

The geochemistry of gossans associated with Sarcheshmeh porphyry copper deposit, Rafsanjan, Kerman, Iran: Implications for exploration and the environment

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Abstract

The Sarcheshmeh copper deposit is one of the world's largest Oligo-Miocene porphyry copper deposits in a continental arc setting with a well developed supergene sulfide zone, covered mainly by a hematitic gossan. Supergene oxidation and leaching, have developed a chalcocite enrichment blanket averaging 1.99% Cu, more than twice that of hypogene zone (0.89% Cu). The mature gossans overlying the Sarcheshmeh porphyry copper ores contain abundant hematite with variable amounts of goethite and jarosite, whereas immature gossans consist of iron-oxides, malachite, azurite and chrysocolla. In mature gossans, Au, Mo and Ag give significant anomalies much higher than the background concentrations. However, Cu has been leached in mature gossans and gives values close or even less than the normal or crustal content (<36.7 ppm). Immature gossans are enriched in Cu (160.3 ppm), Zn (826.7 ppm), and Pb (88.6 ppm). Jarosite- and goethite-bearing gossans may have developed over the pyritic shell of most Iranian porphyry copper deposits with pyrite–chalcopyrite ratios greater than 10 and therefore, do not necessarily indicate a promising sulfide-enriched ore (Kader and Ijo). Hematite-bearing gossans overlying nonreactive alteration halos with pyrite–chalcopyrite ratios about 1.5 and quartz stringers have significant supergene sulfide ores (Sarcheshmeh and Miduk). The copper grade in supergene sulfide zone of Sarcheshmeh copper deposit ranges from 0.78% in propylitized rocks to 3.4% in sericitized volcanic rocks, corresponding to the increasing chalcopyrite–pyrite or chalcocite–pyrite ratios from 0.3 to 3, respectively. Immature gossans with dominant malachite and chrysocolla associated with jarosite and goethite give the most weakly developed enrichment zone, as at God-e-Kolvari. The average anomalous values of Au (59.6 ppb), Mo (42.5 ppm) and Ag (2.6 ppm) in mature gossans associated with the Sarcheshmeh copper mine may be a criterion that provides a significant exploration target for regional metallogenic blind porphyry ore districts in central Iranian volcano–plutonic continental arc settings. Drilling for new porphyry ores should be targeted where hematitic gossans are well developed. The ongoing gossan formation may result in natural acidic rock drainage (ARD).

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1. Introduction

Gossan as defined by Blanchard (1968), Rose et al. (1979), Levinson (1980), Costa et al. (1999), Downing and Giroux (1993), and Jambor and Blowes (1994), is

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the name given to a large mass of residual Fe oxyhydroxide material formed by the oxidation of Fe-bearing sulfide ore deposits.

The process of gossan formation starts with oxidation of pyrite and other sulfides to form Fe oxyhydroxides plus sulfuric acid. The initial product of weathering is typically an amorphous ferric hydroxide expressed as $\text{Fe}(\text{OH})_3$ which gradually crystallizes to goethite or hematite. Other important associated minerals with the Fe oxides are jarosite, gypsum, clay minerals and silica.

During gossan formation, trace elements are strongly adsorbed by the initial amorphous to very fine-grained precipitates. The amount of adsorbed elements decreases in strongly acidic solutions (Rose et al., 1979; Thornber, 1985). At mildly acid to neutral pH values, trace elements are sorbed or coprecipitated with the Fe oxides. Generally, Pb, Cu, and Ag are strongly adsorbed by iron oxides. Elements occurring as anion complexes (Mo, As, Se) are strongly sorbed to Fe oxides under acidic conditions. Gold is generally stable during the weathering of sulfide minerals and is therefore retained

as a primary residual mineral in gossan (Nickel, 1979; Thornber and Nickel, 1983). In sulfide-rich ore deposits, Au may form thiosulfate complexes which, at higher oxidation conditions, are oxidized to sulfates, thereby precipitating gold in the gossan (Nickel, 1979; Plyusnin et al., 1981; Thornber, 1985). Geochemical characteristics of gossans have been used successfully in the exploration for Ni–Cu ores in the lateritic terrain of western Australia (Cox, 1975) to distinguish gossans from ironstones. Costa et al. (1999) and Scott et al. (2001), described comprehensive investigations on the gossans overlying gold and base metal massive sulfide deposits. However, since the work of Blanchard (1968) and Bladh (1982), with the exception of recent work by Chávez (2000), only minimal attention has been given to the exploration, metallogenic and environmental aspects of the gossans or lithocappings that overlie porphyry copper mineralization, although such information may exist in the files of some mining companies.

The Sarcheshmeh porphyry copper deposit, which is the most important copper mine in Iran and is one of the

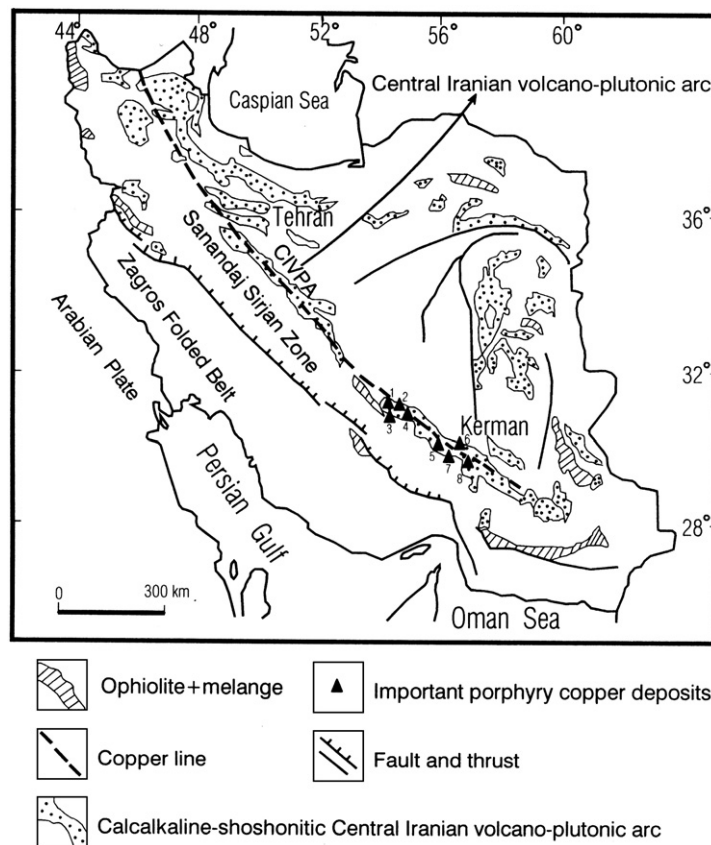


Fig. 1. Map of Iran showing the volcano–plutonic magmatic arc and copper belt. Some important porphyry copper deposits (1=Kader, 2=Gode-Kolvari, 3=Ijo, 4=Miduk, 5=Sarcheshmeh, 6=Dehsiahian, 7=Darrehzar, 8=Chahargonbad) (modified after Bariand et al., 1965; Stocklin, 1968; Taghizadeh and Mallakpour, 1974; Aghanabati, 1990; Aftabi and Anvari, 1992; Aftabi and Atapour, 2000).

largest deposits in the world, is located in the central Iranian volcano–plutonic copper belt. The deposit has been described by Bazin and Hubner (1969a,b), Anonymous (1973), Etminan (1977), Ghorashizadeh (1978), Shahabpour (1982) and Aftabi and Atapour (1997, 2000). However, except for some preliminary studies by Soleymani (1999) and Atapour (2000), no information has been published concerning the geochemical aspects of the Sarcheshmeh gossans. This paper documents exploration, metallogenic and environmental significance of the gossan overlying the Sarcheshmeh deposit.

2. Geological setting

The Sarcheshmeh porphyry copper deposit is situated in southern Iran at 30° N, 56° E; and about 160 km

southwest of Kerman city (Fig. 1). The deposit is within a belt of Eocene volcanic rocks and Oligo-Miocene sub-volcanic granitoid rocks that form part of the 2000 × 50 km central Iranian volcano–plutonic copper belt (Fig. 1). The oldest host rocks at the Sarcheshmeh porphyry copper deposit belong to an Eocene volcano-genic complex, also known as the Sarcheshmeh complex (Fig. 2). The complex consists of pyroxene trachybasalt, pyroxene trachyandesite of potassic and shoshonitic affinity (Aftabi and Atapour, 1997), less abundant andesite and rare occurrences of agglomerate, tuff, and tuffaceous sandstone. These were intruded by a complex series of Oligo-Miocene granitoid intrusive phases such as quartz diorite, quartz monzonite and granodiorite. The frequent association of trachybasalt, trachyandesite, andesite, dacite and ignimbrite and the absence of boninite and tholeiite is the best indication of the continental

