones (C), (modified after Nedimovic, 1973; Jacobsen, 1975; Waterman and Hamilton, 1975; Atapour and Aftabi, 2007).

2011; Bogdanović et al., 2016; Falagan et al., 2017). Also, mining-waste dumps may contain high concentrations of heavy metals (e.g., Cu, Fe, Ni, Zn, Pb, Bi, Mo) and occasionally Au and Ag (Ahmadi et al., 2015; Hunt et al., 2016; Falagan et al., 2017). Moreover, it is widely accepted that pyrite-rich waste rocks also play a positive role as soil additive to neutralize infertile alkaline agricultural soil (Lottermoser, 2011). Additionally, pyrite-rich waste rocks are the widely reported potential source of acid mine drainage (AMD) as well as potentially harmful heavy metal pollution such as As, Pb, Cd, Bi and Se (Ledín and Pedersen, 1996; Benvenuti et al., 1997; Hammarstrom et al., 2005; Diehl et al., 2006; Smith et al., 2006; Nugraha et al., 2009; Sracek et al., 2010; Hudson-Edwards et al., 2011; Jamieson, 2011; Plumlee and Morman, 2011; Modabberi et al., 2013; Dold, 2014; Murray et al., 2014; Jamieson et al., 2015; Yousefi et al., 2015a; Yousefi et al., 2015b; Assawincharoenkij et al., 2017; Khosravi et al., 2017). Tabasi et al. (2017) reported that the mean concentrations of As, Cu, Mo, Ni, Zn, and Re in soil as well as in the shoots and roots of plant species at Sarcheshmeh mine are 18.44, 1280, 25.06, 32.9, 251.82 and 1.7 mg kg⁻¹. These values are much higher than the normal background in non-contaminated soils. Despite these valuable studies, very less attention has been given to the baseline geochemical signatures of the waste rocks dumped around the porphyry copper deposits. > 98 wt% of porphyry copper deposits are dumped as waste rocks, including host rocks, overburden alluvium sediments, iron caps, leached and oxide zones (John et al., 2010). The waste rocks in porphyry copper mines include silicate minerals, oxides, hydroxides, carbonates, phosphates and low-grade sulfide ores. The silicate minerals are the most common gangue minerals and the most abundant sulfides are pyrite, chalcopyrite, molybdenite, marcasite and pyrrhotite, which play a significant role in the acid mine drainage (AMD) production. The chemical properties of iron sulfides, in particular pyrite and other minerals are important as well as the presence or absence of microorganisms, oxygen, temperature, pH

and the Fe⁺²/Fe⁺³ ratios in the rate of acid mine drainage (AMD) generation for releasing toxic elements from the waste rocks (Lottermoser, 2007). The on-going exploitation and extraction of copper and other valuable elements from the porphyry copper ores reduce the copper ore reserves year by year. This increases the demand for copper in the coming years, thus investigation on the waste rocks around the porphyry copper mines may introduce new geochemical data on the alternative exploration techniques to find new copper resources. Also, generation of acid mine drainage (AMD) followed by the release of high concentrations of heavy metals during weathering of sulfide-bearing waste and gossanized waste rocks, merit further development of new remediation techniques for environmental contamination.

1.1. Scope of the study

The Sarcheshmeh porphyry copper mine is one of the giant Miocene continental arc porphyry copper deposits in the world and contains 1.7 G tonnes ore with an average grade of 0.65% copper, 0.02% molybdenum, 1.22 ppm silver, and 0.06 ppm gold (Shafiei, 2014; Parandoush, 2017). The total tonnage of waste rocks is about 2.6 G tonnes, which have not been studied in terms of economic by-product metals and environmental hazards. The primary data on geology and porphyry copper mineralization around the Sarcheshmeh porphyry copper deposit have been described by Bazin and Hübner (1969), Nedimovic (1973), Waterman and Hamilton (1975), Ghorashizadeh (1978), Shahabpour (1982), Shahabpour and Kramers (1987), Soleymani (1999), Khorshidi (2005), Atapour and Aftabi (2007), Shafiei (2014) and Atapour (2017). Previous studies reported some valuable geochemical data on the distribution of toxic elements in water and sediments around the Sarcheshmeh mine (Jannesar Malakooti et al., 2012, 2014; Khorasanipour and Eslami, 2014;

Khorasanipour, 2015; Yousefi et al., 2015a; Khorasanipour and Jafari, 2017). However, there are no records of geochemical data on different types of waste rocks in terms of exploration guides, economic by-product metals, and negative environmental impacts. This investigation explores the geochemical signatures of different types of waste rocks at Sarcheshmeh mine waste dumps to determine if the waste rocks contain economic valuable as well as potential toxic elements. The main objectives of this paper are; (1) to introduce new geochemical baseline for major, minor and trace elements in waste rocks from the Sarcheshmeh porphyry copper deposit (2) to propose the possible exploration guides as well as to identify economic by-product elements, and (3) to evaluate the environmental aspects of potential toxic elements in waste dumps.

2. Geological setting and mining geology

The Sarcheshmeh mine is situated in southeastern Iran at 29°56' 40" N, 55°52' 20" E coordinates, and about 160 km southwest of Kerman city (Fig. 1A). The deposit is one of the giant Miocene continental arc porphyry copper deposits that contains about 1.7 G tonnes ore with an average grade of 0.65% copper and 0.02% molybdenum, 1.22 ppm silver, and 0.06 ppm gold (Shafiei, 2014; Parandoush, 2017). The low concentration of gold and high content of molybdenum in the Sarcheshmeh porphyry copper deposit classify the deposit as a continental arc porphyry copper deposit (Atapour, 2017) rather than a gold-rich island arc or post collision porphyry copper deposit (Muller and Groves, 1997; Sillitoe, 2002). As shown in Fig. 1B and C the oldest host rocks to the porphyry copper mineralization consist of pyroxene trachybasalt and pyroxene trachyandesite of potassic and shoshonitic affinity (Atapour and Aftabi, 2007), less abundant andesite and rare occurrences of tuff, and tuffaceous sandstone. These were intruded by Miocene quartz diorite, quartz monzonite and granodiorite intrusive rocks. The intrusive rocks are intruded by a series of hornblende porphyry, feldspar porphyry and biotite porphyry dykes (Waterman and Hamilton, 1975). The latest stage of magmatic activity includes Neogene ignimbrite, dacite and stratified tuff. The volcano-plutonic complex was folded into an anticline trending east–west, and was subsequently faulted in ENE–WSW direction (Atapour and Aftabi, 2007). The surficial alteration zones cover an area of 1–15 km² and occur as propylitic, sericitic, potassic and argillic along the contacts between the volcanic and intrusive rocks (Aftabi and Atapour, 2010). Fig. 1C shows the details of geological units and alteration zones from the centre outward at the Sarcheshmeh deposit.

3. Mineralization and alteration

The mineralization at the Sarcheshmeh porphyry copper deposit occurs in trachybasalt, trachyandesite, granodiorite and quartz monzonite. The Sarcheshmeh ore body is ellipsoid-shaped about 2300 m long by 1200 m wide and centred in granodiorite and quartz monzonite porphyry stock (Waterman and Hamilton, 1975; Ghorashizadeh, 1978). The hypogene ore zone in the Sarcheshmeh porphyry copper deposit consists of stockworking of pyrite, chalcocopyrite, molybdenite ± primary chalcocite ± bornite and quartz veinlets. According to Aftabi and Atapour (2010), alteration zones from the centre outward at the Sarcheshmeh porphyry copper deposit include potassic, sericitic, propylitic and argillic. The potassic and/or biotitic alteration occurs in the inner zone of the ore body at Sarcheshmeh is characterized by the presence of secondary K-feldspar, biotite, minor sericite, quartz and chlorite, replacing plagioclases and pyroxenes in trachybasalts. Biotitization is observed within the zones of copper mineralization in surficial outcrops, in particular along the contacts between trachybasalt and intrusive rocks. The phyllic alteration occurs as interdistal halo and is the most intensive and common hydrothermal alteration in trachybasalt, Sarcheshmeh porphyry stock and around all other porphyry copper deposits in the area. It is characterized by abundant sericite, granular quartz and minor chlorite, replacing plagioclase, alkali

feldspar and biotite. The argillic alteration is partly developed on the sericitic and propylitic halos and includes kaolinite, illite and chlorite assemblages. The sulfide minerals include abundant pyrite with minor chalcocopyrite, molybdenite and with a pyrite-chalcocopyrite ratio > 10 (Atapour and Aftabi, 2007). The peripheral propylitic distal alteration zone is the most prominent alteration in trachybasalt. The alteration mineral assemblage, include epidote, chlorite, albite, calcite, zeolite, kaolinite, leucoxene, minor sphalerite, galena, pyrite and chalcocopyrite with a pyrite-chalcocopyrite ratio of about 4. The hydrothermal silicate minerals are mainly formed by propylitization of plagioclases, pyroxenes, hornblende and biotite. This type of alteration changes to zeolitic alteration in the most peripheral zone (Atapour and Aftabi, 2007). The minerals in the zeolitic zone occur within veins, veinlets and cavity fillings of zeolites, in close association with calcite, quartz and zeolites such as mesolite and natrolite. The supergene ore zone is comprised of gossanized host rocks. According to Waterman and Hamilton (1975), a layer of leached capping zone averaging 26 m in thickness overlies the supergene sulfide zone. The supergene sulfide blanket is about 37 m in thickness and contains sooty as well as hard chalcocite, digenite and covellite associated with argillic alterations that replace pyrite and chalcocopyrite (Atapour and Aftabi, 2007).

4. Waste rocks

The waste rocks have been dumped around the Sarcheshmeh open pit mine in about 31 sites (Fig. 2) since 1975. Total tonnage of sericitized, propylitized and argillized waste rocks at Sarcheshmeh dumps are 449,523,000 t and the total of the waste dikes include 206,313,000 t (Waterman and Hamilton, 1975), respectively. The more recent estimates on the tonnage of the waste rocks are about 2,600,000,000 t (Parandoush, 2017). Lithologically, the waste rocks are grouped as sulfide-bearing trachybasalt, granodiorite as well as gossanized rocks (Fig. 3A to F). The altered trachybasalt, trachyandesite and granodiorite contain pyrite and chalcocopyrite and show phyllic, argillic and propylitic alterations. The sulfide-bearing waste rocks are enriched in pyrite-chalcocopyrite (5–15 wt%) and are highly sericitized. In addition to pyrite, minor amounts of chalcocopyrite, bornite, chalcocite, covellite, malachite and azurite occur in sulfide-bearing waste rocks. The average copper grade in sulfide-bearing waste rocks is reported to be < 0.25% Cu (Parandoush, 2017). The gossanized waste rocks consist of large blocks of gossan and a leached zone (Fig. 3B) and are composed of hematite, goethite, jarosite and delafossite (CuFeO₂) in stockworking structures (Fig. 3C to F). The boxwork structure is formed by oxidation and dissolution of pyrite and chalcocopyrite during chemical weathering, though they contain minor contents of chalcocite, bornite, covellite and molybdenite. The frequent occurrence of bluish green colors of chalcocite, brochantite and melanterite is a dazzling field aspect of the gossanized waste rocks (Fig. 3G, H and supplementary files 2 and 3, Fig. S2, Table S3, and Fig. S3). Blooms of hydrated metal salts and sulfates have long been recognized as the products of evaporation of acid-sulfate waters formed by chemical weathering of sulfide minerals (Hammarstrom et al., 2005). These include the hydrated copper sulfates such as chalcocite (CuSO₄·5H₂O) and brochantite [Cu₄SO₄(OH)₆], which form during the oxidation and dissolution of chalcocopyrite. Other sulfates include jarosite and melanterite (Fig. 3G and H).

5. Materials and methods

5.1. Sampling

A total of 96 samples, each weighting 2 kg, were collected by a systematic random sampling method from different waste rocks. These piles include 10 residual capped gossans, 16 sulfide-bearing waste rocks, 43 gossanized waste rocks, 23 samples of trachyandesite, trachybasalt and granodiorite, and 4 samples from the secondary sulfate minerals. The sampling sites are shown in Fig. 2. The samples were cut

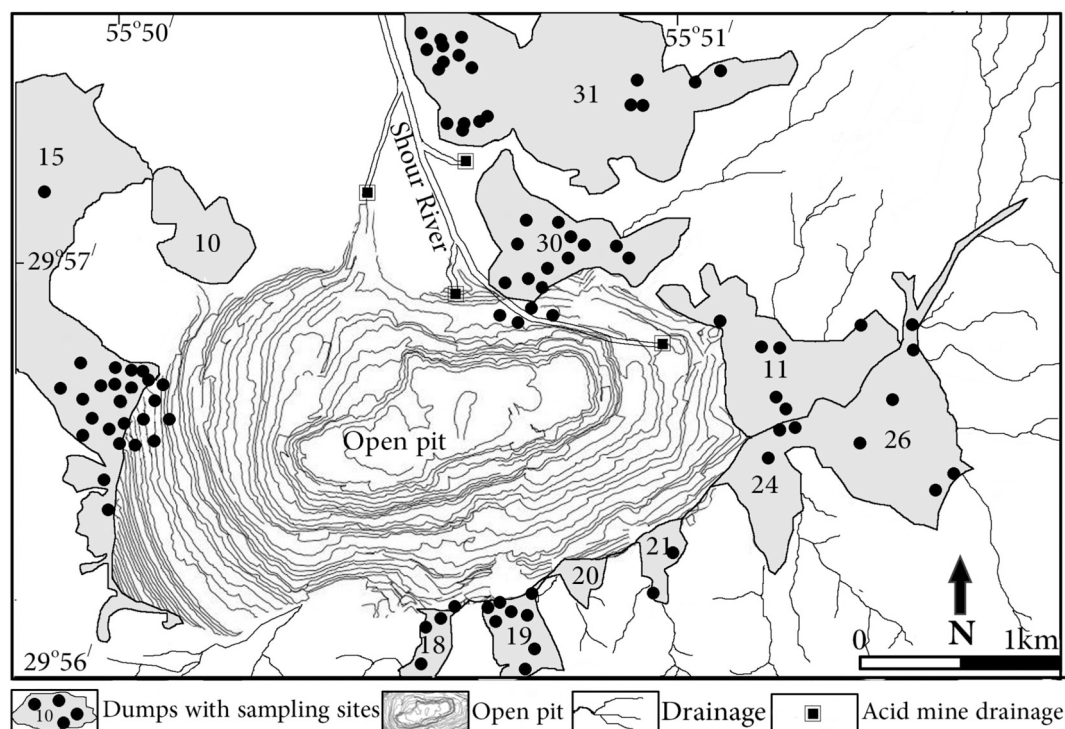


Fig. 2. Map of Sarcheshmeh dumps, showing the position and number of the waste dumps, Sarcheshmeh copper mine open pit and sampling sites (modified after Sahraei Parizi et al., 2005 and Khorasanipour, 2011).

and 35 thin sections and 61 polished sections were prepared for petrographical studies at the Mineralogy Laboratory of the Mining Department of Shahid Bahonar University of Kerman.

5.2. Analytical methods

Samples of about 50 g were submitted to the ALS Minerals Lab. Ireland for a whole rock package of ME-ICP06 including major and trace element analysis. Carbon and sulfur were analysed by combustion furnace (ME-IR08 method). For trace elements including REEs, the samples were digested with a lithium borate fusion procedure (ME-MS81). A four-acid digestion method was employed for the base metals (ME-4ACD81) determination and minor and other trace elements were digested by aqua regia digestion method (ME-MS42). Platinum, palladium and gold were determined by standard lead oxide collection fire assay followed by ICP-MS as well as ICP-AES methods. The loss on ignition (LOI) was calculated by heating the oven dried (110 °C) powdered samples at about 1100 °C in a furnace for an hour, and measuring the weight loss as weight percent. The limit of detection, precision, and accuracy of the elements were tested by using International Standards (AMIS0304, GBAP-8, GEOMS-03, OGGEO-08, OREAS-90 and OREAS-121) and the results are listed in Tables 1–4.

