Hydrothermal Alteration in Porphyry Cu-Mo-Au Mineralizations of the Chagai Arc, Balochistan, Pakistan

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Abstract. Subduction-related east-west trending Chagai Arc located in the western part of Pakistan. This arc is the western extension of Tethyan Magmatic Belt which is about 5000 km long and extends from central Europe, Turkey, Iran, and Pakistan. During the last four decades, several porphyry copper settings were reported from the Chagai Arc. Seven more famous occurrences are selected for the present study owing to more detailed work carried out on them. From west to east these deposits include Saindak, Reko Diq (formerly known as Koh-e-Dalil), Humai, Missi, Durbanchah, Dasht-e-Kain and Ziarat Pir Sultan. Hydrothermal alterations in the porphyry copper setting of Chagai Arc are mostly associated with tonalite porphyry stocks, except Durbanchah and Humai prospects which are hosted in dacite porphyry stocks, whereas Missi Prospect occurs in a granodiorite batholith. The alteration is normally developed in a concentric zonal pattern as observed in the majority of the world deposits, except that absence of a regular argillic and peripheral zone. In most of the occurrences the potassium silicate alteration zone (K-alteration zone) occurs usually within the intrusive porphyry stock, but in Saindak and Reko Diq deposit, some of the adjacent wall-rock sediments, and in Durbanchah setting the microdioritic country rock, has also undergone the K-alteration. Quartz sericitic or phyllic alterations zones are developed in all the occurrences as continuous or discontinuous haloes around the K-alteration zone except in Durbanchah prospect. In Humai prospect an advanced argillic alteration zone is developed around the K-alteration zone. Propylitic alteration has also developed in almost all settings and generally encircles the quartz sericitic alteration. The oxide mineralization is generally represented by goethitic jarosite, hematitic limonites and malachite, with minor pitch limonite, chrysocolla, neotocite, brochantite and molybdate. Hygrope mineralization is represented by pyrite, chalcopyrite and minor bornite. A regular supergene sulfide enrichment is only reported from the Reko Diq deposit and represented by chalcocite and covellite in other deposits restricted incipient type supergene sulfide enrichment is encountered. In terms of ore reserves the Riko Diq deposit is on the top with 2,200 million tons of copper followed by Saindak with 412 million tons and Dasht-e-Kain 350 million tons. Grade wise Reko Diq Deposit is again on the top with 0.53% Cu, 0.01% Mo and 0.3 g/t Au, followed by Saindak with 0.4% Cu, 0.015% Mo and 0.35 g/t Au. Dasht-e-Kain deposit contains 0.35% Cu and 0.015% Mo. Gold has not been reported from the Dasht-e-Kain deposit. From other deposits of the Chagai Arc ore reserves and grade are not reported so far.

Keywords: Hydrothermal Alteration, Porphyry Copper, Tethyan Magmatic Belt, Chagai Arc, Balochistan

1. Introduction

The Chagai Arc located in the western part of Pakistan. This arc is the western extension of the Tethyan Magmatic Belt which is about 5000 km long that extends from central Europe, Turkey, Iran, and Pakistan. During the last four decades, several porphyry copper settings were reported from the Chagai Arc. The main part of the Arc present in the western part of Pakistan. A small component of the arc terrain extends northwards in Afghanistan and towards the west in Iran. The Chagai Arc trends in EW direction, it is around 500 km long and 140 km wide. It is terminated by the Chaman and
Harirud Fault Zones in the east and west respectively and convex towards the south, figure 1 and 2. Several porphyry copper occurrences have been found in the arc, out of which, seven are selected for the present study because relatively more geologic work has been done on them. These include well known Saindak porphyry copper deposit and lesser-known porphyry copper prospects of Reko Diq (formerly known As Koh-e-Dalil), Durbanchah, Hunai, Ziarat Pir Sultan, Missi and Dasht-e-Kain. The eastern part of the Chagai belt between the Chagai Hills and Siah Koh is covered by Recent and Sub-recent alluvial deposits and may also be hosting a few hitherto unknown porphyry prospects [1].

The hydrothermal alteration is generally developed in all the porphyry copper systems and serves as an important tool for the recognition of porphyry copper mineralization in the area [2]. Three hydrothermally altered zones, namely potassium silicate, quartz sericitic (phyllic) and propylitic, have been identified in almost all the porphyry copper occurrences in the region. However, argillic, advanced argillic and a regular peripheral zone as described by Lowell and Giulbert [2], are not developed anywhere in the Chagai Arc. In this paper, an attempt has been made to describe the alteration zones in various deposits/prospects of the Chagai Arc.