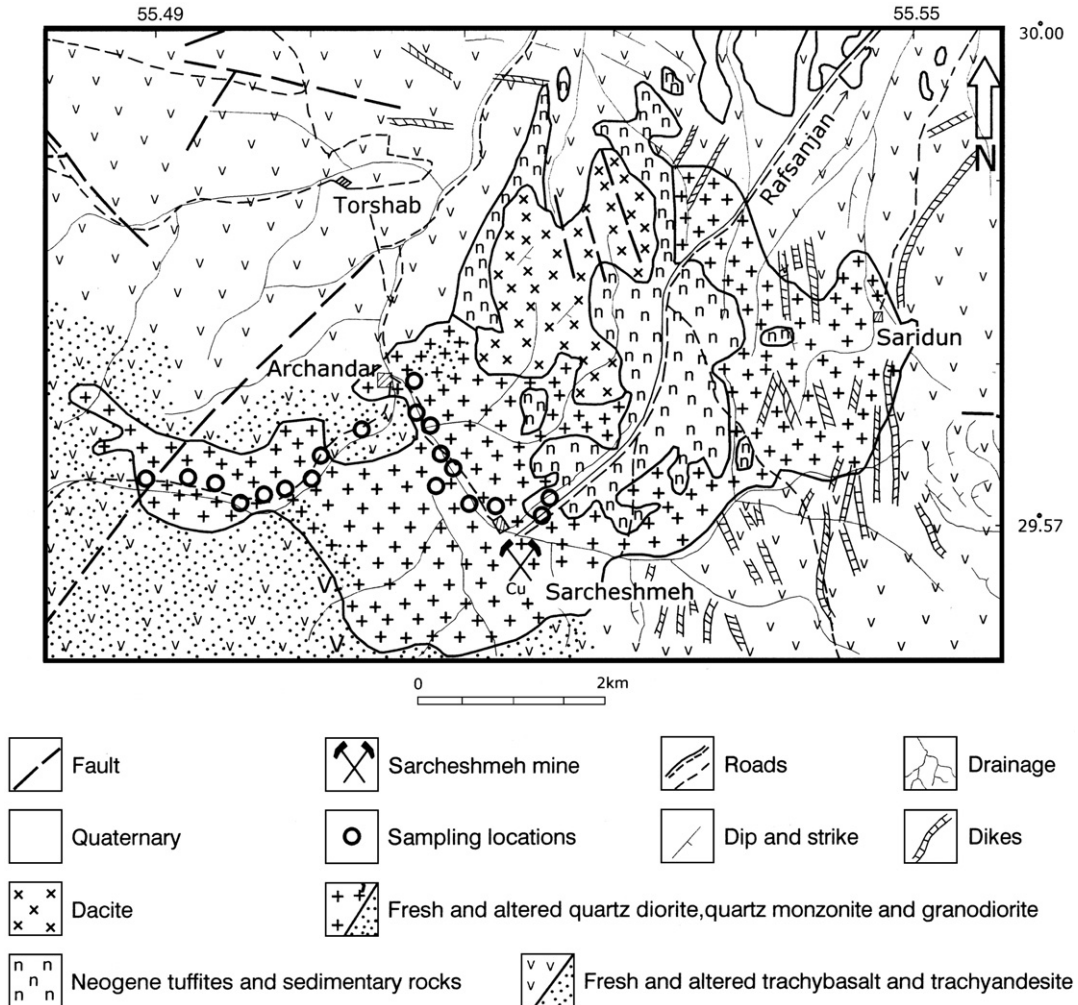


Fig. 2. Geological map around Sarcheshmeh porphyry copper mine (modified after Anonymous, 1973).

margin subduction zone of a volcano–plutonic arc, rather than the island arc (Aftabi, 1997; Aftabi and Atapour, 1997, 2000). The granitoid rocks are cut by a series of intramineral hornblende porphyry, feldspar porphyry and biotite porphyry dykes (Waterman and Hamilton, 1975). The latest stage of magmatic activity includes Neogene ignimbrite, dacite, stratified agglomerate and tuff. The volcano–plutonic complex was folded into an anticline trending east–west, and was subsequently faulted in a ENE–WSW direction.

3. Mineralization

In the Sarcheshmeh area, many zones of stockwork and vein type mineralization occur equally distributed between Eocene volcanics and Oligo-Miocene of quartz diorite, quartz monzonite and granodiorite composition. This plutonic association fits well in the Lowell and Guilbert (1970), model of porphyry copper deposits developed on the continental margin rather than the island arc. It is also noteworthy that at Sarcheshmeh, biotized trachybasalt±trachyandesite are also mineralized by the infiltration of hydrothermal solutions released by sub-volcanic granitoid rocks. The ore body is oval-shaped (Fig. 3), has dimension of 2000 m by 900 m and is centered on the Sarcheshmeh porphyry stock. Within a

2000×900 m area, and to an overall drilled depth of about 150 m, the ore body contains 450 M tonnes averaging 1.13% Cu and 0.03% Mo at a cutoff grade of 0.4% Cu (Waterman and Hamilton, 1975). Au content averages about 0.11 ppm (Bazin and Hubner, 1969a), but more data are needed for further economic evaluation. Table 1 summarizes the mineralization and alteration zones. The presence of well-defined potassic, propylitic, zeolitic, phyllic and argillic alteration halos confirms the porphyry copper system of continental margin type and is inconsistent with a tectonomagmatic model of island arc or immature arc porphyry copper deposit. It became widely accepted that in porphyry copper system of continental margin type, for some reason the magmatic–meteoric water systems encroached one another and developed phyllic–argillic alteration (Sillitoe, 1994). Weathering and erosion have removed a significant percentage of the ore deposit, and the present cycle of erosion may have removed the important lithocappings and supergene ore blanket. Fig. 4 shows field examples of gossans at Sarcheshmeh.

4. Sampling and analysis

20 samples, each weighing 1 kg to 2 kg, were collected from the gossan and lithocapping at the Sarcheshmeh

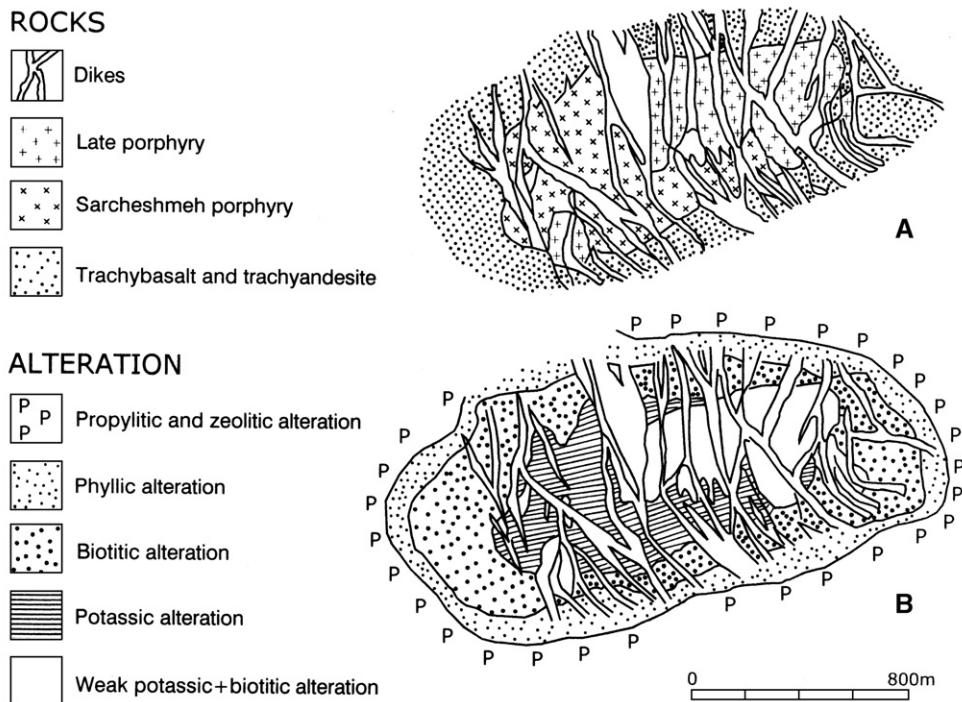


Fig. 3. Geological map of Sarcheshmeh porphyry copper mine (modified after Waterman and Hamilton, 1975; Jacobsen, 1975). A: rock units. B: alteration zones.

deposit. The sample interval was 0.5 to 1 km although, due to difficulty of access, it was not always possible to maintain a uniform sample spacing.

Based on the mineralogical studies, the gossan samples were classified as mature and immature gossans. The mature gossans are characterized by boxwork textures, abundant hematite, some goethite and jarosite and without any carbonate minerals. Some of these are siliceous and may have developed on quartz–chalcopyrite–molybdenite stringers. The immature gossans were found to retain some boxwork textures, but contain abundant carbonate minerals such as malachite, azurite and calcite with variable amounts of goethite, jarosite, hematite and chrysocolla.

Sample analysis was done at the Geological Survey of Iran. Copper, Ag, Mo, Zn, Pb, and other elements were determined by atomic absorption spectrophotometer after extraction with aqua regia (Ward et al., 1969; Price, 1972). Gold was determined by an atomic absorption method (Fletcher, 1981) after digestion and extraction with aqua regia and MIBK (methylisobutylketone), respectively. Two check samples were submitted to the Northwest Geological Research institute of CNNC in China. The precision for different elements ranges from $\pm 0.2\%$ to $\pm 1\%$ at a 95% confidence level. Water samples were analysed by titrimetric, atomic absorption and flame photometric methods.