X-ray diffractograms were recorded at 0.6° 2 θ /min from 10°–35° 2 θ at 40 kv and 20 mA using Cu K α radiation (1.54051 Å). The position of (101) peak was checked by considering an internal standard of quartz for quartz-rich samples. Also, an aluminum specimen holder ($a = 4.0496$ Å) was used to calibrate diffractograms, which are shown in supplementary file 2 (Fig. S2).

The bulk composition of the waste rocks was also determined by scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDX) of Camscan Mv 2300 model at Department of Metallurgy, Shahid Bahonar University of Kerman, Iran, using a tungsten cathode with resolution of 3.5 nm at 30 kv. The rectangular bulk samples of 1 × 1 cm with 5 mm thickness were sputter-coated by gold. The samples were calibrated with K α X-ray lines of internal synthetic and natural

quartz, Al₂O₃, feldspars, wollastonite, Ti, Cr, Mn, Fe, Ni, Cu and Mo standards. The clean surfaces of bulk waste rock samples were bombarded by a 30–50 μ m electron beam at an angle of 90° in 66 s. The results are given in supplementary file 3 (Table S3 and Fig. S3).

6. Results

6.1. Petrography and mineralogy

The waste rocks around the Sarcheshmeh porphyry copper mine contain several types of volcanics, plutonics, sulfide-bearing waste rocks and gossanized waste rocks. The main host rocks include trachybasalt, trachyandesite, granodiorite and quartz monzonite, respectively. Trachybasalt and trachyandesite show porphyritic texture with trachytic, intergranular, glassy groundmass, whereas granitoid rocks display a porphyritic texture with granular groundmass. The major minerals in granitoid rocks are quartz (30%), orthoclase (10–20%), oligoclase (30–40%), biotite (5–10%) and hornblende (10–15%) with minor amounts of apatite, zircon and opaque minerals (5%). The main mineral composition in volcanic rocks are phenocrysts of plagioclase (5–20%), biotite (5–10%), hornblende (5–10%), quartz (0–5%), sanidine (5%). The groundmass of the volcanic rocks contains microlithic plagioclase (30%) and up to 20% of biotite, hornblende, opaque minerals, apatite and zircon. The waste rocks are subjected to various degrees of sericitization, argillization and saururization. The sulfide-bearing waste rocks contain some blocks of oxidized, supergene and hypogene zones of the Sarcheshmeh porphyry copper mine. The most important minerals in these waste rocks are pyrite, chalcopyrite and covellite. The sulfide minerals show vein stockworks, granular, disseminated and veinlet texture (Figs. 4 and 5), though open space filling and replacement textures are also observed. Other minerals include malachite, azurite and delafossite (Fig. 6). There are four generations of pyrite; (1) euhedral, fine-grained and disseminated pyrite grains (> 2%) that are oxidized to hematite and goethite (Fig. 4A, Fig. 5A), (2) boxwork pyrites (> 10%) that are replaced by hematite and goethite and show nest texture (Fig. 5B and C), (3), pyrites (3%) that replace

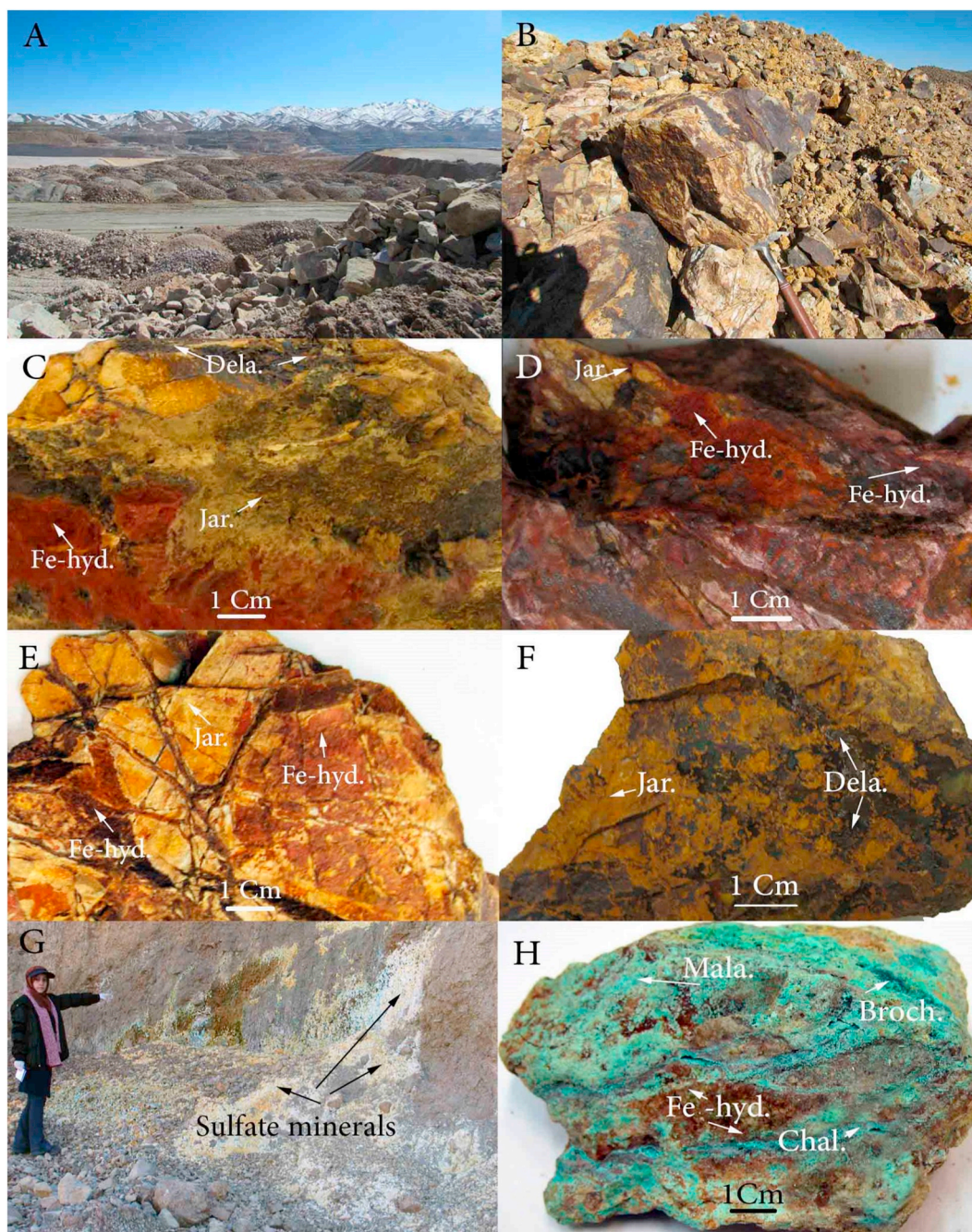


Fig. 3. Gossanized waste rocks at Sarchehmeh waste dumps (A and B), and field samples (B, C, D, E and F) showing hematite (Hem.), Fe-hydroxides (Fe-hyd.), jarosite (Jar.) and delafossite (Dela.), abundance copper-iron sulfate and carbonate minerals; brochantite (Broch.), chalcocite (Chal.) and malachite (Mala.) (G), field samples (H) at Sarchehmeh open pit mine.

biotite cleavages (Fig. 5D) and (4) veinlet pyrites (Fig. 5E) that have been converted to hematite, iron hydroxides, (possibly goethite) and jarosite (Fig. 5F) (Atapour and Aftabi, 2007; Parandoush, 2017). In reflected light, goethite is slightly pleochroic in colors of yellow to gray with bluish tint and displays yellow, red, brown internal reflections (Atapour and Aftabi, 2007; Parandoush, 2017). Optically, jarosite exhibits a high surface relief, amber-yellow to dark brown color with reddish brown pleochroism and occurs as partial pseudomorphic replacement of pyrite crystals in sericitized waste rocks (Atapour and Aftabi, 2007; Parandoush, 2017). This is further supported by the presence of jarosite, natrojarosite, goethite, hematite and other minerals in XRD diffractograms and SEM data in the supplementary files 2 and 3 (Fig. S2, Table S3, and Fig. S3). Chalcocite occurs in two

generations (1) disseminated (Fig. 5D) and (2) replacing the biotite structure (Fig. 5E). Fig. 6 illustrates the possible paragenetic sequences of minerals in different waste rocks. Accordingly, the blocks of slightly fresh volcanic and plutonic waste rocks contain abundant silicate minerals with minor sulfide-hydroxide assemblages, whereas the sulfide-bearing waste rocks are enriched in sulfides and alteration minerals. Contrary, the residual gossans and gossanized waste rocks are mainly composed of supergene hydroxides, oxides, sulfates, hydrous sulfates and hydrous carbonates.

6.2. Geochemistry

The average and range of major, minor and trace element

Table 1
Major element oxides (wt%) in the waste rocks at Sarcheshmeh porphyry copper mine waste dumps (DL = Detection limit).

Locality	ELEMENTS	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅	LOI	Total	S
	DL	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	–	0.01
Sulfide-bearing waste rocks	Min	29.8	10.35	3.6	0.08	0.56	0.06	0.88	0.34	< 0.01	0.11	1.86	94.99	< 0.01
	Max	66.5	18.75	38	10.5	4.54	4.68	4.06	1.1	1.64	0.27	31	101.43	21
	Mean	51.49	15.31	13.08	2.00	2.25	1.86	2.72	0.66	0.27	0.18	9.91	99.71	6.69
	Sd	11.70	3.57	11.15	2.87	1.21	1.80	1.01	0.23	0.47	0.06	8.48	1.76	7.71
Gossanized waste rocks	Min	14.9	2.72	5.56	0.05	0.26	0.01	0.66	0.07	< 0.01	0.01	3.79	87.29	0.05
	Max	65.8	20.2	65.1	2.01	3.48	1.43	5.78	1.14	2.55	0.81	27	101.11	40.8
	Mean	49.95	13.38	19.69	0.29	0.79	0.26	3.36	0.72	0.15	0.27	8.22	97.14	2.45
	Sd	14.38	3.91	14.71	0.45	0.78	0.34	1.27	0.30	0.57	0.21	5.01	4.54	9.05
Residual gossans	Min	29.4	10.9	1.98	0.07	0.42	0.05	1.38	0.61	0.01	0.07	3.33	96.3	0.04
	Max	67.5	23.6	34.6	0.29	3.46	2.62	5.6	1.04	0.58	0.34	12.95	100.4	8.40
	Mean	53.48	18.25	12.92	0.15	1.34	0.49	3.78	0.79	0.12	0.146	7.55	99.11	1.82
	Sd	12.79	3.90	11.05	0.08	1.06	0.94	1.60	0.16	0.21	0.097	3.83	1.43	3.17
Granodiorite*	Mean	66.09	15.73	1.38	3.83	1.74	3.75	2.73	0.54	0.08	0.18	0.45	96.5	–
	Precision	98.28	99.14	99.37	92.75	94.45	100	95.49	100	100	43.43	99.75	99.75	98.07
	Accuracy	94.25	91.64	94.59	96.53	92.61	15.15	68.57	90.55	84.63	95.37	88.82	98.44	91.11

* Cox et al. (1979).

concentrations for sulfide-bearing waste rocks, gossanized waste rocks and residual gossans are shown in Tables 1 to 4. The large variations in major oxides (Table 1) are due to the dissolution and leaching of soluble oxides (SiO₂, MgO, CaO, Na₂O and K₂O). This is indicated by high values of L.O.I, ranging from 1.86 to 12.95 wt%. Also, the high values of Fe₂O₃ (65.1% wt) and sulfur (40.8% wt) in some of the waste rocks indicate the presence of sulfates, sulfides and iron hydroxides-oxides formed by oxidation of pyrite-chalcopyrite. The variations in Na₂O (0.06–4.68%wt) and K₂O (0.88–4.06%wt) is attributed to sericitic and argillic alteration (Table 1). This is also indicated by high values of L.O.I (9.91%wt). The Cu and Mo values in sulfide-bearing waste rocks range from 96 ppm to 4.9 wt% and 0.55 to 30 ppm, respectively. The variations in Cu and Mo contents in gossanized waste rocks are in the range of 141–52,100 ppm and 0.55–2960 ppm, but residual gossans contain 71 to 4660 ppm Cu followed by 8 to 122 ppm Mo (Table 2). These variations are related to the presence of chalcopyrite, molybdenite and malachite. Malachite is bright green, dark green and blackish

green in thin section and shows colourless, yellowish green to deep green pleochroism (Atapour and Aftabi, 2007; Parandoush, 2017). The gold content in gossanized waste rocks is about 0.6 ppm and in residual gossans reaches up to 0.775 ppm (Table 3). However, the REE contents are not significantly enriched.

6.3. Chemical nature of the waste rocks

Table 1 shows large variations of SiO₂ in waste rocks (29.80–66.5% wt). The depletion in the SiO₂ contents of the waste rocks is caused by sulfide oxidation, generation of acid mine drainage (AMD), hydrolysis of silicate minerals and dissolution. This is also reflected in the variable values of L.O.I (1.86–31 wt%). This is further supported by the presence of potassic, phyllic and argillic alteration in the waste rocks. Therefore, the variations in LOI are related to the hydroxyl bearing minerals like sericite, chlorite, epidote and clay minerals in phyllic, argillic and propylitic alteration. The aluminum oxide content ranges from 10.35 to

Table 2
Minor, trace and precious elements (ppm) in the waste rocks at Sarcheshmeh porphyry copper mine waste dumps (DL = Detection limit).