2. Regional Geology
The current geotectonic setting of the Chagai Arc is represented by a Quaternary subduction zone dipping towards the north, an active Makran accretionary zone that is followed by the Chagai-Raskoh magmatic arc and Afghan Block, shown in figure 1. Apparently, this subduction zone setting reflects a continental margin typesetting. The majority of the preceding investigations have preferred this tectonic setting about the origin not only for the Quaternary volcanics but also for the older volcanic rocks up to Late Cretaceous [3, 4, 5, 6, 7, 8, 9, 10]. Siddiqui [11, 12], and Siddiqui et al. [13, 14, 15, 16, 17, 18, 19, 20], have opposed this perspective and documented an oceanic island arc setting for the Late Cretaceous to Paleocene volcanics of the Chagai Arc, transitional character for Eocene and continental margin or Andean type settings for Oligocene to Pleistocene volcanics.

The oldest rock suite developed in the Chagai Arc is a submarine stratified volcanic and volcanoclastic, suite known as Sinjrani Volcanic [21], which is Late Cretaceous in age and is composed mainly of andesitic flows, agglomerates, volcanic conglomerate, tuffs and subordinate amounts of limestone, shale, and sandstone. The total thickness of the Group is about 10,000 m [7], and it has been intruded by the Chagai intrusions [21], which range in size from cupolas and stocks to batholiths and include granite, quartz-monzonite, granodiorite, monzonite, diorite, quartz diorite, and gabbro. These intrusions are as old as Pre-Late Cretaceous [21], and as young as Lower Miocene [22, 23].

Multiple episodes continued in pulsatory fashion were responsible for the emplacement of the volcanic and plutonic rocks of the region [7]. Siddiqui et al. [15, 19], has proposed a link between calc-alkaline volcanism during the Oligocene to Miocene with the formation of porphyry copper deposits in the Chagai Arc.

The Chagai Arc has got tremendous importance for its economic mineral potential. The magmatic rocks are intimately associated with deposits of copper, and iron including the porphyry copper, skarn copper and/or iron, manto-type copper, vein-type copper and volcanogenic sulfur and volcanogenic-stratifiform iron. In addition, zinc, copper and silver-rich Kuroko type sulphide deposits have also been reported.
Figure 1. Geological map of the Chagai-Raskoh Arc terrain and adjoining area showing porphyry copper deposits, after Siddiqui et al. [19].
Figure 2. Schematic cross-section (not to scale) across the Chagai-Raskah Arc terrain and adjoining area, after Siddiqui, [12].
3. Hydrothermal Alteration

Hydrothermal alteration in each of the porphyry copper occurrences is developed in a concentric manner. In each occurrence, the potassium silicate alteration zone (K-zone) occurs in the center, followed outwards by the quartz sericitic and the propylitic alteration zones, but none of the occurrences have regular argillic and peripheral zones proposed by Lowell and Guilbert [2], figure 3. The zones developed are discussed in the following paragraphs.

3.1. Potassium Silicate Alteration Zone (K-zone)

This type of alteration zones occurs centrally within each intrusive porphyry ore prospect; but at Saindak and Reko Diq, some of the adjacent wall rock sediments and, at Durban Chah, microdioritic wall rocks have also undergone such alteration [23, 24], table 1.

At Saindak, K-alteration is mainly associated with three comagmatic tonalite porphyry stocks, named respectively, north, south and east stocks according to their positions. Potassium silicate alteration at Saindak is characterized by the biotite, K-feldspar, quartz anhydrite, epidote, chlorite, tourmaline, pyrite, chalcopyrite, magnetite and minor molybdenite. Biotite occurs disseminated or as replacement of primary hornblende, in veinlets with other minerals and alone on partings. The southern body has a quartz-magnetite type of K-alteration in the center whereas, in the eastern ore body, K-alteration is superimposed by retrograded quartz sericitic alteration [22].

At Reko Diq, potassium silicate alteration is generally associated with five tonalite porphyry stocks, some neighboring host-rock sediments have also undergone the same alteration, K-alteration. In this prospect, is characterized by the biotite, K-feldspar, quartz, tourmaline, magnetite, pyrite, chalcopyrite and minor molybdenite. The main eastern body is centered by quartz-magnetite type of K-alteration, and retrograded quartz sericitic alteration has developed towards its eastern boundary. At Reko Diq deposit, the K-zone is partially destroyed by the emplacement of post-mineralization dacite porphyry intrusions [25, 26]. At Humai prospect, potassium silicate alteration is restricted to a dacite porphyry stock and is represented by chlorite after biotite, quartz, magnetite and minor pyrite and chalcopyrite [5].

The largely concealed Durban Chah porphyry copper prospect has a small outcrop of K-alteration, restricted in a marginal part of alluvial depression bordered by andesites of Sinjani Volcanic Group. Potassium Silicate alteration at this prospect is associated with a dacite porphyry stock and is represented by biotite, K-feldspar, quartz, chlorite, and minor pyrite, chalcopyrite and molybdenite [27, 28].