5. Results

The average and variation in elemental concentrations for gossan samples, primary ore and supergene sulfide zone are shown in Table 2. The best means of presenting geochemical data is histograms and probability plots (Howarth, 1984; Garrett, 1989; Moon et al., 2006). This is indicated in Fig. 5. It is evident that mature and immature gossans are separated into two populations in Table 2 and Fig. 5. The mature gossans are enriched in Au (59.6 ppb), Mo (42.5 ppm) and Ag (2.6 ppm), but depleted in Cu (<36.7 ppm). The highest values for Au, Mo, and Ag in gossans are significantly higher than the mean values of the primary hypogene and supergene ore zones. Molybdenum and silver values are not significantly enriched or depleted compared to those of primary hypogene or supergene ore zones. The immature gossans contain high values of Cu (160.3 ppm), Zn (826.7 ppm) and Pb (88.6 ppm). The distribution of the elements in mature and immature gossans is similar to those gossans reported by Scott et al. (2001). According to Table 2, Au, Mo, and Ag in mature gossans are strongly enriched, relative to the primary hypogene and supergene ore zones. Copper is

Table 1
Mineralogical and geochemical characteristics of different zones at Sarcheshmeh porphyry copper mine

Zones	Mineralogy	Alteration	Geochemical signature
Gossan Lithocapping Leached zone	Hematite, goethite, jarosite, delafossite, gypsum and basaluminite	Argillic (kaolinite)	Mo and Au, are retained in gossans, whereas S and Cu are leached downward. Copper subsequently precipitated as supergene sulfides.
Sulfide Supergene Blanket Zone	Chalcocite \pm digenite \uparrow \downarrow Covellite	Argillic \pm sericitic	Soluble copper ion replaces pyrite as sooty or hard chalcocite.
Hypogene ore zone	Pyrite, chalcopyrite, molybdenite \pm primary chalcocite \pm bornite+ quartz stringers	Sericitic, potassic (k-silicate) and an outer propylitic and zeolitic in volcanic rocks	No supergene leaching but hydrothermal enriching of Cu, Mo and Au as stockworkings.
Fresh stock	Quartz monzonite \pm granodiorite \pm quartz diorite	Weak deuteric alteration	No significant leaching or enriching

particularly anomalous in the immature gossans, where it occurs as malachite and chrysocolla. It is noteworthy, that the highest value for copper (233 ppm) is 124 times lower than those of the primary hypogene and supergene ore zones. Zinc and lead values in immature gossans are higher than those of primary hypogene and supergene ore zones. Nickel and cobalt values in immature gossans are 5 to 6 times enriched, relative to those of primary hypogene and supergene ore zones. Other elements considered are not significantly enriched or depleted, relative to primary hypogene and supergene ore zones.

Water samples (Table 3) have elemental values much higher than the background values for surface waters and ground waters (Turekian, 1977). However, the Sarcheshmeh River contains higher values than the acceptable concentrations (Environmental Protection Agency, 1991). The pH values are acidic and also below acceptable levels, which should be >6.5 (United States Environmental Protection Agency, 1986).

The geochemistry of different elements in gossans will be discussed as the following:

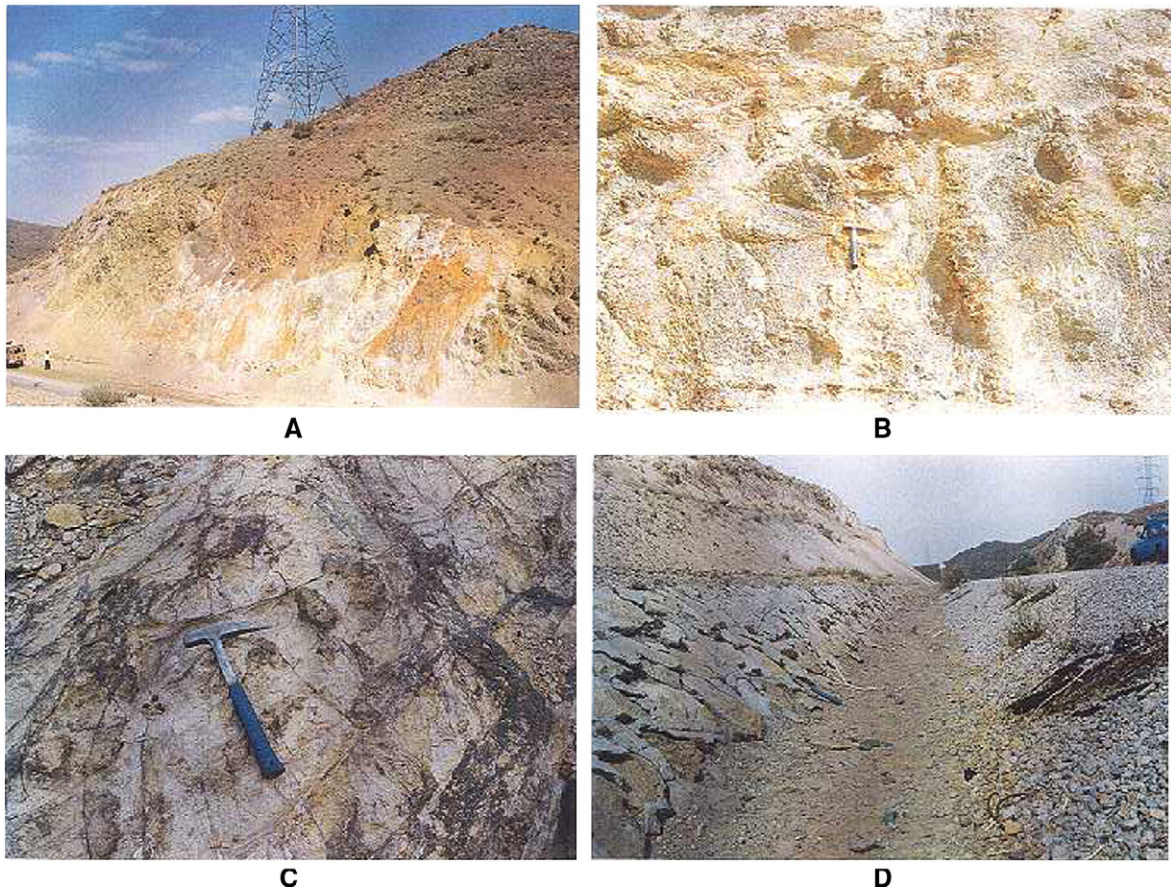


Fig. 4. Field aspects of gossan formation (Fig. 4A=jarositic gossans and leached zone close to Sarcheshmeh porphyry copper mine, Fig. 4B=Goethitic and jarositic gossans overlying stockworking and vein-type mineralization close to Sarcheshmeh porphyry copper mine, Fig. 4C=hematitic gossans overlying Sarcheshmeh porphyry copper ore. Fig. 4D=dismantling of road embankment as a result of ongoing gossan formation.

5.1. Gold

Gold values in gossan samples range from <20 to 200 ppb (Table 2 and Fig. 5A) with the higher values

occurring in the jarosite–goethite associated with the stockworks (Fig. 4B). The highest gold values of the immature gossans represent a significant enrichment, relative to the primary hypogene and supergene ore

Table 2

Average and range of metal content in gossan samples, supergene ore and hypogene ore around Sarcheshmeh porphyry copper deposit, Kerman

Elements	Mean (all gossans)	Range	Mature gossans	Immature gossans	Supergene ore	Hypogene ore
Au (ppb)	59	<20–200	59.6	35.4	110	100
Ag (ppm)	2.33	<1–4	2.6	0.9	16	4.3
Cu (ppm)	80	2–233	36.7	160.5	19900	8900
Mo (ppm)	68	<20–336	42.5	21.5	500	400
Pb (ppm)	64.6	7–204	50.5	88.6	400	50.4
Zn (ppm)	371.5	9–2993	89.4	826.7	800	96
Cr (ppm)	280	28–541	180.8	471.1	–	41
Cd (ppm)	3.2	1–8	2.6	4.1	–	–
Ni (ppm)	24.3	4–67	16.8	41.2	–	36
Co (ppm)	44	5–139	33.8	58.6	–	14
Mn (ppm)	548	8–2050	429.1	943.7	1089	155
S%	0.62	0.05–3.6	0.34	1.1	–	–
Fe%	5.21	0.17–12	3.89	6.9	5.99	6.8
Al%	8.8	1.2–22	8.2	9.35	8.22	8.1

zones, although the immature gossans are less likely to be enriched in gold (Table 2). It is probable that during weathering of gold bearing sulfides in porphyry ores, gold forms thiosulfate complexes (Nickel, 1979; Thornber, 1985). During intense oxidation, thiosulfates are oxidized to sulfate, precipitating gold (Thornber, 1985). Plyusnin et al. (1981), found that during sulfide oxidation, gold goes into solution, probably in the form of thiosulfate complexes. As thiosulfate is easily oxidized, the gold is not likely transported far. This is

consistent with the high values of gold associated with goethite and gypsum in some gossan samples.