Locality	ELEMENTS	Cu	Mo	Pb	Zn	Cr	Ni	Co	Sn	W	V	Re	Se	Ag	Au	Pt	Pd
	DL	1	1	2	2	10	1	1	1	1	5	0.001	0.2	0.5	0.001	0.005	0.001
Sulfide-bearing waste rocks	Min	96	< 1	6	33	< 10	1	3	1	1	69	< 0.001	0.6	< 0.5	0.001	< 0.005	< 0.001
	Max	52,100	30	135	17,000	250	120	281	5	55	275	0.023	16.3	6.3	0.311	0.003	0.003
	Mean	2954.6	4.97	31.17	1665	33.5	29.17	55.42	2.25	17.17	146.33	0.0033	5.82	1.34	0.0443	0.001	0.0011
	Sd	4753	8.35	35.01	4846.6	68.8	38.87	82.97	1.48	18.55	70.03	0.01	6.20	1.98	0.0857	0.00083	0.00074
Gossanized waste rocks	Min	141	< 1	1.1	26	< 10	0.75	0.75	1	7	41	< 0.001	1.9	< 0.5	0.1675	< 0.005	0.0014
	Max	63,900	2960	551	2570	430	35	58	16	95	395	0.153	68.6	87	0.608	0.0066	0.005
	Mean	3168.2	180.22	107.06	365.3	50.9	9.67	8.90	4.48	42.76	219.38	0.011	13.45	5.7	0.085	0.0015	0.0020
	Sd	4989.9	640.75	169.6	611.5	96.3	9.18	12.51	3.16	23.51	104.2	0.04	16.12	18.7	0.167	0.0015	0.0014
Residual gossans	Min	71	8	4	12	< 10	2	1	1	10	103	< 0.001	2.8	< 0.5	0.012	< 0.005	0.001
	Max	4660	122	758	861	20	31	55	9	58	309	0.043	15.2	13.4	0.775	0.0019	0.003
	Mean	1612.8	33.00	204.4	276	9.71	14.14	14.43	3.57	31.57	177.7	0.01	7.43	3.71	0.15	0.0010	0.0021
	Sd	1784.5	41.57	279.7	304.2	5.35	12.14	20.23	2.82	17.25	73.16	0.02	4.05	5.33	0.283	0.0006	0.0009
Crust*	Mean	55	1.5	12.5	70	100	75	25	2	1.5	135	0.0005	0.05	0.07	0.004	0.002	0.004
	Granodiorite**	Mean	30	1	15	60	20	20	10	2	2	100	0.0005	0.05	0.07	0.004	0.006
Hypogene ore***	Mean	6500	200	50.4	96	41	36	14	1.7	29	–	0.0018	2.5	1.22	0.06	0.004	0.002
	Supergene ore***	Mean	24,300	220	–	–	–	–	–	–	–	–	–	1.55	0.114	–	–
EF/sulfide-bearing waste rocks	Mean	0.45	0.02	0.62	17.34	0.82	0.27	0.64	2.64	1.47	–	5.55	2.33	1.10	0.74	0.25	0.57
EF/gossanized waste rocks	Mean	0.49	0.90	2.12	3.81	1.24	0.27	0.64	2.64	1.47	–	22.22	5.38	4.67	1.42	0.38	1.00
EF/residual gossans	Mean	0.25	0.17	4.06	2.88	0.24	0.39	1.03	2.10	1.09	–	11.11	2.97	3.04	2.50	0.25	1.05
Precision	Mean	98.06	89.13	86.5	97.1	94.28	85.43	96.99	100	92.74	97.54	100	95.1	100	–	100	–
Accuracy	Mean	85.69	–	–	92.26	100	–	–	86.53	100	95.03	100	–	–	85.01	87.59	85.66

* Rose et al. (1979).

** Levinson (1980).

*** Bazin and Hübner (1969), Atapour (2007), Atapour and Aftabi (2007) and Shafiei (2014).

Table 3

Minor, trace and special elements (ppm) in the waste rocks of Sarcheshmeh porphyry copper mine waste dumps (DL = Detection limit).

Locality	ELEMENTS	Ba	Sr	Rb	Li	Cs	Te	Tl	U	Th	Hf	Zr	As	Sb	Bi	Ga	In	Nb	Ta
	DL	0.5	0.1	0.2	10	0.01	0.01	0.02	0.05	0.05	0.2	2	0.1	0.05	0.01	0.01	0.005	0.2	0.1
Sulfide-bearing waste rocks	Min	30.2	16	30.9	4.87	1.65	0.01	0.09	0.28	0.48	1.1	36	1.2	0.12	0.18	8.9	0.01	0.8	0.1
	Max	1285	539	155	40	11.75	7.17	1.37	4.75	16.1	3.7	133	425	85	16.25	43.2	0.375	9.4	0.6
	Mean	505.8	211.8	96.7	11.19	5.23	1.67	0.31	2.40	6.79	2.50	91.50	48.7	12.61	3.02	17.7	0.081	4.08	0.29
	Sd	463.3	195.9	33.1	10.07	3.02	2.42	0.40	1.46	6.42	0.86	31.53	119	28.63	4.63	8.6	0.104	2.63	0.178
Gossanized waste rocks	Min0.5	15.7	8.8	27.1	4.87	0.96	0.22	0.08	1.14	0.38	0.4	15	4	0.27	0.59	3.5	0.009	0.11	0.1
	Max	1015	222	213	40	22.7	23.9	0.78	7.8	18.05	4	140	425	130	163	39.8	7.81	13.3	0.7
	Mean	307.84	87.81	139.7	8.48	6.79	3.20	0.23	2.90	3.88	2.61	91.00	83.53	10.24	10.87	16.6	0.442	3.45	0.24
	Sd	261.50	71.32	51.24	8.13	4.62	5.67	0.17	2.00	4.38	0.98	34.25	122	27.90	34.97	7.08	1.68	2.69	0.143
Residual gossans	Min	185.5	19.2	68	4.867	3.49	0.09	0.1	1.36	0.33	0.8	33	1.1	0.24	0.82	11.5	0.006	1.1	0.1
	Max	981	671	229	10	10.95	10.9	0.56	2.5	6.19	3.5	155	425	4.1	43.8	60.8	0.883	5.3	0.2
	Mean	512.8	182.6	148.9	8.53	5.66	3.22	0.25	1.90	3.81	2.17	87.57	102	1.61	8.62	21.3	0.24	3.24	0.17
	Sd	296.2	224.4	53.44	2.50	2.65	4.49	0.17	0.40	2.22	0.99	45.41	149	1.67	15.93	17.6	0.37	1.74	0.05
Crust*	Mean	425	375	90	20	3	0.001	0.45	2.7	10	3	165	1.8	0.2	0.17	15	0.1	20	2
Granodiorite**	Mean	500	450	120	25	2	0.001	0.5	3	10	2	140	2	0.2	0.14	18	0.1	20	2
Hypogene ore***	Mean	300	–	2.65	–	–	0.56	0.05	4	3.15	–	–	220	220	3.3	18.53	0.04	2.85	0.2
EF/sulfide-bearing waste rocks	1.68	–	36.5	–	–	2.98	6.2	0.6	2.1	–	–	–	0.22	0.06	0.92	0.96	2.03	1.43	1.46
EF/gossanized waste rocks	1.02	–	52.7	–	–	5.71	4.6	0.72	1.23	–	–	–	0.38	0.05	3.29	0.90	11.05	1.21	1.20
EF/residual gossans	1.7	–	56.1	–	–	5.75	5	0.47	1.2	–	–	–	0.46	0.01	2.61	1.15	6.00	1.14	0.85
Precision	87.26	98.60	96.53	100	87.22	92.1	98.1	87.12	87.24	88.35	96.32	95.55	97.00	97.70	96.86	89.90	91.05	100	
Accuracy	96.90	92.24	95.94	–	92.79	–	93.45	95.01	96.35	96.95	90.34	98.00	97.62	94.11	87.01	92.60	97.93	87.24	

* Rose et al. (1979).

** Levinson (1980).

*** Bazin and Hübner (1969), Atapour (2007), Atapour and Aftabi (2007) and Shafiei (2014).

18.75 wt%, indicating the presence of feldspar, sericite and most likely clay minerals in the waste rocks. The biplot geochemical diagrams of $\text{Na}_2\text{O} + \text{K}_2\text{O} - \text{SiO}_2$ (Fig. 7A and B) display that the composition of the volcanic waste rocks is close to the field of basalt, picritic basalt and basaltic andesite. However, this classification differs from the pristine petrographical and geochemical nature of the petrographically known trachybasalt and trachyandesite. The granitoid rocks plot within the field of synodiorite and quartz diorite. The dissimilarity of chemical names to those of the petrographical classification of the waste rocks is due to the leaching of Ca, Na, K, and Si ions by hydrolysis during hydrothermal alteration and chemical weathering. The mobility, solubility, and leaching of the aforementioned elements have also been

pointed out by Brownlow (1995).

6.4. Minor and trace elements

It is accepted that the characteristic suite of porphyry chalcophile and precious elements in waste rocks could provide significant exploration, economic and environmental signatures (Hettler et al., 1997; Wu et al., 2009; Lottermoser, 2011; Bogdanović et al., 2016; Falagan et al., 2017; Yin et al., 2018). In this regard each element has been described as below:

Table 4

Rare earth elements (ppm) in the waste rocks at Sarcheshmeh porphyry copper deposit (DL = Detection limit).

Locality	Elements	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Sc	ΣREE
	DL	0.5	0.5	0.03	0.1	0.03	0.03	0.05	0.01	0.05	0.01	0.03	0.01	0.03	0.01	0.5	1	–
Sulfide-bearing waste rocks	Min	2.8	5.9	0.94	4.7	1.34	0.37	1.89	0.23	1.29	0.27	0.75	0.13	0.69	0.12	7.4	6	34.82
	Max	38.9	72.4	7.78	29.9	5.79	1.72	6.41	0.94	6.13	1.45	4.38	0.65	4.22	0.66	43.5	26	250.83
	Mean	19.02	34.75	4.02	16.44	3.27	0.94	3.28	0.5	3.02	0.66	1.92	0.29	1.86	0.3	18.29	14.16	122.72
	Sd	14.14	23.91	2.43	8.58	1.4	0.36	1.31	0.19	1.3	0.33	1.02	0.14	1.01	0.15	9.75	6.92	72.94
Gossanized waste rocks	Min	2.4	4.5	0.64	2.8	0.66	0.2	0.68	0.11	0.63	0.12	0.36	0.06	0.41	0.06	3.4	4	21.03
	Max	42.2	74.3	8.17	31.2	7.61	3.15	9.41	1.25	7.54	1.55	4.5	0.72	4.4	0.62	36.3	30	262.92
	Mean	13.54	26.37	3.12	13.48	3.05	0.95	3.51	0.58	3.41	0.73	2.12	0.32	2.1	0.33	18.61	18.19	110.41
	Sd	10.19	17.49	1.74	6.67	1.62	0.63	1.9	0.26	1.59	0.33	0.99	0.15	0.93	0.14	8.23	8.76	61.62
Residual gossans	Min	2.3	5.6	0.61	2.9	0.54	0.28	0.58	0.15	1.12	0.33	1.01	0.17	1.04	0.16	8	12	36.79
	Max	36.4	69.8	7.41	28.2	5.8	1.86	4.42	0.84	5.18	1.13	3.14	0.42	2.76	0.42	26.9	27	221.68
	Mean	20.11	39.08	4.27	16.54	3.16	0.87	2.36	0.41	2.59	0.59	1.73	0.25	1.75	0.28	14.72	18	126.71
	Sd	14.53	25.4	2.66	10.21	1.91	0.53	1.22	0.22	1.3	0.27	0.73	0.09	0.55	0.08	6.6	5.32	71.62
Crust*	Mean	30	60	8.2	28	6	1.2	5.4	0.9	3	1.2	2.8	0.48	3	0.5	30	16	196.68
Granodiorite**	Mean	36	40	40	26	6.8	1.2	–	1.3	3.2	1.6	4.8	0.5	3.6	–	–	10	–
Hypogene ore***	Mean	15.9	30.5	–	–	–	–	–	–	–	–	–	–	–	–	3.5	–	–
EF/sulfide-bearing waste rocks	1.2	1.1	–	–	–	–	–	–	–	–	–	–	–	–	–	5.2	–	–
EF/gossanized waste rocks	0.05	0.86	–	–	–	–	–	–	–	–	–	–	–	–	–	5.3	–	–
EF/residual gossans	1.2	1.2	–	–	–	–	–	–	–	–	–	–	–	–	–	4.1	–	–
Precision	98.99	96.14	95.89	97.68	95.48	96.03	93.71	92.68	95.32	89.45	86.84	91.95	99.66	86.33	99.28	100	–	–
Accuracy	92.49	97.86	97.41	95.75	92.01	91.09	99.59	97.18	97.41	91.36	93.2	90.96	97.04	98.42	95.51	–	–	–

* Rose et al. (1979).

** Levinson (1980).

*** Bazin and Hübner (1969), Atapour (2007), Atapour and Aftabi (2007) and Shafiei (2014).

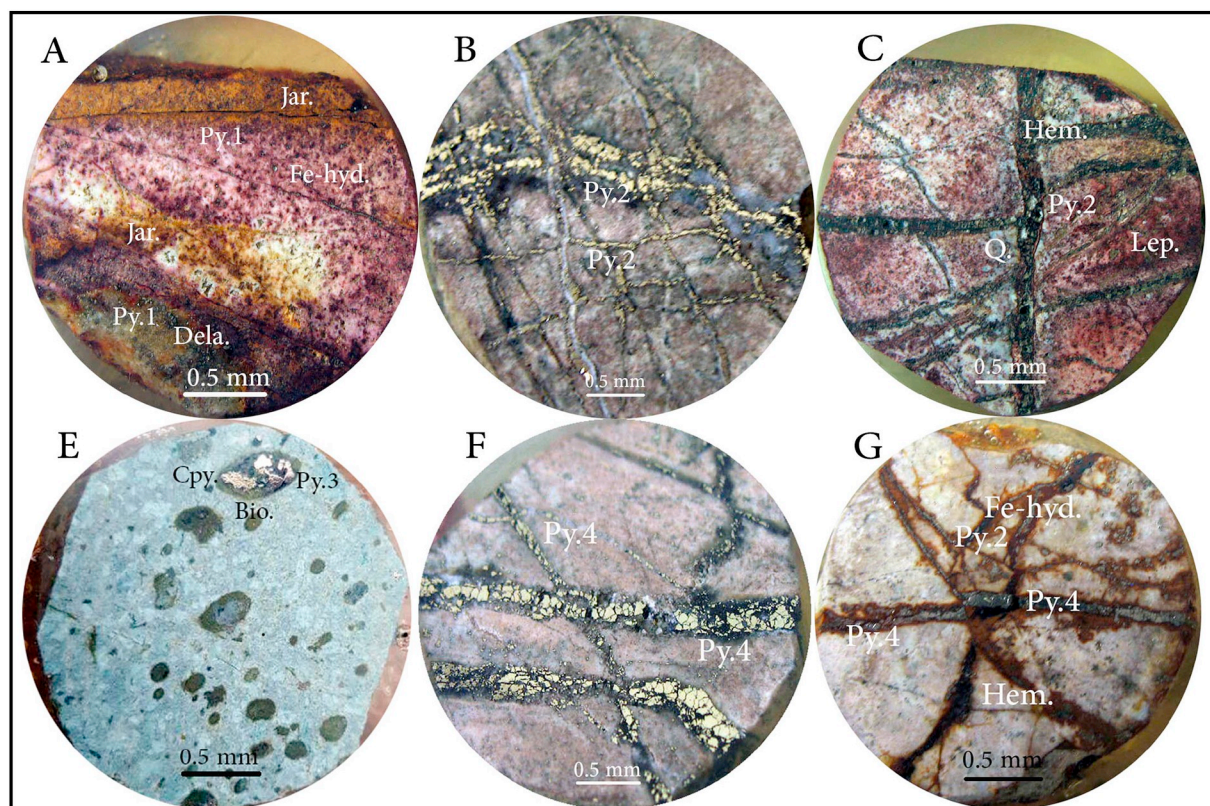


Fig. 4. Disseminated pyrite (Py.) in sulfide-bearing waste rocks samples (A), boxworks of pyrites in gossanized waste rocks (B) that are replaced by hematite (Hem.), Fe-hydroxides (Fe-hyd.) and lepidocrocite (Lep.) associated with quartz (Q.) (C) pyrite and chalcopyrite (Cpy.) replacing biotite (Bio.) cleavages in altered host rocks. (D) and pyrite veinlets (E) which have been converted to hematite, Fe-hydroxides and jarosite (Jar.) in gossanized waste rocks (F).

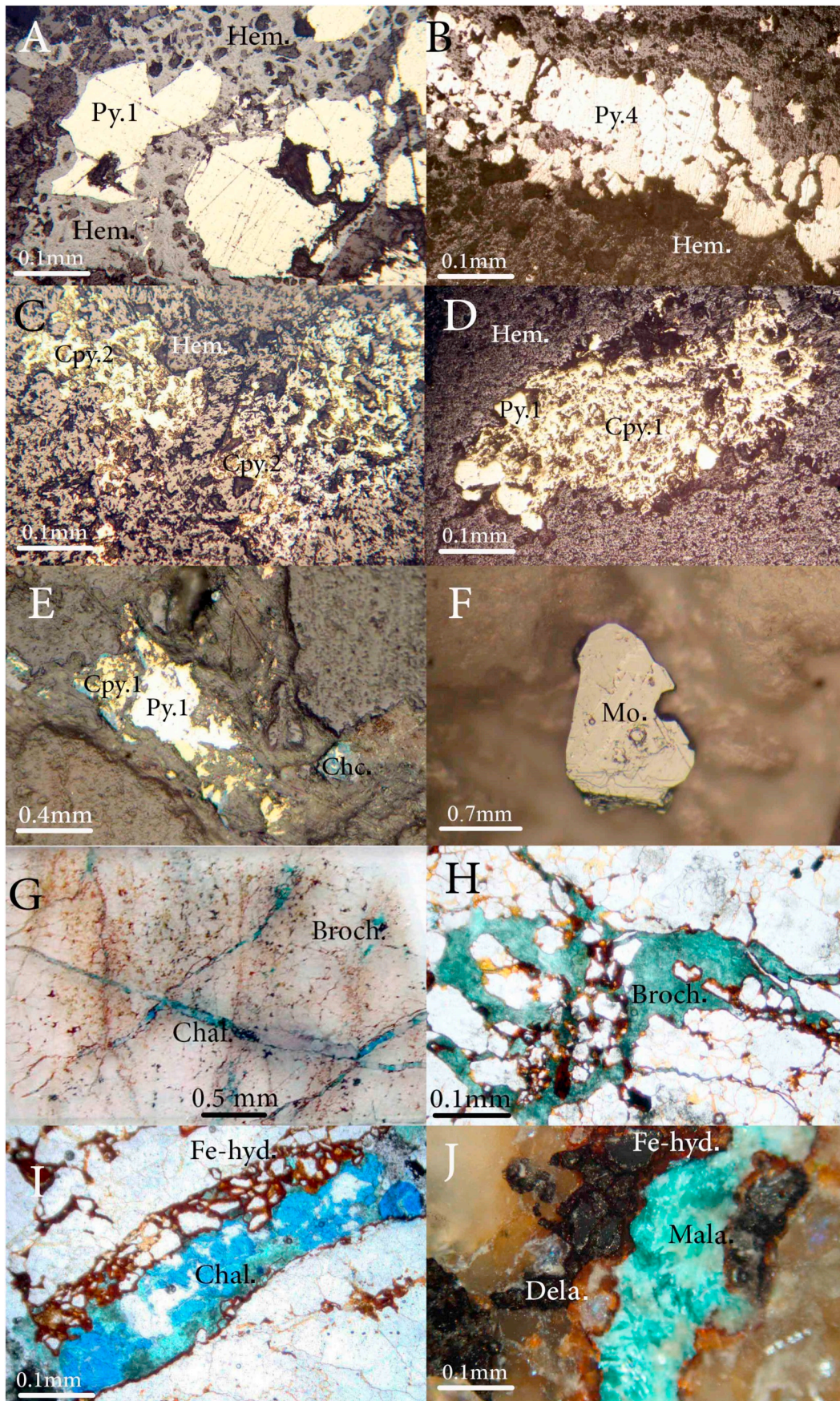
6.4.1. Copper (Cu)

The average copper values in sulfide-bearing waste rocks, gossanized waste rocks and residual gossans are about 2954.60 ppm, 3168.20 ppm and 1612.80 ppm (Table 2), respectively. These values are about 53–105 times over the background content of the fresh granodiorite, but lower than those of supergene and hypogene ore zone (Table 2) at Sarcheshmeh mine, though very close to the copper cut-off grade for future copper mining. The highest value of copper in the waste rocks reaches up to 63,900 ppm, which is close to the mid-grade to high grade wastes (Anonymous, 2011) and may be considered as the future copper resources (Anonymous, 2011). The cut-off grade for future copper mining is reported to be about 0.2% Cu (Seredkin et al., 2016). The presence of copper sulfates in the waste rocks (Atapour, 2007; Khorasanipour, 2015; Parandoush, 2017) suggests that Cu^{2+} is significantly leached at pH range of 5 to 6 (De Vos and Tarvainen, 2006) from the precursor copper sulfides (chalcopyrite) during oxidative chemical weathering of the waste rocks. This is possible as copper exhibits extensive supergene enrichment because of the high and low solubility of Cu-sulfates and Cu-sulfides, respectively (Levinson, 1980; Sillitoe, 2005). This is also supported by the occurrence of malachite, chrysocolla and goethite in residual gossans (Scott et al., 2001; Atapour, 2007; Atapour and Aftabi, 2007). The best means of presenting geochemical data is by histograms and probability plots (Howarth, 1984; Garrett, 1989; Moon et al., 2006). The frequency histogram, cumulative percentage and box plot diagram (Fig. 8A) indicate anomalous positive skewness and lognormal distribution for copper. The high content of Cu is related to presence of malachite, azurite, chalcantite and antlerite in residual gossans as well as the waste rocks (Atapour, 2007; Atapour and Aftabi, 2007; Parandoush, 2017) with minor contribution from chalcopyrite. The high anomalous values of copper in residual gossans and gossanized waste rocks in the Sarcheshmeh mining area are caused by chemical weathering of

sulfides. The copper contents occur at concentrations > 53 times greater than the natural background concentrations of the geochemical cycle, thus are of environmental concern.

6.4.2. Molybdenum (Mo)

The mean values of molybdenum follow 4.97 ppm, 180.22 ppm and 33 ppm in sulfide-bearing waste rocks, gossanized waste rocks and residual gossans, respectively (Table 2), though the highest value of Mo in gossanized waste rocks reaches up to 2960 ppm. This is confirmed by the presence molybdenite in polished sections (Fig. 5F). Fig. 8B, shows the positive skewness distribution with anomalous contents of molybdenum in the waste rocks. Upon weathering, molybdenite decomposes, releasing molybdenum into solution (Nickel, 1979). In its higher oxidation states, molybdenum has an intermediate ionic potential, hydrolyses readily and probably is precipitated as ferrimolybdate (Nickel, 1979; Levinson, 1980; Seo et al., 2012). It is also suggested that during oxidation of Mo-bearing sulfides in the waste rocks, Mo is released as molybdate and is stable over a wide range of pH conditions, from strongly alkaline to pH 3–4 (Frascoli and Hudson-Edwards, 2018). The association of high molybdenum values in gossanized waste rocks may be related to the presence of the ferrimolybdate or probably ilsemanite (Nickel, 1979; Levinson, 1980). Frascoli and Hudson-Edwards (2018) also suggested that Mo is strongly adsorbed by Fe (III) oxyhydroxides in acidic and oxidizing sulfidized waste rocks. Moreover, in supergene zones, oxidized molybdenum occurs predominantly as the immobile acid molybdate anion (HMoO_4^-), and in the groundwater as the relatively mobile molybdate anion (MoO_4^{2-}) (Levinson, 1980; Atapour and Aftabi, 2007; Frascoli and Hudson-Edwards, 2018). This may indicate that in the gossanized waste rocks, where Cu is strongly leached, molybdenum is retained in the gossan and could be used as a possible pathfinder for prospecting porphyry copper ores (Levinson, 1980; Atapour and Aftabi, 2007). The highest Mo value (2960 ppm) in the



(caption on next page)

Fig. 5. Disseminated pyrite (Py.) (A), vein type pyrite in sulfide-bearing waste rocks (B), disseminated chalcocopyrite (Cpy.) (C), photomicrograph, showing chalcocopyrite replacing biotite in altered host rocks (D), replacement of chalcocopyrite by chalcocite (Chc.) in gossanized waste rocks (E), molybdenite (Mo.) in gossanized waste rocks, replacement of chalcocopyrite by chalcocite (Chal.) and brochantite (Broch.) (E) and (F), chalcocite and iron hydroxide (Fe-hyd.) (I) malachite (Mala.) and iron hydroxide and delafossite (Dela.) (J) in gossanized waste rocks.

gossanized waste rocks is higher than in the supergene ore zone (0.02%, Shafiei, 2014). In supergene zones developed on porphyry copper deposits, molybdenite (MoS₂) or ferrimolybdate [Fe₂ (MoO₄)₃·nH₂O] are the dominant Mo minerals (Mc Candless et al., 1993), although Frascoli and Hudson-Edwards (2018), reported Mo-bearing minerals, minerals adsorbing Mo (ferrihydrite) [Fe₃³⁺O₃·0.5(H₂O)] and mineral enable to structurally incorporate Mo (jarosite) [KFe₃³⁺(OH)₆(SO₄)₂] as well as ferrimolybdate [Fe₂ (MoO₄)₃·nH₂O], molybdate (MoO₃) and tugayinovite (MoO₂), respectively. It is notable that ferrihydrite [Fe₃³⁺O₃·0.5(H₂O)] most likely adsorbs Mo-aqueous species during chemical weathering of the waste rocks. In this regard, Mo may be released as anionic molybdate species which could release highly anomalous values of Mo up to 4–2000 magnitudes over the natural background values of the crustal abundances in soil and sediments around the Sarcheshmeh mining area. It is suggested that such high concentrations of Mo (Politis

et al., 2017) could be considered as an environmental threat.

6.4.3. Rhenium (Re)

The average rhenium content in sulfide-bearing waste rocks, gossanized waste rocks and residual gossans is 0.0033 ppm, 0.011 ppm and 0.01 ppm (Table 2), 6–22 magnitudes higher than the granodiorite and crustal abundance. Rhenium is mainly produced as a by-product of molybdenum and copper refinement from Cu–Mo porphyry and sediment-hosted deposits. Re-bearing molybdenite occurs as ReS₂ solid solution with molybdenite (Leybourne and Cameron, 2008) and contains more than 1 wt% Re, but has been found in porphyry-style Cu–Mo deposits (Ekström and Hålenius, 1982; Sinclair et al., 2009; Voudouris et al., 2013). The Re concentration in molybdenite is mainly controlled by the composition of the ore-forming solution, the nature and source of the host rocks, the modal content of molybdenite in a given deposit, and

Minerals	Host rocks		Sulphide-bearing waste rocks	Gossanized waste rocks	Residual gossans
	Trachybasalt and trachyandesite	Quartz diorite, quartz monzonite and granodiorite			
Olivine	-----				
Clinopyroxene	-----				
Hornblende	-----	-----			
Biotite	-----	-----	-----		
Labradorite	████████				
Oligoclase	-----	████████			
Orthoclase	-----	████████			
Anorthoclase	-----				
Quartz		████████	-----	-----	-----
Apatite	-----	-----			
Magnetite	-----	-----			
Hematite			-----	████████	████████
Goethite			-----	████████	████████
Lepidocrocite				-----	-----
Pyrite	-----	-----	████████	-----	-----
Chalcocopyrite	-----		████████	-----	-----
Molybdenite	-----		-----	-----	-----
Chalcocite	-----	-----	-----	-----	-----
Covellite			-----	-----	-----
Bornite	-----	-----	-----	-----	-----
Chalcanthite				-----	-----
Brochantite				-----	-----
Melanterite				-----	-----
Antlerite				-----	-----
Jarosite				-----	-----
Malachite				-----	-----
Azurite				-----	-----
Chrysocolla				-----	-----
Calcite	-----	-----	-----	-----	-----
Sericite	-----	-----	-----	-----	-----
Chlorite	-----	-----	-----	-----	-----
Epidote	-----	-----	-----		
Zeolite	-----				
Clay minerals	-----	-----	-----	-----	-----

Major ██████████ Minor ----- Trace -----

Fig. 6. Mineral paragenesis in sulfide-bearing and gossanized waste rocks and residual gossans at Sarcheshmeh porphyry copper mine dumps.

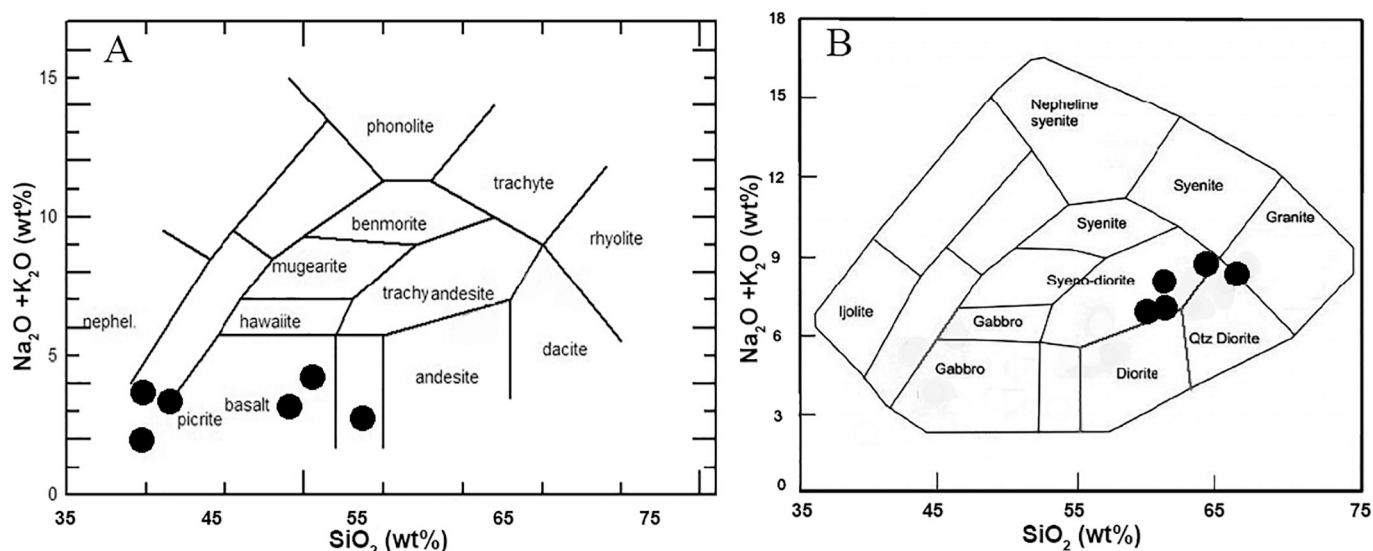


Fig. 7. $K_2O + Na_2O$ versus SiO_2 diagram of (Le Maitre, 2002) for the volcanic (A) and plutonic rocks (B).

the physicochemical conditions of ore formation (Voudouris et al., 2013). The economic grade of rhenium for porphyry Cu-Au and porphyry Mo deposits are almost comparable in the range of 0.01 to 0.6 g/t, suggesting that there is no difference between the Re content of Mo-dominant and Cu-dominant porphyry deposits of comparable tonnage (Voudouris et al., 2013). The average content of Re in molybdenite at Sarcheshmeh porphyry copper deposits is 192 ppm and changes between 11 and 517 ppm (Aminzadeh et al., 2011). The mean Re content in porphyry copper deposits is 0.01 ppm (Sinclair and Jonasson, 2014), but the cut-off grade for future mining is reported to be about 3.5–4 ppm Re (Seredkin et al., 2016). Fig. 8C shows a positive anomalous skewness distribution for Re in the waste rocks. Re content in some samples of hypogene ore zone at Sarcheshmeh mine is 0.0018 ppm (Atapour, 2007), but in gossanized waste rocks reaches up to 0.01 ppm, six times more than the hypogene ore zone. Freydl et al. (1997) found considerable Re concentrations in chalcopyrite, sphalerite, bornite and pyrite at El Teniente porphyry copper deposit that range from 0.053 to 0.18 ppb, whereas in pyrite from the Andacollo porphyry copper deposit, Re concentrations reach up to 100 ppb. During supergene alteration, some molybdenites were found to have experienced some Re loss, which has been structurally incorporated into ferrimolybdate (Leybourne and Cameron, 2008). However, Re was enriched in secondary minerals, some intergrowth with molybdate (MoO_3), and powellite $[Ca(Mo,Re)O_4]$ (Mc Candless et al., 1993). Rhenium extraction is performed as a by-product of molybdenite, but has no apparent deleterious effect on the geochemical cycle (Politis et al., 2017).