5.2. Silver

Silver, although it does not show a pattern identical to that of Au (Fig. 5A and B), is anomalous in a few samples of jarositic and goethitic gossan, above the stockwork. The concentration factor for Ag is much higher than that of Au and is close to the typical grade for primary hypogene

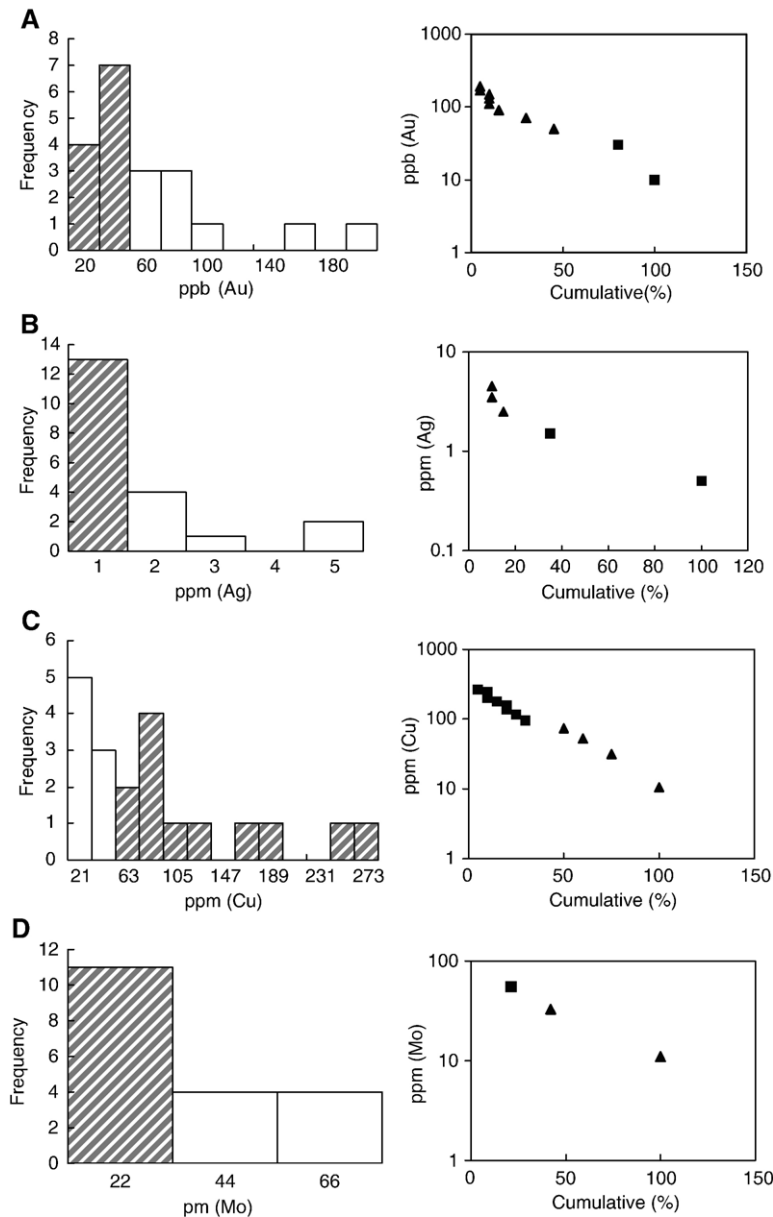


Fig. 5. Histograms and probability plots of different elements in gossan samples around Sarcheshmeh copper mine (Fig. 5A=Au, Fig. 5B=Ag, Fig. 5C=Mo, Fig. 5D=Cu, Fig. 5E=Pb, Fig. 5F=Zn, Fig. 5G=Cr, Fig. 5H=Cd, Fig. 5I=Ni, Fig. 5J=Co, Fig. 5K=Mn, Fig. 5L=Fe, Fig. 5M=Al).

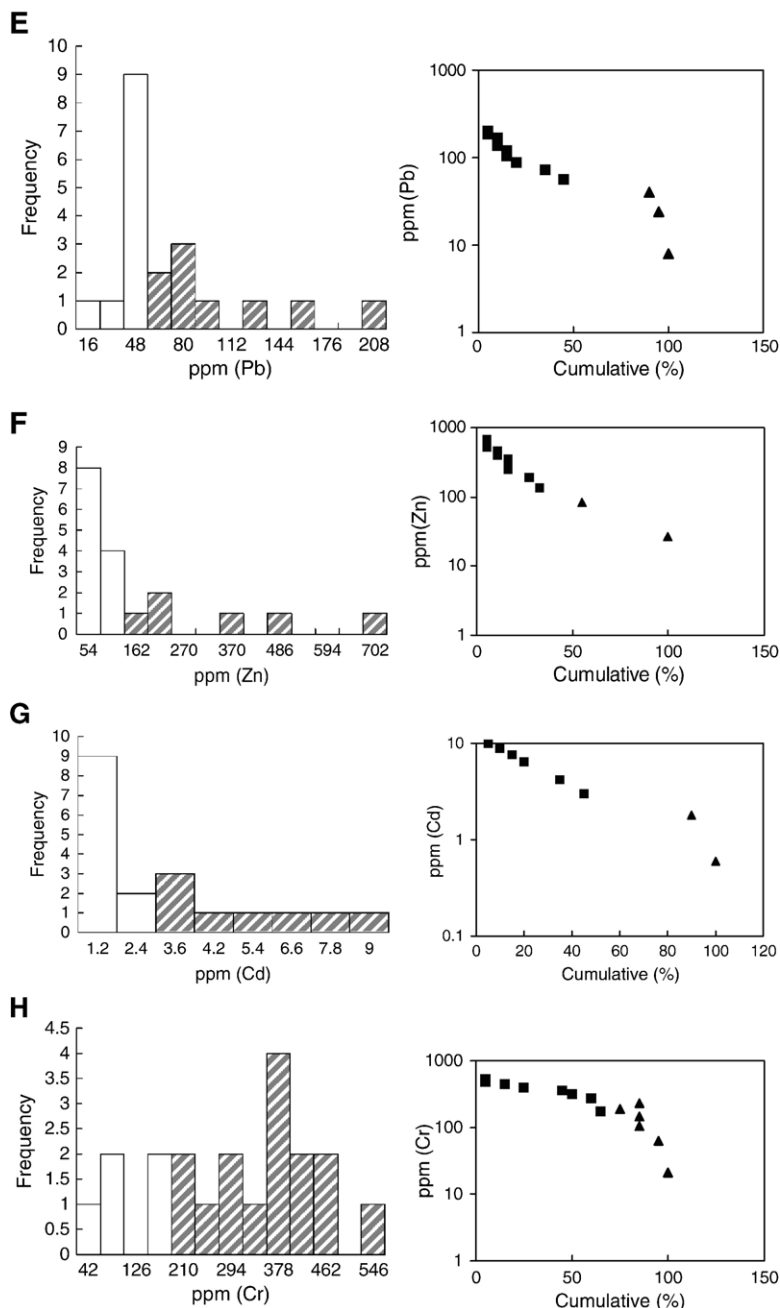


Fig. 5 (continued).

porphyry copper deposits (Table 2). It is possible that the higher concentration of Ag is related to the formation of native silver or chlorides (cerargyrite) similar to that which occur in the oxidized zone of Chilean porphyry copper deposits (Maynard, 1983). It is also likely that the Ag is in jarosite (Scott et al., 2001). Silver occurs in the structure of tetrahedrite, chalcopyrite, galena and bornite (Rankama and Sahama, 1950). During supergene processes, silver

will be released as sulfate and chloride ions and may retain in mature gossans (Rankama and Sahama, 1950).

5.3. Molybdenum

The Mo values range from <20 to 336 ppm (Table 2 and Fig. 5D). Most of the samples with anomalous Mo contents are associated with mature gossans and

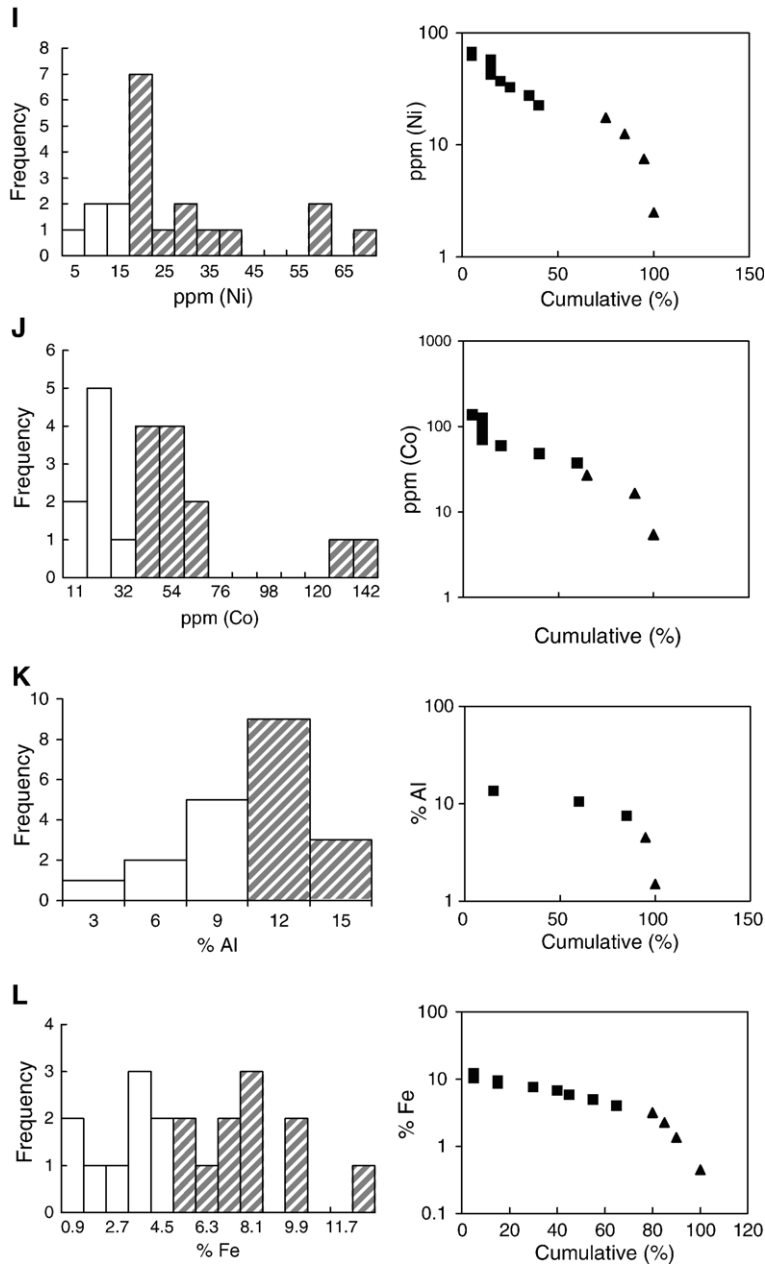


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brecciated–silicified jarosite and goethite, derived from the oxidation of quartz–chalcopyrite–molybdenite stringers. The highest Mo values in gossans are close to those of primary hypogene and supergene ore zones (Table 2). Molybdenite is a common mineral in the potassic–phyllic zone of the Sarcheshmeh porphyry copper mine. Upon weathering, it decomposes, releasing molybdenum into solution (Nickel, 1979). In its higher oxidation states, molybdenum has an intermediate ionic potential, hydrolyzes readily and probably is precipitated as

ferrimolybdate (Nickel, 1979; Levinson, 1980). The association of high molybdenum values in mature gossans may be related to the presence of the ferrimolybdate or probably ilsemannite (Nickel, 1979; Levinson, 1980). It is suggested that in supergene zones and soil environments, oxidized molybdenum occurs predominantly as the immobile acid molybdate anion and in the groundwater as the relatively mobile molybdate anion (Levinson, 1980). This indicates that in mature gossans, where Cu is strongly leached

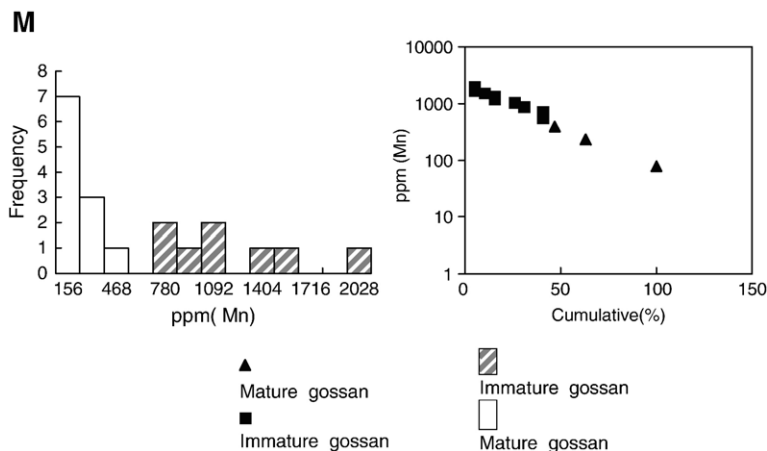


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molybdenum is retained in the gossan and could be used as a possible pathfinder for prospecting porphyry copper ores (Levinson, 1980).

5.4. Copper

The samples with anomalous Cu values are fewer than those of Au, Ag and Mo (Table 2 and Fig. 5C). Copper is highly soluble under acid conditions, and in mature gossans, the Cu values are commonly close or less than the background concentration. The low Cu values, which range from 2 to 233 ppm are associated with jarositic gossan, which forms under acidic conditions. Comparison of Cu values in gossans with either primary hypogene ore or supergene sulfide ore (Table 2), suggests that in most samples Cu is significantly leached. Copper is the one element which exhibits extensive supergene enrichment because of its high sulfate and low sulfide solubility (Levinson, 1980). In immature gossans, Cu occurs in malachite, chrysocolla, jarosite and goethite as reported by Atapour (2000) and Scott et al. (2001).

The average copper content in gossan samples of the Sarcheshmeh porphyry copper is about 80 ppm, but on average, 2% copper has been reported by Waterman and

Hamilton (1975), in the sulfide blanket zone of the Sarcheshmeh porphyry copper deposit. Similar low copper values of about 100 ppm copper in gossans overlying high-grade enriched ore has been reported at Ruth porphyry copper, Ely, Nevada by Rose et al. (1979).

In contrast to Cu, which is leached from the mature cappings overlying high-grade enriched zone of the Sarcheshmeh porphyry copper deposit, Mo, Au and Ag are enriched in the same mature gossan samples up to 336 ppm, 200 ppb and 6 ppm respectively (Table 2). Similar cases of Mo and Au enrichment in cappings and soils from which much of Cu is leached are reported in Puerto Rico (Learned and Boissen, 1973). From the following cases of the gossans overlying porphyry copper deposits, it is evident that molybdenum and gold play a significant exploration role in prospecting for the porphyry copper ores by sampling the mature gossans over the blind ore deposits (Tables 3 and 5).

5.5. Lead

Due to its low solubility, (Nickel, 1979) anomalous values of Pb are not frequent (Table 2 and Fig. 5E). The lead values range from 7 to 204 ppm. Thus, higher values may be related to the precipitation of Pb as

Table 3

Geochemical composition of springs and rivers draining the Sarcheshmeh porphyry copper deposit (all values are in ppb except for sulfate ion in ppm)

Location	Temperature	pH	SO ₄ ⁻²	Cu	Fe	Zn	Mn	Pb
Sarcheshmeh (river)	17	5.9	750	8000	3000	100	1000	80
Sarcheshmeh (spring)	18	6.4	320	200	200	32	140	30
Sarcheshmeh (Torshab) (spring)	17	6.3	310	300	300	52	180	50

plumbojarosite, plumbogummite or adsorption by manganese and iron oxides in malachite-rich immature goethitic gossans formed at near neutral to alkaline pH (Nickel, 1979; Thornber, 1985). The highest lead values occur in immature gossans and are enriched relative to the primary hypogene ore (Table 2), although rare occurrences of galena or other lead-bearing sulfide minerals have been reported in the hypogene zone at Sarcheshmeh porphyry copper mine (Aftabi and Atapour, 1997).

5.6. Zinc

Zinc values in gossan samples range from 9 to 2993 ppm (Table 2 and Fig. 5F). As the Zn is soluble at low pH, the anomalous values are related to the adsorption and precipitation at low pH in jarosite and goethite or in immature goethitic–malachitic gossans at high pH. Zinc values in mature gossans are close to that of primary hypogene ore zone. In immature gossans, Zn is almost ten orders of magnitude higher than the primary hypogene ore, but close to that of the supergene sulfide ore (Table 2). During gossan formation, zinc is released to the pore water by the oxidation of sphalerite or other zinc-bearing sulfide and silicate minerals. Zinc goes readily into solution as sulfate and chloride ions at low pH and precipitates in jarosite and goethite as reported by Rankama and Sahama (1950). Smith (1982), found that the solubility of zinc as chloride and sulfate ions is very high at low pH values, but did not give the exact values. Moncur et al. (2005), reported the presence of zinc in all of the Fe oxyhydroxides. Therefore, the occurrence of zinc in immature gossans at Sarcheshmeh porphyry copper mine indicates that the zinc precipitation may be due to coprecipitation or colloidal adsorption by Fe oxyhydroxides.

5.7. Chromium

Chromium does not show significant anomalous values in gossans. The values range from 28 to 541 ppm (Table 2 and Fig. 5H). The higher values of Cr in immature gossans are about ten times higher than that of the primary hypogene ore zone. However, the high values may be related to the dissolution of Cr replacing iron in pyrite and chalcopyrite of porphyry copper ores (Boyle, 1974). Another possibility is the release of chromium, replacing aluminum in the aluminosilicate minerals such as muscovite or sericite (Moncur et al., 2005) and biotite of potassic and phyllic alteration. The soluble chromium released by the dissolution of sulfide and aluminosilicate minerals at higher oxidation condi-

tion may coprecipitate with the goethitic gossans at high pH levels.