6.4.4. Gold (Au)

The highest gold values in some gossanized waste rocks samples (dump-11 and dump-24) and residual gossans in the Sarcheshmeh mine wastes in SW of the open pit range from 0.085 to 0.775 ppm, almost 22 to 193 times more than global granodiorite and crustal abundances (Table 2). The average gold content in residual gossans is 0.15 ppm, 1.3 to 2.5 orders higher than the supergene and hypogene ore grades at Sarcheshmeh mine. The histogram, cumulative percentage and box plot diagram (Fig. 8D) (see supplementary file for basic terms of statistics) for Au show anomalous positive skewness and lognormal distribution with three subpopulations (Fig. 8D), representing sulfide-bearing waste rocks, gossanized waste rocks and residual gossan. The cut-off grade for future mining is reported to be about 0.25–0.3 ppm Au (Seredkin et al., 2016). The oxidation and weathering of gold bearing inclusions in sulfide minerals produce gold bearing thiosulfate complexes (Nickel,

1979; Thornber, 1985). During intense oxidation, thiosulfates are oxidized to sulfate, precipitating gold (Thornber, 1985). As thiosulfate is easily oxidized, the gold is not likely transported far (Nickel, 1979; Thornber, 1985; Assawincharoenkij et al., 2017). It has also been suggested (Yesares et al., 2015) that gold enrichment in gossan or gossanized waste rocks may follow in four stages; (1) dissolution of gold inclusions in chalcopyrite and pyrite during oxidative chemical weathering as chloride complexes, (2) transportation of gold during gossanization, (3) destabilization of gold complexes by Fe-redox reactions and finally, (4) Au co-precipitation by Fe-oxyhydroxides. This is consistent with the high values of gold associated with goethite and gypsum in residual gossans and gossanized waste rocks, though so far, no gold grains are observed, microscopically in the Sarcheshmeh gossans. Up to date, gold has no distinctive environmental concern during porphyry copper mining (Hettler et al., 1997) because it is most likely insoluble and has minimal bioaccumulation in geochemical cycles.

6.4.5. Silver (Ag)

The average silver content in sulfide-bearing waste rocks, gossanized waste rocks and residual gossans is 1.34 ppm, 5.7 ppm and 3.71 ppm (Table 2), almost 4.6 magnitudes higher than the hypogene ore grade (1.22 ppm) at Sarcheshmeh mine (Table 2) and more than the cut-off grade for future mining (0.25–0.3 ppm Ag, Seredkin et al., 2016). As shown in Fig. 8E, the frequency diagram, cumulative percentage and box plot diagram show positive skewness and lognormal distribution. During oxidative chemical weathering, silver is liberated from the structure of sulfide minerals (e.g., pyrite and chalcopyrite) as chloride complexes and concentrated in supergene gossanized zones by adsorption of Fe-oxyhydroxides or as native silver, cerargyrite and silver bearing sulfates (possibly jarosite) (Levinson, 1980; De Vos and Tarvainen, 2006). It is possible that the higher concentration of silver is related to the formation of the aforementioned minerals in the Sarcheshmeh waste rocks. It is suggested that Ag is replaced in the structure of galena, chalcopyrite, tetrahedrite, bornite and pyrite (Rankama and Sahama, 1950; Levinson, 1980; Reich et al., 2013), similar to the cases reported by Atapour and Aftabi (2007) and Scott et al. (2001). Silver is more soluble in acidic and highly oxidative environments of high ionic strength, in which soluble complexes with anions, in particular chlorides can form (Levinson, 1980; De Vos and Tarvainen, 2006). Under most conditions, Ag salts are insoluble at pH values > 4.0, but at pH values between 4.0 and 8.0, Ag and Pb will be co-precipitated by Fe-oxyhydroxides (Lottermoser et al., 1999; De Vos and Tarvainen, 2006).

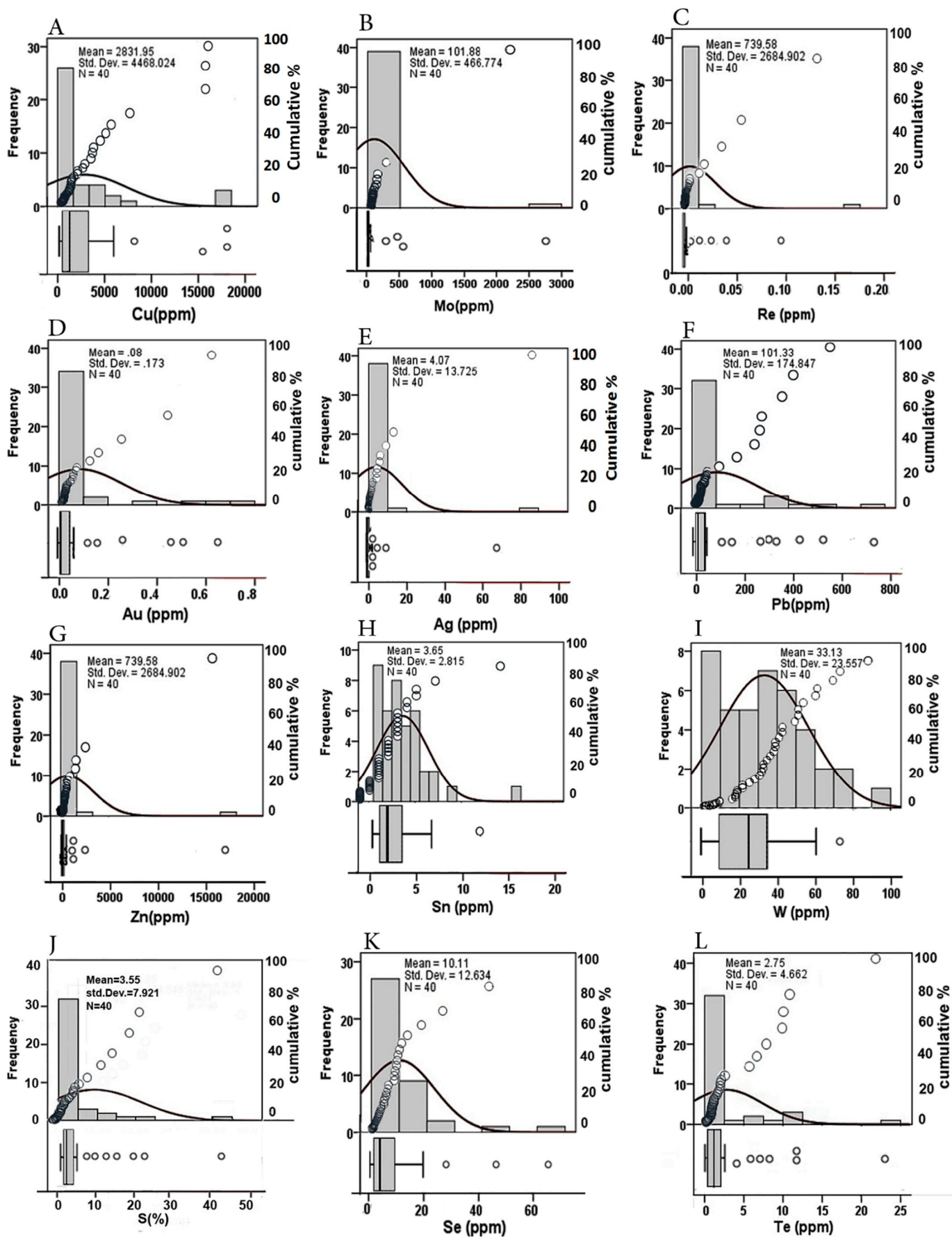


Fig. 8. Histogram, box plot and cumulative percentage diagrams of minor and trace elements in the waste rocks.

In terms of pH solubility, the equilibrium pH of the pore water-waste rocks at Sarcheshmeh waste rocks varies from 4 to 8.1 (Jannesar Malakooti et al., 2014).

6.4.6. Lead (Pb)

The average lead contents in sulfide-bearing waste rocks, gossanized waste rocks and residual gossans are 31.17, 107 and 204.4 ppm (Table 2). The highest value reaches up to 758 ppm in residual gossans, four times higher than the hypogene ore zone at Sarcheshmeh mine. This may be due to the rare occurrences of galena in propylitized waste rocks. Lead often has been found in residual gossan as plumbojarosite and plumbogummite (Nickel, 1979; Thornber, 1985). The frequency histogram, box plot and cumulative percentage diagram (Fig. 8F) show anomalous positive skewness and lognormal distribution of lead in the waste rocks. In areas of sulfide mineralization Pb^{2+} is mobilized by acidity (e.g., below pH 6) derived from the weathering of galena and other sulfide minerals (De Vos and Tarvainen, 2006). Lead also forms complexes with organic anions, chloride, hydroxide, and insoluble or poorly soluble sulfide, sulfate, carbonate and phosphate minerals (Levinson, 1980; De Vos and Tarvainen, 2006) such as anglesite ($PbSO_4$), cerussite ($PbCO_3$) and pyromorphite, $[Pb_{10}(PO_4)_6Cl_2]$. The highly anomalous values of lead in the waste rocks of the Sarcheshmeh mine dumps are 2–8 times greater than the natural background and crustal abundances, and thus are high enough to be an environmental concern.

6.4.7. Zinc (Zn)

The average Zn concentrations are 1665 ppm in sulfide-bearing waste rocks, 365.3 ppm in gossanized waste rocks and 276 ppm residual gossan (Table 2). Fig. 8G shows an anomalous positive skewness distribution for zinc. The enrichment of Zn in gossanized waste rocks and residual gossans is due to the dissolution of sphalerite in a low pH environment during chemical weathering and its precipitation with iron oxides and hydroxides in gossans (Atapour and Aftabi, 2007). The weathering of sphalerite or other zinc-bearing sulfide and silicate minerals can release Zn^{+2} into solution and precipitate it as sulfate and chloride ions at low pH and or co-precipitates with goethite and ferrihydrite (Rankama and Sahama, 1950; Levinson, 1980). However, the presence of white color gossalarite could not be excluded. Zinc mobility in the environment is greatest under oxidizing, acidic conditions and more restricted under reducing conditions (De Vos and Tarvainen, 2006). The Zn concentrations in sulfide-bearing waste rocks and gossanized waste rocks are 2–5 times over the natural background values. Under oxidative chemical weathering of Zn-rich sulfides in the waste rocks, soluble Zn enters into soil-groundwater systems and contaminates the environment.

6.4.8. Tin (Sn)

The average Sn contents in sulfide-bearing waste rocks, gossanized waste rocks and residual gossan are 2.25 ppm, 4.48 ppm and 3.57 ppm, respectively (Table 2) and the highest value reaches up to 16 ppm in gossanized waste rocks, eight times more than the crustal abundance (Table 2). Soluble tin is possibly formed by oxidation and dissolution of stannite (Cu_2FeSnS_4) and then is probably adsorbed by iron hydroxide during gossan formation (De Vos and Tarvainen, 2006). Fig. 8H indicates a positive skewness distribution in the waste rocks. The mobility of Sn is highly pH dependent and Sn^{2+} is only present in acid and reducing environments (De Vos and Tarvainen, 2006), but Sn follows the behaviour of Fe and Al and remains in the weathered residue along with hydroxides of these metals. Under these conditions, waste rocks are weathered and Sn is released and entered the cycle of water and soil (Kabata-Pendias, 2011).

6.4.9. Tungsten (W)

The mean concentrations of tungsten in sulfide-bearing-waste rocks, gossanized waste rocks and residual gossan are 17.17 ppm, 42.77 ppm

and 31.5 ppm (Table 2), but the highest content reaches up to 95 ppm in gossanized waste rocks. This value is eighty times higher than the average of the W in granodiorite (Table 2 and Fig. 8I). Tungsten could replace Mo in the structure of molybdenite, thus the high values of W in gossanized waste rocks may be due to oxidation of molybdenite that precipitates tungstite (WO_3) and W-hydroxide $[WO_2(OH)_2]$ in gossans (De Vos and Tarvainen, 2006). Chemical weathering of the aforementioned minerals in the waste rocks releases soluble W, which finally enters through soil and groundwater cycle.

6.4.10. Sulfur (S)

The average values of sulfur in sulfide-bearing waste rocks, gossanized waste rocks and residual gossans are 6.69 wt%, 2.42 wt% and 1.816 wt%, but reach up to 40.8 wt% in gossanized waste rocks. This is also supported by a positive anomalous skewness and lognormal distribution of sulfur in the waste rocks (Fig. 8J). Comparison with the abundance of the sulfur in natural background and crustal abundances (0.03 wt%) indicates enrichments by factors of 80–1360. This enrichment is related to the abundance of non-weathered pyrite-chalcocopyrite inclusions and the presence of sulfates such as chalcantite, brochantite, antlerite, jarosite, and gypsum (supplementary files 2 and 3, Fig. S2, Table S3, and Fig. S3). The frequent occurrence of sulfate minerals points to the acidic conditions during oxidative weathering of sulfide-rich waste rocks, which possibly leads to the generation of sulfuric acid. This acid has corrosive effects as well as moderate chronic toxicity to the geochemical cycles.

6.4.11. Selenium (Se)

Selenium displays considerable variations in different types of waste rocks, with 5.82 ppm, 13.45 ppm, and 7.93 ppm in sulfide-bearing-waste rocks, gossanized waste rocks and residual gossans, respectively. The mean content of Se in Sarcheshmeh waste rocks is 10.1 ppm, 202 times higher than the granodiorite and crustal abundances (Table 2) and shows positive anomalous skewness and lognormal distribution in Fig. 8K. Selenium is most likely replacing sulfur in pyrite-chalcocopyrite, released during oxidative chemical weathering of these sulfides in the waste rocks, and is soluble under oxidizing and basic conditions. However, when the Eh decreases, it precipitates as native Se, secondary selenides (Levinson, 1980; Kabata-Pendias, 2011). In this regard, the high values of Se in gossanized waste rocks and residual gossans may be due to the oxidation Se-bearing sulfides and precipitation of selenides, native Se and or co-precipitation with Fe-oxyhydroxides, similar to the cases reported by Levinson (1980), Eby (2004) and De Vos and Tarvainen (2006). The highly anomalous values of Se in the waste rocks are > 100 magnitudes over the natural background and crustal abundances and thus, selenium is an element of environmental concern in the Sarcheshmeh mining areas.

6.4.12. Tellurium (Te)

Tellurium displays variable concentrations from 0.01 ppm in sulfide-bearing waste rocks up to 23.9 ppm in gossanized waste rocks (Table 3), 10–23,900 magnitudes higher than granodiorite and crustal abundances. Fig. 8L indicates a positive anomalous skewness and lognormal distribution for Te in different waste rocks.

During weathering processes, tellurium is oxidized as telluric complexes and can be adsorbed by iron hydroxides. Telluric acid $[Te(OH)_4]$ is soluble in aqueous solution, although Te^{4+} gradually oxidises to Te^{6+} mainly as $H_5TeO_6^-$ (De Vos and Tarvainen, 2006). Tellurium is also released as TeO_3^{2-} from the structure of pyrite and molybdenite (Levinson, 1980; De Vos and Tarvainen, 2006) and under oxidizing conditions Te is adsorbed by Fe-oxyhydroxides or occurs as tellurites in sediment and soil. Soluble Te may enter into the water cycle. As such, the enrichment of Te in gossanized waste rocks and residual gossans is most likely related to the adsorption of tellurides by Fe-oxyhydroxides.