5.8. Cadmium

Cadmium values are anomalous and range from 1 to 8 ppm in gossan samples (Table 2 and Fig. 5G). The values in immature gossans are higher than those of the mature gossans (Table 2). Cd is more soluble than Zn and may show similar geochemical character to that of zinc at low pH (Thornber and Nickel, 1983; Thornber, 1985). At high pH and oxidizing conditions, Cd is adsorbed by immature goethitic gossans (Thornber, 1985; Scott et al., 2001). The absence of cadmium minerals at Sarcheshmeh porphyry copper mine, may indicate that the low values of Cd occur in the structure of sphalerite or other sulfide minerals as proposed by Boyle (1974).

5.9. Nickel

Nickel values in the gossan samples are low (Table 2 and Fig. 5I). High Ni values are related to immature gossans. The average values are very identical to that of primary hypogene ore zone (Table 2). Ni is likely to be a minor component in the structure of pyrite, chalcopyrite and other sulfides in porphyry copper ores (Boyle, 1974). So, these minerals do not release significant values of nickel during supergene processes. This may be related to the low normal concentration of the element in porphyry copper ores and high solubility and mobility of Ni at all pH (Jambor and Blowes, 1994) during gossan formation, which has no exploration significance at Sarcheshmeh porphyry copper ores.

5.10. Cobalt

Cobalt content ranges from 5 to 139 ppm (Table 2 and Fig. 5J). The pattern of cobalt values in mature and immature gossans is very similar to that of nickel. The average values in immature gossans are up to four orders of magnitude, relative to the primary hypogene ore zone. Although Co solubility is similar to that of nickel, it may be precipitated as stanniferite (Mason and Moore, 1982) and or adsorbed by manganese oxides and goethitic gossans (Nickel, 1979). The main source of cobalt is pyrite, which is very common at Sarcheshmeh porphyry copper mine (Boyle, 1974; Aftabi and Atapour, 1997). During supergene and weathering, Co could be incorporated in the structure of goethite (Moncur et al., 2005).

5.11. Manganese

Manganese content ranges from 8 to 2050 ppm (Table 2 and Fig. 5M). Mn sorbs other elements retained in the gossans and thus may be significant (Thornber, 1985). The Mn values in immature gossans are higher than those of mature gossans and primary hypogene ore zone by a factor of two and nine respectively (Table 2). This indicates that Mn oxyhydroxides precipitate at higher oxidation potential, which is favored at higher pH values (Thornber, 1985). This is indicated by the presence of wad and manganite in malachitic cappings at Sarcheshmeh porphyry copper mine. The primary sources of Mn are in the structure of pyrite and chalcopyrite in hydrothermal and porphyry ore deposits (Boyle, 1974).

5.12. Sulfur

Total sulfur values average about 1.46% and range from 0.5% to 3.6% in gossan samples. The sulfur values in immature gossans appear to be higher than that of the mature gossans (Table 2). This may be related to the presence of hydrous sulfate minerals such as brochantite and antlerite in immature gossans (Nickel, 1979; Thornber, 1985). The higher values could be related to the presence of jarosite and gypsum in mature gossans. The higher values of S in jarositic gossan are an association also reported for Au–Ag–Cu ores that have a gold–jarosite–goethite assemblage (Stoffregen, 1987).

5.13. Iron

The iron content of gossan samples ranges from 0.17% to 12% (Table 2 and Fig. 5L). The Fe values for immature gossans are similar to those of primary hypogene ore and somehow close to the supergene sulfide ore. Higher anomalous values are associated with goethitic and hematitic gossans formed at high pH level and oxidation state. Low values are correlated with jarositic gossans and leached cappings formed under very acidic conditions (Smith, 1982). Most of the elements are adsorbed or coprecipitated by iron oxides of the gossans. The main sources of iron at Sarcheshmeh porphyry copper mine are pyrite and chalcopyrite (Aftabi and Atapour, 1997). During oxidation of iron sulfides, iron precipitates as Fe oxyhydroxides, hematite, jarosite and goethite (Thornber, 1985; Atapour, 2000).

5.14. Aluminum

The average Al value in gossan samples is about 9% (Table 2 and Fig. 5K) and some high anomalous values

are associated with jarositic gossans and kaolinite in leached zones. Low values are related to the replacement of aluminum in goethitic gossans. Aluminum shows a rather similar values in immature gossans, mature gossans, primary hypogene ore and supergene sulfide ore (Table 2). This indicates that Al is readily hydrolyzed at neutral pH and commonly precipitates in the form of clay minerals, allophane, alunite and jarosite as proposed by Thornber (1985).

6. Discussion and implications of exploration, metallogenesis and environmental assessment

Gossans are oxidized caps that form due to sulfide oxidation, dissolution and precipitation of secondary minerals and pervasive rock leaching. Gossans have been geochemical targets for mineral exploration, and have led to the discovery of numerous major ore deposits. In spite of comprehensive investigations of gossan geochemistry, only minor attention has been given to the geochemical aspects of trace elements in gossans associated with porphyry copper ores.

6.1. Exploration considerations

To give the exploration significance of lithocappings, it is important to look at the distribution of gossans on the porphyry copper metallogenetic district at the Kerman province (Tables 3 and 5 and Fig. 6). It is evident from Table 5, that porphyry copper such as Miduk with hematitic gossans show reasonable sulfide supergene enrichment with an average of 1.5% Cu. Data on the chalcopyrite–pyrite or chalcocite–pyrite ratios at Sarcheshmeh mine are not available. According to Alpers and Brimhall (1989) and Waterman and Hamilton (1975), the chalcopyrite–pyrite ratios in hypogene ore is almost equivalent to that of chalcocite–pyrite ratios of supergene ore. Based on microscopic studies and geochemical analyses of some samples from hypogene and supergene ores in the altered volcanic rocks, the chalcopyrite–pyrite or chalcocite–pyrite ratios, supergene copper grade, hypogene copper grade and related cappings are shown in Table 4. Accordingly, the supergene copper grade increases almost more than twice that of hypogene ore from propylitized to sericitized trachybasalt. In this relation, the possible pyrite–chalcopyrite ratios in hypogene ore for different porphyry copper ores are indicated in Table 5. At Sarcheshmeh, the supergene blanket beneath the hematitic cappings may contain on average up to 2% Cu (Waterman and Hamilton, 1975). In contrast to Sarcheshmeh and Miduk, at Darrehzar the sulfide supergene blanket below the malachite-rich