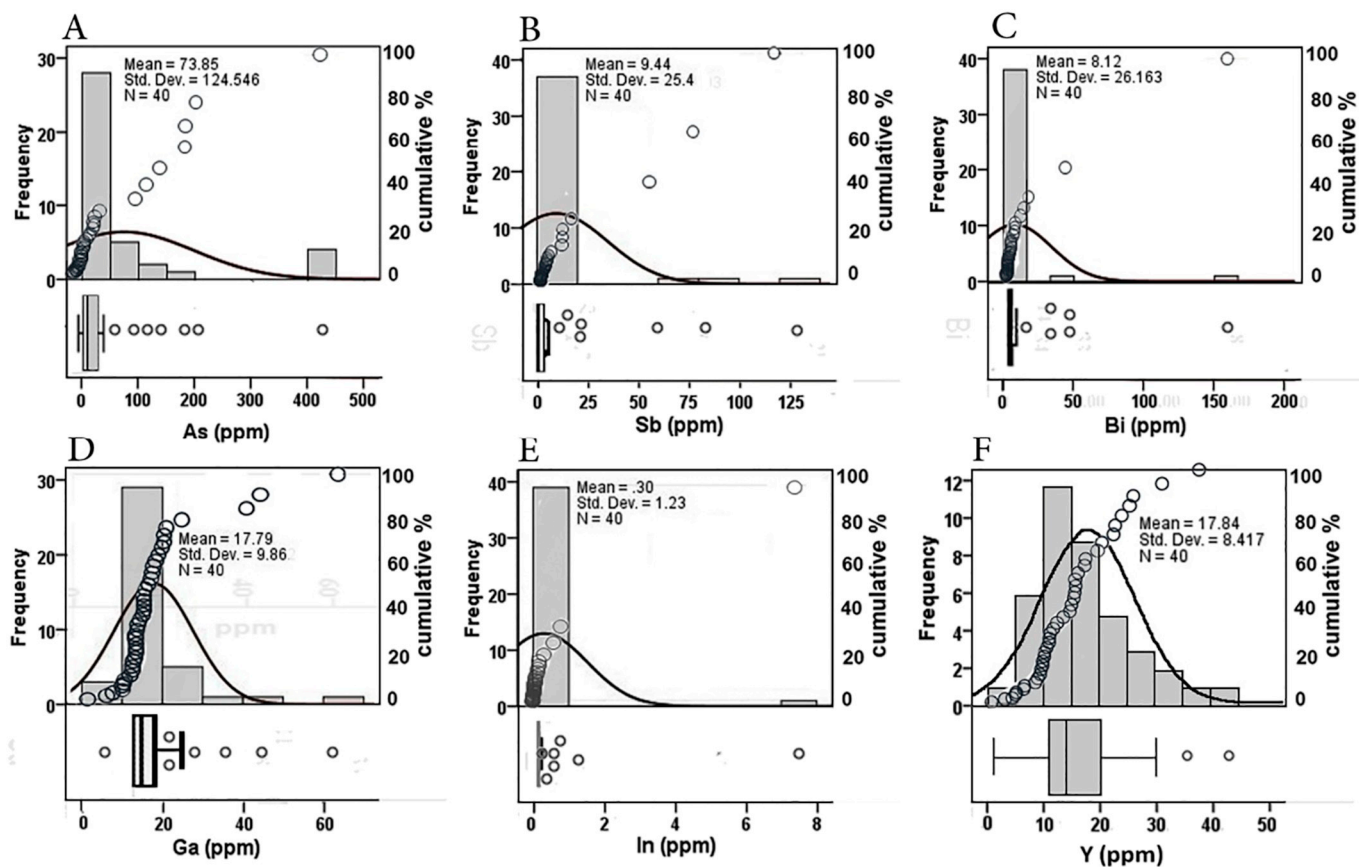


Fig. 9. Histogram, box plot and cumulative percentage diagrams of elements in the waste rocks.

6.4.13. Arsenic (As)

The average content of arsenic in sulfide-bearing waste rocks, gossanized waste rocks and residual gossans follows 48.68, 83.53 and 102.19 ppm, 24.34 to 51 magnitudes higher than granodiorite and crustal abundances. This is reflected in histogram, box plot and cumulative diagram of As (Fig. 9A), which illustrates a positive anomalous skewness and lognormal distribution. The highest arsenic level (425 ppm) in gossanized waste rocks could be due to the colloidal adsorption by Fe-oxyhydroxides (Levinson, 1980; Atapour and Aftabi, 2007; Plumlee and Morman, 2011; Smith et al., 2013). In this respect, Reimann et al. (2003) suggested that arsenic minerals and compounds are readily soluble, but arsenic migration is limited, because of the strong sorption by Fe-oxyhydroxides. Arsenate ions are known to be co-precipitated by Fe-oxyhydroxides and goethite, though, ferrihydrite more strongly adsorb arsenic due to its higher surface area (Kabata-Pendias, 2011; Reimann et al., 2003). Arsenic is more strongly adsorbed at weak acidic than near neutral pH conditions on to Fe-oxyhydroxides (Plant et al., 2004). Arsenic is readily incorporated in the pyrite and chalcopyrite and during oxidative chemical weathering of these minerals, it is released causing highly anomalous values of arsenic into Shour river, springs and soils around the Sarcheshmeh mine surroundings (Khorasanipour, 2011; Khorasanipour et al., 2011; Khorasanipour and Eslami, 2014; Khorasanipour, 2015; Khorasanipour and Jafari, 2017). Importantly, the concentration of arsenic in the waste rocks is almost > 24 times greater than the natural background and crustal abundances, which is certainly of environmental concern.

6.4.14. Antimony (Sb)

Antimony shows large variations in waste rocks, as its content in sulfide-bearing waste rocks reaches up to 12.61 ppm, five times higher than antimony in granodiorite and crustal abundance. The highest value of antimony is 130 ppm in gossanized waste rocks. Fig. 9B shows

histogram, box plot and cumulative percentage diagram of Sb, where the data show a positive anomalous skewness and lognormal distribution. Antimony is soluble at moderate pH (4–8) and is adsorbed by iron oxyhydroxides, but antimony oxide (Sb_2O_3) is poorly soluble (De Vos and Tarvainen, 2006). Antimony replaces iron in pyrite (Levinson, 1980; Smith et al., 2013; Shao et al., 2018), and during chemical weathering soluble Sb is drained into soil and groundwater system (Levinson, 1980; Smith et al., 2013). This is supported by high values of Sb (11.75–56.20 ppm) in soils around the waste dumps in the Sarcheshmeh mining area (Khorasanipour and Aftabi, 2010). Although antimony is not as toxic as arsenic, the highly anomalous values of this element in the Sarcheshmeh waste rocks may be of environmental concern.

6.4.15. Bismuth (Bi)

The Bi values range from 16.25 ppm in sulfide-bearing waste rocks up to 163 ppm in gossanized waste rocks. The mean value in gossanized waste rocks is about 10.8 ppm, three magnitudes higher than the Sarcheshmeh ore zone (Table 3), but 50 fold over the natural background and crustal abundances. The histogram, box plot and cumulative percent diagram of Bi in waste rocks show a positive anomalous skewness with lognormal distribution (Fig. 9C). Bismuth is reported to replace in the structure of pyrite, galena, sphalerite and chalcopyrite (Nickel, 1979; Levinson, 1980). The enrichment of bismuth in gossanized waste rocks is related to the adsorption of the element by iron oxide and hydroxides (Nickel, 1979; Thornber, 1985). Bismuth has low mobility under most environmental conditions and in aqueous solutions most commonly occurs as the trivalent cation Bi^{3+} (1.10 Å), which is relatively similar to Pb^{2+} (1.26 Å) (Eby, 2004; Kabata-Pendias, 2011). Like As, Sb and Pb, Bi is also readily adsorbed by secondary Fe and Mn oxyhydroxides, oxides and organic matter in soil and stream sediments

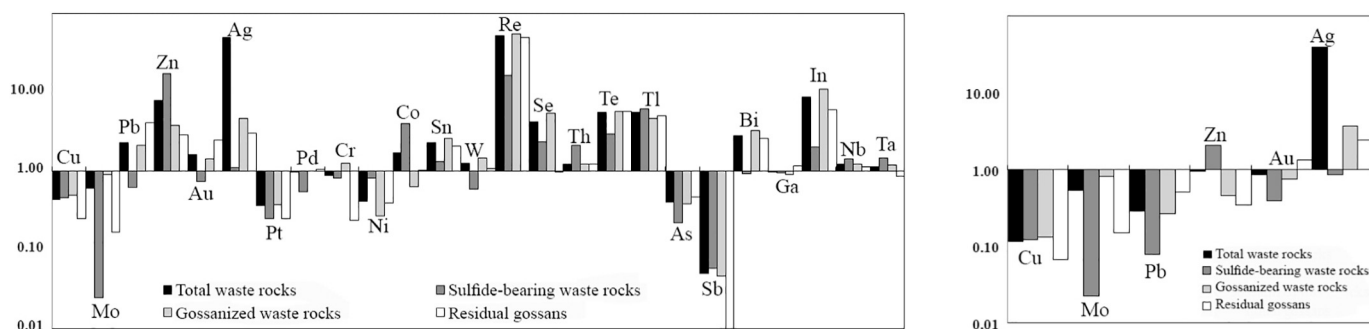


Fig. 10. Enrichment factor for some elements in the waste rocks normalized to the Sarcheshmeh hypogene and supergene ore zones.

Table 5

A summary of normative minerals, NP, S (%) AGP (AP), NAP and NNP data in the waste rocks of the Sarcheshmeh mining area.

Sample	Statistics	Q	Or	Ab	An	C	Hy	Mag	Il	Hem	Ap	Ru	Cc	Total	NP	S %	AGP	NAP	NNP
Sulfide-bearing waste rocks	Mean	26.27	18.30	16.67	8.09	7.41	6.19	0.62	0.37	14.58	0.45	0.47	1.30	100.22	89.67	3.73	116.56	26.89	-26.89
	Max	40.13	26.77	40.52	39.08	13.74	13.90	6.83	1.25	44.98	0.69	1.18	6.33	101.01	177.39	8.01	250.31	196.06	134.31
	Min	11.01	7.83	0.60	-0.43	0.00	1.07	0.00	0.02	1.62	0.30	0.00	0.08	99.26	12.53	0.53	16.69	-134.3	-196.06
Gossanized waste rocks	Mean	38.43	22.46	2.33	-0.30	10.59	2.22	0.29	0.13	22.28	0.67	0.75	0.54	100.40	21.50	0.91	28.44	6.93	-6.93
	Max	54.01	44.17	12.81	9.18	16.10	9.40	6.17	1.87	74.28	2.06	1.19	2.92	101.94	98.87	10.80	337.50	319.35	97.00
	Min	11.03	6.40	0.14	-4.95	2.19	0.74	0.00	0.00	6.22	0.00	0.00	0.08	100.08	-2.18	0.05	1.56	-97.00	-319.35
Residual gossans	Mean	37.28	24.19	4.58	-0.22	14.82	3.76	0.02	0.27	14.21	0.37	0.73	0.18	100.19	25.16	1.82	56.74	31.58	-31.58
	Max	51.07	36.49	24.48	0.94	25.18	10.04	0.13	1.22	38.15	0.92	1.16	0.25	100.27	47.54	8.40	262.50	217.21	32.85
	Min	7.29	9.39	0.44	-1.26	7.98	1.10	0.00	0.02	2.07	0.18	0.00	0.08	100.08	13.86	0.04	1.25	-32.85	-217.21

(De Vos and Tarvainen, 2006). The highly anomalous concentrations of Bi in the waste rocks are much higher than the geochemical background in the Sarcheshmeh mining areas and compared to arsenic and antimony, are less likely of environmental concern.

6.4.16. Gallium (Ga)

The average concentration of Ga is about 60.80 ppm in residual gossan, 43.20 ppm in sulfide-bearing waste rocks and 39.80 ppm in gossanized waste rocks, almost two times more than the Sarcheshmeh ore zone. This is also illustrated in histogram, box plot and cumulative percentage diagram of Ga in waste rocks, indicating a positive anomalous skewness with lognormal distribution (Fig. 9D). Gallium is a trivalent element and replaces in the structure of aluminum-rich silicate minerals and less likely copper sulfides as gallite (CuGaS_2) (De Vos and Tarvainen, 2006). Gallium is generally immobile in the geochemical cycle, but is most likely mobile under acid conditions, in particular in acidic environments (Levinson, 1980; De Vos and Tarvainen, 2006). Chemical weathering of silicate-rich and sulfide-rich (chalcopyrite) waste rocks could release Ga and precipitates as gallium hydroxide or songheite $\text{Ga}(\text{OH})_3$, but under acidic pH, soluble gallium may drain into soils and water cycle (Kabata-Pendias, 2011).

6.4.17. Indium (In)

The mean indium contents in sulfide-bearing waste rocks, gossanized waste rocks and residual gossans are 0.081, 0.442 and 0.24 ppm, and the highest values reach up to 7.81 ppm in gossanized waste rocks (Table 3). This value is almost eleven times higher than the indium content in the Sarcheshmeh ore zone (0.04 ppm). Fig. 9E indicates frequency histogram, box plot and cumulative percentage diagram of indium with a positive anomalous skewness and lognormal distribution. Indium is reported to replace in the structure of chalcopyrite (Levinson, 1980; Kabata-Pendias, 2011). Oxidative chemical weathering of the waste rocks releases indium as $\text{In}(\text{OH})^{2+}$, which at pH range of 5–9 precipitates as dzahlindite $\text{In}(\text{OH})_3$ or is adsorbed by iron hydroxides.

6.4.18. REEs and Yttrium (Y)

The average concentrations of total rare earth elements (ΣREEs) in sulfide-bearing waste rocks, gossanized waste rock and residual gossan

follow 122.72, 110.41 and 126.71 ppm (Table 4), somehow lower than the crustal abundance (196.68 ppm, Table 4). These values are also similar to the values of ΣREEs in granodiorite (120.1 ppm), although the highest values reach up to 262.92 ppm in the gossanized waste rocks. The average value of yttrium is 18.29 ppm in residual gossan, 18.61 ppm in sulfide-bearing waste rocks and 14.27 ppm in gossanized waste rocks. However, the highest values of Y reach up to 43.5 ppm in gossanized waste rocks. These values are higher than the crustal abundances for Y (30 ppm) (De Vos and Tarvainen, 2006). The high concentrations of REEs and Y in gossanized waste rocks are attributed to the sorption of these elements by iron hydroxides (Liu et al., 2017). The REEs and Y are reported to replace in silicate minerals, oxides, phosphates, carbonates and to a lesser extent in the sulfide minerals (Jones et al., 1996; Zhao and Jiang, 2007). The solubility of the REEs + Y depends on pH and soluble forms, which occur as the free ion ($\text{REE}^{3+} + \text{Y}^{3+}$) or as F^- , OH^- , SO_4^{2-} , CO_3^{2-} , or PO_4^{3-} complexes under acid conditions and low temperature (Lee and Byrne, 1992; Wood, 1990; Voudouris et al., 2013; Randive et al., 2014). Haas et al. (1995) and Voudouris et al. (2013) suggest that at low temperature and pressure, stability of the REEs complexes increases slightly from La to Lu. Both Y and the heavy REEs (Gd to Lu) form more stable complexes than light REEs (La to Sm), particularly with carbonate and sulfate anions in alkaline solutions. Yttrium displays very low mobility under all environmental conditions (De Vos and Tarvainen, 2006) and most likely, it can be treated as trivalent REEs (Van Middlesworth and Wood, 1998). In acid and sulfate-rich waters, REEs + Y remain dissolved below pH 5.1, but between pH 5.1–6.6 they partitioned, co-precipitated or adsorbed by iron hydroxides (Jones et al., 1996; Verplanck et al., 2004; Liu et al., 2017). In this regard, under oxidative chemical weathering of the waste rocks, REEs and Y are dissolved and mobilized through hydrolysis, dissolution and oxidation of silicate, phosphate, carbonate and sulfide mineral via acid mine drainage (AMD), but at pH > 5.1 are adsorbed by Fe-oxyhydroxides in gossanized waste rocks.