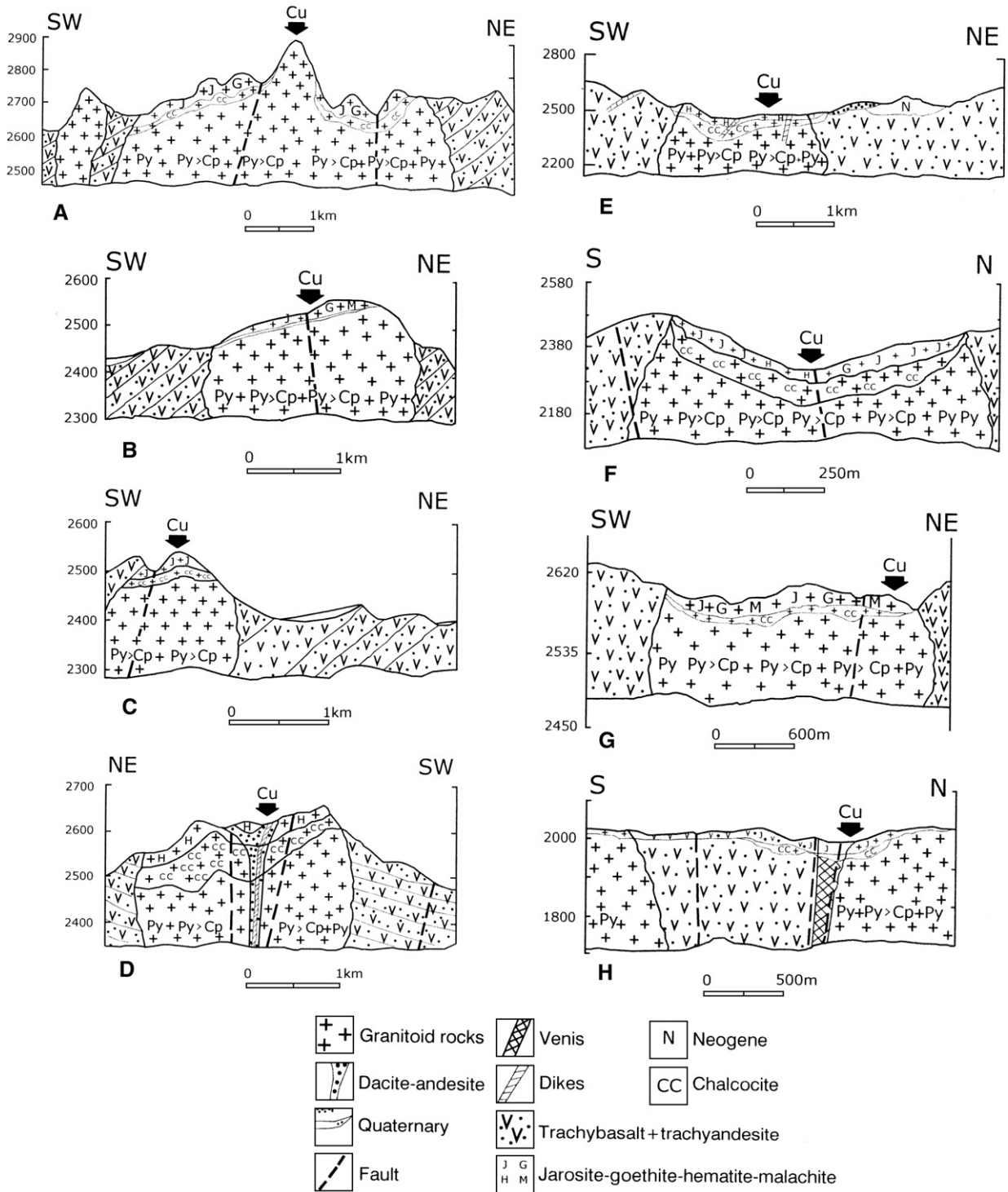


Fig. 6. The possible simplified schematic cross sections in different porphyry copper mineralization, showing the relationship between hypogene zone, gossan mineralogy and supergene sulfide-enriched zone. Fig. 6A=Kader, Fig. 6B=Gode-Kolvari, Fig. 6C=Ijo, Fig. 6D=Miduk, Fig. 6E=Sarcheshmeh, (volcanic rocks dipping northeast), Fig. 6F=Darrehzar, (volcanic rocks dipping north-northwest), Fig. 6G=Dehsiah, (volcanic rocks dipping northeast), Fig. 6H=Chahargonbad, (volcanic rocks dipping north-northeast). Py=pyrite, Cp=chalcocyanite, J=jarosite, G=goethite, H=hematite, M=malachite. The scale of zones in cross sections are approximate.

immature jarositic–goethitic blanket contains about 0.8% Cu. Geochemically, most of the mature lithocappings are anomalous for Mo and Au in particular those of Darrehzar and Chahargonbad.

There may be several important factors for the diversity of jarositic, hematitic and goethitic cappings overlying the Iranian porphyry copper deposits, which could be interpreted as the following:

1–In porphyry Cu deposits dominated by pyrite and chalcopyrite, leaching is well developed with most of the leached copper going to the formation of the sulfide enrichment blanket, beneath an hematitic gossan (Sarcheshmeh and Miduk porphyry copper deposits). This occurs in the ore shell, which lies at the potassic–phyllic alteration boundary, containing 5–10% pyrite and pyrite–chalcopyrite ratio from 1.5 to 2.5 as mentioned by Lowell and Guilbert (1970) and Aftabi and Atapour (1997). The main ore minerals in this zone at Sarcheshmeh porphyry copper mine are stockwork and veinlets of chalcopyrite, pyrite, molybdenite and bornite. Therefore, much of the deep supergene leaching and enrichment of Cu in Sarcheshmeh and Miduk porphyry copper deposits may be related to the high acid generating and low buffering capacities of the quartz–sericite alteration, superimposed on the earlier potassic alteration developed in intensely brecciated and faulted zones.

Alpers and Brimhall (1989), considered phyllic (sericitic) alteration as a nonreactive gangue that develops hematitic cappings. In nonreactive phyllic alteration similar to the Sarcheshmeh copper mine, the oxidation of sulfide minerals with pyrite–chalcopyrite ratios about 1.5 is observed to form only hematite. In such gossans, pH stays low enough so that cupric hydroxyl-sulfates such as antlerite and brochantite do not form, instead maximum possible amount of copper ion is mobilized downward to the supergene sulfide zone.

2–Porphyry coppers with high ratio of pyrite to chalcopyrite between 4 to 10 (Alpers and Brimhall, 1989), could develop immature goethitic, jarositic and malachitic cappings with a very weak or even no important sulfide enrichment blanket zone. This would be the case for God-e-Kolvari. In this case, the mineralized zone occurs in potassic alteration, having low sulfide content, but molybdenite higher than anywhere else in the deposit (Lowell and Guilbert, 1970; Aftabi and Anvari, 2006). Mineralization occurs as disseminated pyrite (up to 5%), chalcopyrite, and molybdenite. In this type of alteration, with increasing pyrite–chalcopyrite ratios from 4 to 10, a systematic change in mineralogy from hematite to goethite and finally jarosite will occur.

3–Porphyry coppers with much higher ratio of pyrite to chalcopyrite greater than 10 (Alpers and Brimhall, 1989), occur in pyrite shell of some porphyry copper ores with argillic, phyllic and/or propylitic alteration zones (Lowell and Guilbert, 1970). Sulfide mineralization forms both as veins and disseminations with up to 15% pyrite and develops jarositic cappings overlying a thin sulfide enrichment blanket. During weathering of these deposits, nearly all ferric hydroxide occurs as jarosite with minor goethite. According to Sillitoe and Mckee (1996), the hematitic cappings developed on phyllic alteration zone will have a better sulfide enrichment blanket zone than the goethitic–jarositic ones formed over argillic and potassic or propylitic alterations.

The high pyrite–chalcopyrite ratios in most of the porphyry copper ores of the world may be related to the subducted pyrite-rich banded iron formations or massive sulfide deposits of the precursor oceanic crust. The metallogenic significance of this process has not been understood. However, it is proposed (Aftabi and Anvari, 2006) that most of the pyrite-rich porphyry ores and iron oxides Cu–Au deposits such as El Laco (Chile), Qaleh-

Table 4

Average chalcopyrite–pyrite or chalcocite–pyrite ratios, hypogene and supergene copper-grade at Sarcheshmeh porphyry copper deposit (Waterman and Hamilton, 1975 and this study)

Host rocks and alteration halo	Chalcopyrite–Pyrite or chalcocite–pyrite ratios	Average hypogene–copper grade (%)	Average supergene–copper grade (%)	Cappings
Propylitized trachybasalt	0.3	0.4	0.78	Jarosite > goethite > hematite
Sericitized trachybasalt	0.4	0.65	1.25	Hematite > jarosite > goethite
Sericitized ± biotized trachybasalt	0.6	1.2	1.98	Hematite > goethite
Sericitized ± biotized trachybasalt	3	1.89	3.4	Hematite
Sericitized quartz monzonite	0.9	0.89	1.78	Hematite > goethite
Sericitized ± biotized quartz monzonite	1.4	1.2	2.4	Hematite

Table 5

Mineralogical, pyrite–chalcopyrite ratios and geochemical characteristics of gossans overlying some important porphyry copper deposits of Iranian continental volcano–plutonic magmatic arc (Aftabi and Atapour, 2000; Soleymani, 1999; Anonymous, 1973, and this study)

Porphyry deposits	Volcano–plutonic rocks	Hypogene mineralization	Supergene sulfide mineralization	Gossan and leached zone (average meters)	Geochemical signature (average for all gossans)
Kader	Trachybasalt trachyandesite diiorite, quartz diiorite	Py, Cp, Po, \pm Mol \pm Sp Cu=0.1% Py/Cp=12	Chalcocite \pm covellite Cu=0.2%	(30 m) jarosite> goethite> hematite> malachite	Mo=8 ppm Au=20 ppb
Ijo	Trachybasalt, trachyandesite diiorite, quartz diiorite	Py, Cp, Po Mol, Bn Cu=0.4% Py/Cp=3	Chalcocite \pm covellite native copper Cu=0.8%	(20 m) jarosite> hematite> malachite> chrysocolla> azurite	Mo=30 ppm Au=58 ppb
Gode–e Kolvari	Trachybasalt trachyandesite diiorite, quartz diiorite \pm granodiorite	Py, Cp, Mol Cu=0.1% Py/Cp=12	Weak or non existence Cu=0.2%	(10 m) goethite> jarosite> hematite> malachite> azurite>cuprite	Mo=40 ppm Au=32 ppb
Miduk	Trachybasalt trachyandesite dacite–andesite diiorite, quartz diiorite	Py, Cp, Mol Cu=0.1–0.4% Py/Cp=3–12	Chalcocite covellite Cu=1–3%	(25 m) hematite> goethite> malachite> azurite	Mo=82 ppm Au=78 ppb
Sarcheshmeh	Trachybasalt, trachyandesite dacite–andesite quartz diiorite, quartz monzonite granodiorite	Py, Cp, Mol Cu =0.89% Py/Cp=1.5	Chalcocite, digenite Covellite Cu=1.99%	(26 m) hematite>> goethite>jarosite	Mo=68 ppm Au=59 ppb
Darrehzar	Trachybasalt trachyandesite dacite–andesite diiorite, quartz diiorite	Py, Cp, Mol Bn, Po, Tet, En, Sp, Cu=0.3% Py/Cp=4.5	Chalcocite \pm covellite Cu=0.6%	(30 m) goethite> hemalite> jarosite> malachite> azurite> chrysocolla	Mo=54 ppm Au=68 ppb
Dehsiahan	Trachybasalt trachyandesite monzonite quartz monzonite, monzogranite \pm granodiorite	Py, Cp, Mol, Bn, Po, Sp, Ga, Tet Cu= 0.05 Py/Cp=24	Chalcocite \pm covellite \pm Bornite Cu=0.1%	(10 m) goethite> hematite> malachite> azurite	Mo=10 ppm Au=24 ppb
Chahargonbad porphyry- vein type	Trachybasalt trachyandesite quartz diiorite granodiorite	Py, Cp, Sp, Ga, Tet, Mol, Cu= 0.44–1.67% Py/Cp=0.4–3.5	chalcocite \pm Covellite Cu=0.8%– 3.2%	(14 m) goethite> hematite>>jarosite> malachite>chrysocolla	Mo=56 ppm Au=110 ppb

Py=pyrite, Cp=chalcopyrite, po=pyrrhotite, Mol=molybdenite, Bn=bornite, Tet=tetrahedrite, En=enargite, Sp=sphalerite, Ga=galena.