6.4.19. Other elements

The rest of elements including Pt, Pd, Tl, Nb, Ta, Li, Zr and Hf show background concentration and do not show significant variations in the waste rocks.

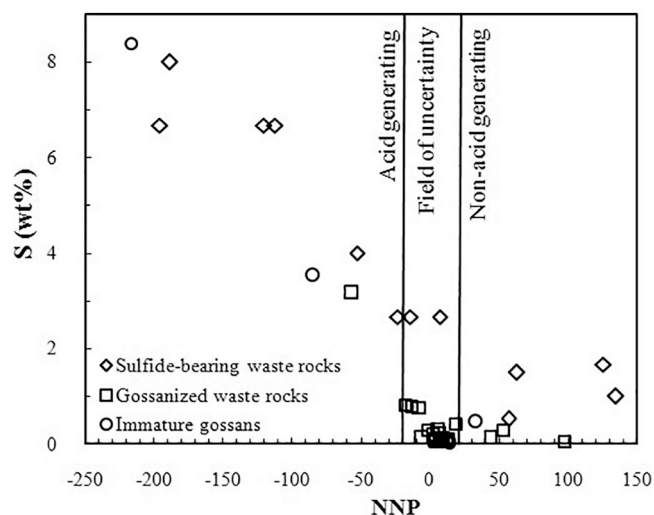


Fig. 11. Evaluation of acid mine drainage (AMD), using sulfur-NNP biplot diagram (Ferguson and Morin, 1991).

6.4.20. The enrichment factors through Sarcheshmeh ore zone

The enrichment factors were calculated by dividing the average elemental contents in the waste rock through the average concentrations in the Sarcheshmeh ore zone (Tables 2, 3, 4 and Fig. 10). The highest enrichment factors in waste rocks follow Au (2.5), Pt (0.38), Pd (1.05), Ag (4.67), Cu (0.49), Mo (0.90), Pb (4.06), Zn (17.34), Sn (2.64), W (1.47), Re (22.22), Se (5.38), Te (5.75), Tl (4.1), As (0.46), Sb (0.06), Bi (3.29), Ga (1.15), In (11.5), La (1.2), Ce (1.2) and Y (4.1), respectively. Among these, the highest enrichment factors include for Re (22.22), Se (5.38), Ag (4.6), Te (5.71), Tl (4.6), Bi (3.29) and In (11.05) in gossanized waste rocks (Tables 2 and 3) are notable. However, the enrichment factors for some elements in waste rocks normalized to the supergene ore zone are not significant, except for silver which displays an enrichment factor of 34.

7. Possible prediction of acid generation and neutralization potential of the waste rocks

This section explores the possible prediction of acid mine drainage (AMD) generation during oxidative chemical weathering of the waste rocks. In this regard, the acid generation potential or acid potential (AGP or AP), neutralization potential (NP), net acid potential (NAP) and net neutralization potential (NNP) of the waste rocks are calculated. The calculations are based on the methods proposed by (1) Plumlee (1999) and Abrosimova et al. (2015). $AGP (AP) = S_{sulfide} \times 31.25$, which is expressed in terms of kilograms of calcium carbonate to neutralize the acid generated by oxidation of sulfide minerals in 1000 kg of the waste rocks (Plumlee, 1999). NP is neutralization potential of the waste rocks and is expressed by the below equation (Lawrence and Scheske (1997): $NP = \text{normative wt mineral (g)/100} \times \text{mol wt calcite/mol wt mineral} \times 1000 \text{ kg/ton} \times \text{relative reactivity of mineral in the waste rocks}$. The results are followed by $NNP = NP - AGP$ and $NAP = AGP - NP$. AGP is calculated by using sulfur content of only sulfide minerals and NP is calculated by calculating the normative minerals of the waste rocks, respectively. The summary of the results are shown in Table 5 and Fig. 11. As shown in Fig. 11, the majority of the sulfide-bearing waste rocks and only two samples of the immature gossans, which contain > 3 wt% S, plot on the field of potentially acid generating sources. However, the gossanized waste rocks as well as some of the immature residual gossans with < 3 wt% S reflect either a very weak nature of acid generation or are plotted within the field of uncertainty. Accordingly, the sulfide-bearing waste rocks at the Sarcheshmeh mining area are considered as the main source of acid mine drainage (AMD), which covers an area of about

Table 6 Pearson's correlations coefficients in the waste rocks at Sarcheshmeh porphyry copper mine waste dumps.

Pearson's correlations coefficients		Fe	Cu	Mo	Au	Ag	Pb	Zn	Sn	W	Re	Se	Te	S	As	Sb	Bi	Ga	In	ΣREE
Fe	1	0.108	-0.097	0.291	0.405	0.295	-0.119	0.388	0.176	-0.199	0.312	0.460	0.657	0.460	0.179	0.365	0.462	0.300	0.396	-0.688
Cu		1	0.556	0.122	0.195	0.001	0.525	0.004	-0.016	0.289	0.444	0.058	0.084	0.058	0.265	0.032	0.163	-0.066	0.190	-0.096
Mo			1	0.043	0.004	-0.076	0.323	-0.043	0.323	0.355	0.776	-0.079	0.013	-0.017	0.013	-0.017	-0.046	-0.182	-0.030	0.007
Au				1	0.540	0.614	-0.010	0.411	-0.029	-0.063	0.004	-0.085	0.512	-0.085	0.374	0.049	0.488	0.214	0.495	-0.385
Ag					1	0.543	0.038	0.721	0.011	-0.057	-0.033	-0.071	0.808	-0.071	0.049	0.031	0.974	0.429	0.992	-0.225
Pb						1	0.029	0.308	0.025	-0.165	-0.164	-0.164	0.607	-0.164	0.531	0.211	0.500	0.332	0.491	-0.239
Zn							1	-0.106	-0.200	-0.063	-0.063	0.056	0.005	-0.034	-0.034	-0.059	0.040	-0.014	0.055	-0.003
Sn								1	0.407	-0.016	-0.016	-0.150	0.686	-0.221	-0.085	0.046	0.791	0.611	0.737	-0.294
W									1	0.152	0.152	0.066	0.066	-0.163	0.104	0.242	0.004	0.012	-0.025	-0.227
Re										1	0.225	0.444	0.053	-0.006	0.194	-0.090	-0.084	-0.060	0.063	0.338
Se											1	0.240	0.053	0.240	0.094	0.355	-0.099	-0.306	-0.095	-0.231
Te												1	0.053	-0.014	0.307	0.847	0.601	0.794	-0.403	-0.403
S													1	-0.058	0.094	-0.065	-0.150	-0.070	-0.399	-0.269
As														1	-0.031	0.299	-0.095	-0.013	-0.269	-0.190
Sb															1	-0.004	0.102	-0.043	-0.043	-0.267
Bi																1	0.573	0.985	0.985	-0.267
Ga																	1	0.455	0.455	-0.265
In																		1	1	-0.215
ΣREE																				1

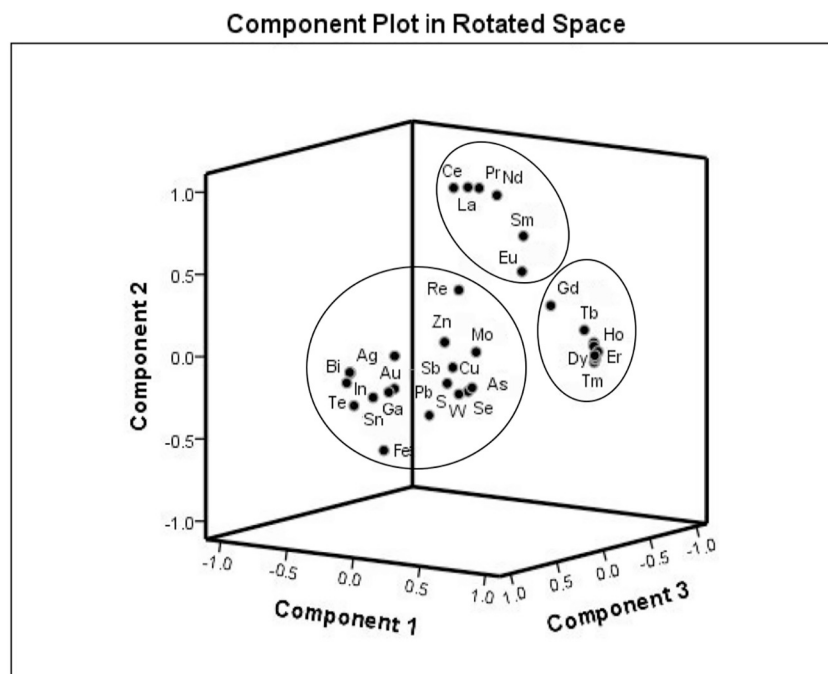


Fig. 12. Principal components analysis diagram of different elements in the waste rocks.

2 km² and contributes to distribution of heavy metal contaminants via geochemical cycle.

8. Statistical approach

In order to explore the elemental association in different waste rocks, correlation coefficient, cluster analysis and principal components analysis were employed.

8.1. Correlation coefficient

The Pearson correlation coefficient has been applied for interelement relationships (Levinson, 1980). Accordingly, the Pearson correlation coefficients were calculated after log-transformation of the elements concentration (Table 6). In this regard, elements pairs with significant correlation coefficient are emboldened. The results indicate that there is a positive correlation between Fe, Cu, Te, Bi, S, In, Sb, Ag, Au, Pb, As and Sn. This is most likely related to chalcophile nature of these elements, replacing in the structure of sulfates (melanterite, chalcantite) and sulfides (pyrite, chalcopyrite) in the waste rocks (Levinson, 1980; De Vos and Tarvainen, 2006). There is also a close positive correlation between Fe, Pb, Au and Ag in the gossanized waste rocks. The frequent occurrence of Fe-oxyhydroxides in the gossanized waste rocks, may explain the possible co-precipitation or adsorption of the aforementioned elements by Fe-oxyhydroxides. However, Au and Ag might occur as minute inclusions in chalcopyrite, pyrite and galena (Levinson, 1980, Page: 871–872). Moreover, Ag is mainly reported to replace in the structure of galena (Levinson, 1980).

Also, Te indicates a positive correlation with Fe, Au, Ag, Pb and Sn. This may be due to the chalcophile nature of Te, essentially being constrained to sulfide and low-temperature supergene minerals (De Vos and Tarvainen, 2006). The positive correlation between Se and S could be related to the substitution of Se in the structures of sulfide–sulfate minerals. It is noteworthy that Se is a chalcophile element, which more widely presents as an accessory element replacing sulfur in the structure of pyrite, chalcopyrite, molybdenite, pyrrhotite and sphalerite (De Vos and Tarvainen, 2006). The most notable point is that most of the elements anticorrelate with REEs, which may form as independent lithophile hydroxide phases (Jones et al., 1996) in the waste rocks during

supergene processes.

8.2. Principal components analysis (PCA)

The principle components analysis explores the associations between elemental groups in Fig. 12 and Table 7, and show eight principal-components with eigenvalues greater than 1. PC1 contains about 32.79% of the total variance and mainly includes Gd–Tb–Dy–Ho–Er–Tm–Yb–Lu–Y association. This may reflect the occurrence of REE + Y hydroxides in the waste rocks and most importantly it indicates that the REEs + Y have similar radii and geochemical properties. This is also indicated in Table 7, where there is no significant correlation between REEs and other chalcophile elements. PC2 displays about 17.16% of the total variance and shows another significant association of La–Ce–Pr–Nd–Sm–Eu in the waste rocks, which possibly indicates association of the light REEs. PC3 illustrates about 12.25% of total variance and includes Ag–Sn–Te–Bi–Ga–In association, reflecting the chalcophile nature of these elements in the waste rocks. PC4 includes about 8.70% of the total variance and explains a Cu–Mo–Re–Se link that gives positive genetic relation as well as characteristic suite of porphyry chalcophile elements in the gossanized and sulfide-bearing waste rocks. PC5 depicts about 6.11% of the total variance and is related to Fe–Se–Sb–As–Eu–Gd link, indicating chalcophile nature of some elements and possibly adsorption of few REEs by Fe-oxyhydroxides. PC6 accounts about 5.19% of the total variance and indicates Au–Pb–As association of siderophile-chalcophile elements in the waste rocks. PC7 includes about 4.36% of the total variance and possibly shows a strong Cu–Zn association related to the presence of copper-zinc sulfates or Zn-rich sulfides. PC8 displays about 3.05% of the total variance and is related to Sn–W group that may occur as oxides or hydroxides in the waste rocks.

8.3. Cluster analysis

The method is based on the centroid linkage (Reimann et al., 2003) and the dendrogram of elements (Fig. 13) and indicates two cluster branches. The first cluster branch shows chalcophile association and includes two subgroups; Ag, In, Te, Bi, Te, Sn and Ga, followed by Fe, S, Au, Pb, As, Sb, Cu, Zn, Mo, Se, W and Re. Both of the subgroups occur in

Table 7
Principal components analysis, rotated components matrix in the waste rocks at Sarcheshmeh porphyry copper mine waste dumps.