Zari (Iran) and other iron–copper ores associated with the Iranian porphyry copper belt could be considered as porphyry-vein iron–copper ores, rather than a simple model of iron-oxide Cu–Au (IOCG) ores. The age, continental arc settings, potassic, phyllic and argillic alteration zones in IOCG ores are very similar to those

of typical porphyry copper deposits as reported by Aftabi and Anvari (2006).

4–Reactive or nonreactive host rocks, alteration halo and minerals may play another important role for the diversity of lithocappings. In this case, with a low pyrite to chalcopyrite ratio in hypogene zone, the sulfide

enrichment zone may not develop economically, if the host rocks are reactive. Reactive cappings include feldspars, chlorite, mafic minerals (biotite), carbonates and montmorillonite (Rose et al., 1979) and nonreactive rocks are composed of quartz, chalcedony, kaolinite, and alunite (Rose et al., 1979; Langmuir, 1997). For example, alteration zones containing pyrite, chalcopryrite, feldspars, chlorite, biotite, carbonates and montmorillonite during gossan formation, due to low amounts of pyrite and the presence of carbonates increase the pH of most of the sulfuric acid solution produced during weathering. Thus, in the presence of carbonate minerals, cupriferous solutions react with carbonates to precipitate copper as malachite, chrysocolla, azurite, cuprite or copper sulfate minerals such as brochantite and antlerite and no economic enrichment zones may develop. If the hypogene zone contains moderate contents of pyrite and small amount of reactive minerals or nonreactive minerals, most of the soluble copper sulfate is leached downwards, replacing pre-existing pyrite and chalcopryrite, forming a thick enrichment blanket of sooty or hard chalcocite. In case of abundant pyrite and chalcopryrite and nonreactive gangue or host rocks almost all soluble Cu is leached to leave even less than the background values in cappings overlying high-grade porphyry copper enriched ores. This case is reported by Learned and Boissen (1973) at Ruth porphyry copper deposit, Ely, Nevada. At Sarcheshmeh the presence of abundant pyrite, chalcopryrite, and molybdenite, associated with abundant nonreactive quartz–sericite–stringers or quartz stockworkings have produced two economic sulfide enrichment zones in eastern and western part of the ore zone. These exactly coincide with the two eastern and western phyllic ore shell zones. The average Cu values in gossan samples is about 80 ppm and thus, more Cu is leached downward, than retained in the cappings. Therefore, the economic sulfide enrichment zones were possibly developed on the quartz–stringers sericitic–pyrite shell superimposed on the earlier K-silicate or potassic alteration at Sarcheshmeh porphyry copper deposit. The supergene sulfide zone at Sarcheshmeh averages 37 m and contains sooty chalcocite and chalcocite replacing pre-existing pyrite and chalcopryrite ± bornite. It is thin over low-grade hypogene ore and thickens over high-grade hypogene ore (Waterman and Hamilton, 1975).

5–Complex structural features such as large faults, shear zones, and breccia zones are associated with several Iranian porphyry copper deposits in particular Kader. In this case, porphyry copper deposits with jarositic–goethitic cappings might have developed their sulfide enrichment ore zones as a distal supergene

blanket far from the proximal hypogene zones through the plumbing fault systems. To illustrate the exploration and metallogenic aspects of the Iranian porphyry copper system, the idealized profiles of hypogene mineralization, supergene and gossans over typical porphyry copper deposits are shown in Fig. 6.

6.2. Environmental considerations

The significance of gossan formation, mine drainage and natural drainage waters as well as the solution and precipitation processes of metals and minerals, has been a major focus of environmental investigation (Jambor and Blowes, 1994; Plumlee et al., 1994). Table 4 shows the results of chemical composition of rivers and springs draining from the Sarcheshmeh porphyry copper deposit. The high values for sulfate ion, copper, iron, manganese, zinc and lead classifies the Sarcheshmeh River as a very polluted drainage. Sahraei Parizi and Karimi Nasab (2001), considered the Sarcheshmeh River as a contaminated drainage. The river is drained from the eastern part of the Sarcheshmeh ore body, reacting with copper rich zones and possibly pyrite-rich dumped tailings. Some of the ongoing gossan formation disturbs and dismantles embankment of the roads (Fig. 4D). The dynamics of acid rock drainage (ARD) and ongoing gossan formation associated with active springs have been observed in many places around porphyry copper ores in the area. The deposition of basaluminite, jarosite and goethite is obvious around these springs. Ferricrete is unconsolidated surficial material cemented by Fe oxyhydroxides in water drainages (creeks) or slopes downstream of weathering sulfide-rich rocks and pyrite-rich dumped tailings around the Sarcheshmeh mining area. Also, ongoing gossan formation is a feature commonly noted on acid generating pyrite-rich waste dumps and tailings of the area. Some of these might form immature copper carbonates or oxides cappings with minor supergene sulfide ores, which could become economic in the future as proposed by Downing and Giroux (1993). Some of the embankments of roads are weathered and dismantled due to the ongoing gossan formation (Fig. 4D). This may be related to the near neutral pH values of mine and natural drainage and or springs draining from the porphyry copper ores. As a result of pH decrease, related to the downstream from springs, the liberated waters into the environments can still generate acid, damaging the geoenvironmental cycle as reported by Garrells and Christ (1965). Therefore, for rivers and springs with even pH levels near neutral around the Iranian porphyry copper deposits, there may be a risk of

acid rock drainage (ARD) that could damage the environmental ecosystems. When such acidic streams encroach non-acidic drainages, Fe oxides are found to be precipitated and gravels or creeks to become stained in some places along roads (Fig. 4D). Darkening and chlorosis of leaves in some plants around the Sarcheshmeh, Dehsiahan and Darrehzar mining areas may be related to the high concentration of iron, copper and acid rock drainage (ARD) in soils and sediments developed on immature gossans. Similar effects of high iron and copper values in plants have been reported by Brooks (1972).

7. Conclusions

The gossans around the Sarcheshmeh porphyry copper deposit have the following features:

1. Mature surficial gossans are composed of abundant hematite with some goethite, jarosite and possibly alunite and are enriched in Au (59.6 ppb), Ag (2.6 ppm) and Mo (42.5 ppm), but depleted in Cu (<36.7 ppm), Zn (<84.4 ppm) and Pb (<50.5 ppm).
2. Immature surficial gossans include Fe oxides associated with abundant malachite, azurite and chrysocolla and are enriched in Cu (160.5 ppm), Zn (826.7 ppm) and Pb (88.6 ppm).
3. Au and Mo values in mature gossans of many Iranian porphyry copper ores are anomalous and could be used as a possible regional geochemical and metallogenic exploration guide for porphyry copper ores.
4. Mature hematitic gossans developed over nonreactive phyllic alteration zone with pyrite–chalcopyrite ratios about 1.5, containing quartz–chalcopyrite–molybdenite stringers are enriched in Mo, but depleted in Cu and may give the indication for a high-grade supergene chalcocite blanket zone of the Sarcheshmeh porphyry copper ores, averaging 1.99% Cu, more than twice than that of 0.89% Cu in the hypogene ore.
5. Immature malachite–jarosite- and goethite-bearing gossans probably indicate non-economic or weak supergene sulfide-enriched ores.
6. Immature malachitic gossans may not always be associated with an enriched supergene blanket zones at all.
7. Hypogene porphyry copper ores with nonreactive alteration haloes (quartz–sericite stringers) and hematitic gossans are the most promising porphyry copper ores.
8. Jarosite and malachite-bearing gossans are commonly developed over the chalcopyrite-poor, but pyritic shell of porphyry copper ores with pyrite–chalcopyrite ratios greater than 10 and generate acid rock drainage (ARD) that may impose serious environmental impacts on the ecosystems due to the acid generation of natural drainage systems of rivers or springs.
9. Regional metallogenic ore districts may be masked by mature hematitic gossans overlying the promising supergene-enriched zones and drilling targets may be oriented where these hematitic gossans are well developed.
10. Porphyry copper ores with steep faults and shear zones (Kader) may perform extended percolation and migration of supergene solutions, thus forming distal supergene blanket- enriched zones.
11. Most of the porphyry copper ores have developed gossan zones, supergene sulfide zones and acid rock drainage (ARD), which may continue into the future.
12. Natural drainage water systems and springs with even near neutral pH and high base metal values disturb the geoenvironmental cycle, giving rise to a geochemical kill zone.

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