Elements	Rotated component matrix								
	Component								
	1	2	3	4	5	6	7	8	
Fe	-0.212	-0.657	0.422	0.054	0.375	-0.020	-0.123	-0.210	
Cu	0.066	-0.089	0.127	0.600	-0.011	0.120	0.700	-0.112	
Mo	0.131	-0.011	-0.031	0.892	-0.058	0.042	0.081	0.129	
Au	-0.144	-0.191	0.465	0.054	-0.127	0.645	-0.041	-0.052	
Ag	-0.147	-0.027	0.934	0.068	-0.034	0.173	0.032	-0.082	
Pb	-0.002	-0.093	0.486	-0.121	0.160	0.723	-0.018	0.025	
Zn	-0.088	0.031	-0.005	-0.088	0.005	-0.029	0.943	-0.048	
Sn	-0.059	-0.185	0.814	-0.005	-0.077	-0.084	-0.104	0.420	
W	0.037	-0.269	0.021	0.387	0.190	-0.069	-0.221	0.715	
Re	0.032	0.363	0.014	0.586	-0.064	-0.149	-0.046	0.030	
Se	0.016	-0.274	-0.108	0.828	0.372	0.069	-0.059	-0.019	
Te	-0.178	-0.241	0.851	-0.056	0.263	0.148	-0.001	0.008	
S	-0.306	-0.457	-0.146	0.109	0.092	-0.272	-0.045	-0.626	
As	0.042	-0.249	-0.115	0.057	0.122	0.832	0.058	0.049	
Sb	-0.050	-0.213	0.021	0.001	0.861	0.122	-0.013	0.117	
Bi	-0.150	-0.083	0.969	-0.005	-0.060	0.060	0.043	-0.032	
Ga	-0.084	-0.185	0.611	-0.306	-0.055	-0.118	0.051	0.331	
In	-0.144	-0.022	0.945	0.032	-0.091	0.103	0.052	-0.092	
La	-0.098	0.951	-0.116	-0.004	-0.060	-0.133	-0.022	0.005	
Ce	0.010	0.966	-0.116	-0.020	-0.047	-0.122	-0.007	-0.033	
Pr	0.086	0.967	-0.128	0.001	-0.013	-0.137	-0.010	-0.035	
Nd	0.224	0.939	-0.122	0.008	0.123	-0.125	-0.003	-0.063	
Sm	0.443	0.716	-0.094	0.037	0.492	-0.030	0.004	-0.109	
Eu	0.432	0.500	-0.094	0.180	0.674	0.037	0.028	-0.091	
Gd	0.659	0.318	-0.080	0.099	0.627	0.026	0.028	-0.028	
Tb	0.886	0.187	-0.117	0.160	0.329	0.009	0.074	-0.016	
Dy	0.957	0.117	-0.118	0.150	0.133	0.012	0.034	-0.017	
Ho	0.985	0.064	-0.122	0.027	0.031	0.000	-0.014	-0.008	
Er	0.989	0.048	-0.080	0.047	-0.013	-0.017	-0.003	0.013	
Tm	0.982	0.022	-0.098	0.043	-0.012	0.020	-0.013	0.030	
Yb	0.982	0.029	-0.097	0.009	-0.020	0.005	-0.052	0.084	
Lu	0.965	-0.001	-0.109	-0.016	-0.057	-0.010	-0.055	0.126	
Y	0.960	0.095	-0.113	-0.091	-0.015	-0.089	-0.038	-0.004	
Initial eigenvalues	Total	10.82	5.66	4.04	2.87	2.01	1.715	1.44	1.01
	% of variance	32.79	17.16	12.25	8.70	6.11	5.19	4.36	3.05
	Cumulative%	32.79	49.96	62.21	70.91	77.02	82.22	86.59	89.65

Extraction method: principal component analysis.

Rotation method: Varimax with Kaiser normalization.

sulfates and sulfides minerals in the waste rocks and have a significant relationship to Fe and S and show chalcophile nature of the aforementioned elements. The second cluster is related to lithophile elements and includes REEs which consists of two subgroups. The first one includes HREE (Ho, Er, Tm, Yb, Tb, Dy, Lu, Y), followed by the second group of LREE (Sm, Eu, Gd, Ce, Pr, La, Nd), which probably either occur as independent REEs hydroxide phases or less likely adsorbed by Fe-oxhydroxides in the waste rocks.

9. General discussion

Mining of high tonnage and low-grade ores such as porphyry copper deposits produces large volumes of waste rocks that are dumped on the land surface. It is reported that > 98% of porphyry copper systems are dumped as waste rocks (John et al., 2010). These waste rocks may be considered as a potential source of valuable elements as well as a pollution hazard system. The following discussion explores the possible exploration, economic and environmental significance of the Sarcheshmeh porphyry copper mine wastes.

9.1. Exploration significance

To give the exploration significance of residual gossans and waste rocks, it is important to look at the distribution of trace and precious elements in different waste rocks. Previous studies (Rose et al., 1979;

Levinson, 1980) have not given enough geochemical data on the exploration significance of gossans or gossanized waste rocks around porphyry copper deposits, except for the few data reported by Atapour and Aftabi (2007).

Elemental enrichment and depletion in different waste rocks may give a guiding exploration clue for future exploration targets. For example, although the average gold value (0.044 ppm) in sulfide-bearing waste rocks are lower than residual gossans (0.15 ppm) and gossanized waste rocks (0.085 ppm), the contents are almost 10–37 magnitudes higher than the non-mineralized granodioritic porphyry stock at Sarcheshmeh porphyry copper area (Atapour, 2007). This indicates that in the sulfide-bearing waste rocks, gold occurs as inclusion in the fine-grained disseminated pyrite and chalcopyrite. During oxidative chemical weathering and gossanization of the waste rocks, the soluble compounds are leached, but gold is enriched in the residual gossan and gossanized waste rocks. This is supported by the highest values of gold in residual gossans (0.775 ppm) and gossanized waste rocks (0.608 ppm). In this regard, gold sampling of residual gossans or gossan floats in the alluvium may indicate the concealed porphyry ores under the cover of the leached zones at greater depth. There are also elevated values of Mo (2960 ppm), Ag (87 ppm) and Se (68 ppm) in the gossanized waste rocks, thus Mo, Ag and Se could also be considered as other exploration targets for unexposed porphyry deposits by using surficial gossan sampling.

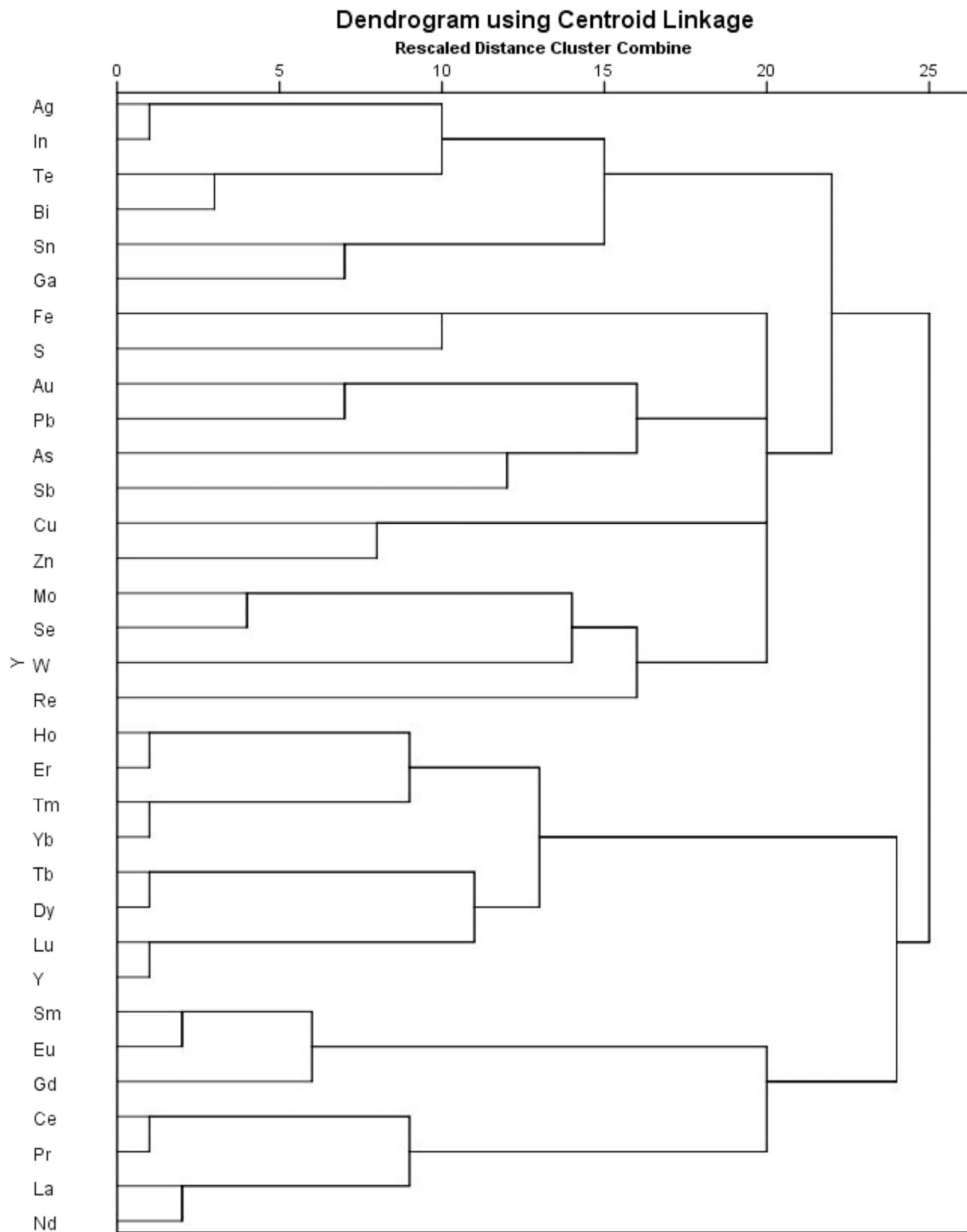


Fig. 13. Dendrogram of cluster analysis of different elements and precious metals in the waste rocks.

9.2. Possible economic by-products

Waste rocks could contain elements with lower and uneconomic concentrations to be economically recoverable at the time of porphyry copper exploitation. However, as some of the elements may have critical or strategic applications, they should be reevaluated for future resources. Some of these elements are considered to be of strategic and

critical elements for future resources (Seredkin et al., 2016). The average contents of Cu, Mo, Pb, Zn, Ag, Sn, W, Re, Se, Te, Bi, Ga, In, Nb, Ta, Au and their total weight within 2.6 billion tonnes of the waste rocks at Sarcheshmeh mine dumps are shown in Table 8.

The occurrence of sulfate minerals in the waste rocks may be regarded as other possible economic by-product minerals. Copper sulfates have different applications in the fields of agriculture, industry,

Table 8
Total weight of different elements within 2.6 Gt of the waste rocks.

Elements	Average (ppm)	Resources (tonnes)
Cu	3225	8.4×10^6
Mo	119	312×10^3
Pb	115	300×10^3
Zn	750	1.95×10^6
Ag	61	158×10^3
Sn	4	10×10^3
W	37	95×10^3
Re	0.01	27
Se	10	27×10^3
Te	3	8×10^3
Tl	0.28	726
Bi	9	24×10^3
Ga	18	48×10^3
In	0.35	902
Nb	3	9×10^3
Ta	0.23	598
Au	0.1	255

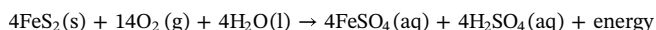
chemistry and medicine (USDA, 1995). In this regard, copper sulfate mineral ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) is used for production of blue and green paints, in the coloring of cotton and silk fabrics, hair dye, production of fungal toxins, electroplating as electrolyte, as well as a dye for glass, glue, ceramic, and bacteria filling for green flame in fireworks (USDA, 1995). The use of these minerals in agriculture is also commonly used as an antifungal agent to control bacterial viruses and fungal diseases of plants, patches of leaves and pests (Beckman, 2008).

9.3. Environmental considerations

It is logic to consider the waste rocks as a double-edged sword that may have positive economic by-products as well as negative environmental impacts. In this regard, the high concentrations of potentially toxic elements in sulfide-bearing waste rocks and generation of acid mine drainage (AMD) released by oxidative chemical weathering of sulfide minerals can pose risks to ecosystems and humans (Hudson-Edwards and Dold, 2015).

One of the most environmental hazards in the waste rocks at the Sarcheshmeh porphyry mine is related to sulfide-bearing waste rocks that contain up to 15% pyrite and chalcocopyrite. When these sulfide minerals are exposed to oxygen, water and catalyzed by microbial activity, their oxidation lead to the formation of sulfate ion, toxic metals and acid mine drainage (AMD) (Atapour and Aftabi, 2007; Khorasanipour and Eslami, 2014; Abrosimova et al., 2015). Depending on the rate of pyrite-chalcocopyrite oxidation, availability of moisture and oxygen and presence of oxidizing bacteria (Frascoli and Hudson-Edwards, 2018) within the waste rocks, the pH is often very low, between 2.9 and 3.5 (Shafaei Tonkaboni et al., 2011).

The relationship between net neutralization potential (NNP) and sulfur content in the waste rocks indicates that the waste rocks with > 3 wt% sulfur are potential source of AMD. It is notable that some samples with < 3 wt% sulfur have no significant potential of AMD. This may be due to the presence of minute inclusions of sulfide minerals in a closed system of some resistant minerals (e.g., quartz), which resist to the chemical weathering of the sulfide mineral inclusions. The acid mine drainage (AMD) in the Sarcheshmeh mine dumps was probably formed according to reaction proposed by Lottermoser (2007):



Further reactions of sulfuric acid with soluble copper, iron and zinc lead to the formation of iron-copper-zinc sulfates. Acid leaching by acid mine drainage (AMD) is a serious hazard to surface runoff, groundwater, and soil that may lead to crop pollution, high cancer rates, and animal deformity (Wu et al., 2009; Yin et al., 2018). The highest

selenium (68.6 ppm) and rhenium (0.155 ppm) in the Sarcheshmeh waste rocks may also be toxic at higher levels, causing hair and nail loss, skin disorders, nerve damage and abdominal cramps (De Vos and Tarvainen, 2006), though this depends on the bioavailability of Se which is controlled by the type of minerals and their solubility. Although Mo is an essential elements for life in ecosystems, the very high values of the element up to 4000 ppm (Frascoli and Hudson-Edwards, 2018) and similar high Mo contents (2960 ppm) in the Sarcheshmeh mine wastes are in the risk level of Mo contamination in water cycle, soil and sediments. Moreover, the AMD in the Sarcheshmeh mining area covers an area of about 2 km², which poses serious environmental risks in the Sarcheshmeh mining area.

10. Conclusions

This investigation highlights the geochemical signatures of different waste rocks around the Sarcheshmeh porphyry copper mine dumps and gives the following conclusions:

There are two main types of sulfide-bearing and gossanized waste rocks at Sarcheshmeh porphyry mine dumps. The waste dumps consist of sericitized, argillized and propylitized trachybasalt and granodiorite with up to 15 percentage pyrite-chalcocopyrite. The gossanized waste rocks are composed of hematite, goethite, jarosite, malachite, chalcantite, brochantite and delafossite with a similar mineralogy to the residual immature gossans. The Sarcheshmeh waste rocks contain important critical and strategic elements (Au, Ag, Cu, Mo, Pb, Zn, W, Re, Se, Te, As, Sb, Bi, Ga, In), which are enriched 4–1360 magnitudes over the crustal abundances, thus they may be considered as the possible future resources. Some of these elements even display higher values than the granodiorite and hypogene ore zone at the Sarcheshmeh mine. The anomalously high contents of gold (0.775 ppm), molybdenum (122 ppm), Se (68.6 ppm) and Ag (87 ppm) in residual gossans as well as Au (0.608 ppm) and Mo (2960 ppm) in gossanized waste rocks are considered as the potential exploration guides in surficial supergene zones over the concealed porphyry copper ores. Importantly, the highest values Cu (6.39% wt) and Mo (2960 ppm) in the waste rocks are higher than the present cut-off grade at Sarcheshmeh mine (0.65% Cu and 0.02% Mo). The on-going demand for the critical and strategic elements together with exploitation of high-grade ores merits much further research for extraction of the aforementioned elements from the waste rocks. In this regard, the total weight of the critical and strategic elements within 2.6 Gt of the waste rocks around the Sarcheshmeh mine ranges from 24 to 8.4×10^6 t (Table 8). The S-NNP diagram reveals that the sulfide-bearing waste rocks have the greatest potential for generating acid mine drainage (AMD) in the Sarcheshmeh mining area. Acid mine drainage (AMD) and the high contents of some potentially toxic elements, including Cu (6.39 wt%), Mo (2960 ppm), As (425 ppm), Sb (130 ppm), Bi (163 ppm), In (7.81), Se (68.6 ppm) and sulfur (40.8% wt) are globally-recognized as environmental hazards that may danger the ecosystems of the surrounding areas of the Sarcheshmeh mine.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.gexplo.2019.01.002>.

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