At Ziarat Pir Sultan, the alteration is mainly associated with two tonalite porphyry stocks and K-alteration is exhibited by biotite and quartz with minor pyrite, chalcopyrite and molybdenite [28]. At Missi prospect, potassium silicate alteration zone has not been observed on the surface, but it is expected to occur below the quartz sericitic zone [5].

At Dashte Kain, the alteration is mainly associated with two tonalite porphyry stocks, named eastern and western stocks by position. The later stock is invaded by an intrusive breccia pipe. K-alteration is centered in each stock and is characterized by biotite, K-feldspar, anhydrite, chlorite, carbonate, sericite, and kaolinite with minor magnetite, pyrite, chalcopyrite, pyrrhotite, molybdenite, bornite, and enargite. A considerable part of the K-zone of the western stock has been superimposed by retrograded quartz sericitic alteration [29].

3.2. Quartz Sericitic or Phyllic Alteration Zone

The quartz sericitic alteration zone has developed as continuous and/or discontinuous halos around potassium silicate alteration zone in all the porphyry Cu settings of the Chagai belt, except at Durban Chah where it has not been encountered, whereas at Humai an advanced argillic zone has been found around K-zone, table 1.
Quartz sericitic alteration at Saindak ranges from pervasive to veinlet-controlled and comprises quartz, sericite, anhydrite, pyrite and minor chalcopyrite and molybdenite. Pyrite is locally abundant and may attain more than 10% by volume of the rock [22]. At Reko Diq deposit, quartz sericitic alteration is partially concealed by Recent alluvial deposits in the middle of a deeply eroded stratovolcano. The sericitization is also partially superimposed and surrounded by propylitized volcanic rocks. The characteristic mineral assemblages of the prospect are quartz, sericite, pyrite, and chlorite [25, 26, 30]. At Humai prospect, an advanced argillic alteration zone is developed around K-zone instead of quartz sericitic alteration, which is represented by alunite, quartz, sulphur, and pyrite [5]. There is no quartz sericitic alteration zone at Duroanchah, at least on the surface and K-alteration is directly surrounded by propylitic zone. At Ziarat Pir Sultan, quartz sericitic alteration occurs as a discontinuous halo around K-zone and is exhibited mainly by sericite, quartz, and pyrite [28]. Quartz sericitic alteration at Missi prospect is widely developed and characterized by sericite, quartz, and pyrite with minor chalcopyrite and molybdenite. At Dashte Kain, quartz sericitic alteration zone partly encircles the K-alteration and is represented by quartz, sericite, and pyrite. At places, this alteration is also superimposed over a hydrothermal intrusion breccia. The northern portion of quartz sericitic alteration at Dasht-e-Kain is alluvium covered.
Table 1. Different porphyry Cu-Mo-Au settings of the Chagai Arc, Balochistan, Pakistan: [5, 15, 22, 23, 25, 27, 30, 31, 49].

| NAME OF PORPHYRY COPPER SETTING | GEOLOGY AND AGE | HOSTING ROCK | PROPYLITIC ZONES | HYDROTHERMAL ALTERATION ZONES | AREA OF ALTERATION | ORE GRADE | ORE RESERVE |
|---------------------------------|----------------|--------------|------------------|------------------------------|------------------|-----------|-------------|
| SAFINAEK                        | Paleocene      | Dacite to andesite porphyry (1 body) | Not determined | Quartz, sericite, pyrite and chalcopyrite | 1.1 Km² | Not determined | 150 |
| REKO DIQ (Former Koh-e-Dalil)   | Paleocene      | Dacite to andesite porphyry (1 body) | Not determined | Quartz, pyrite, magnetite, calcite | 9.75 Km² | Not determined | 500 |
| HUMAI (Chagai Arc)              | Late Cretaceous | 10.9 x 0.7 Ma* | Not determined | Not determined | 1 Km² | Not determined | 100 |
| DURBANCHAH (Li-Cr. -Miocene)    | Late Cretaceous | 21.0 x 0.7 Ma* | Not determined | Not determined | 2.5 Km² | Not determined | 200 |
| ZIARAT PIR SULTAN               | Late Cretaceous | 31.6 x 1.2 Ma* | Not determined | Not determined | 3 Km² | (a) 35% (b) 0.15% | 350 |

*aAge of Mineralization, [22, 23, 31, 49].
3.3. Propylitic Alteration Zone

The propylitic alteration zone is widely developed in all the porphyry copper settings so far found in the Chugai belt and generally encircles the quartz sericitic alteration zone, Table 1. At Saindak, the area beyond the quartz sericitic zone represents the propylitic alteration and its outer limits were defined as the outer limits of pervasive pyritization. This alteration at Saindak is typified by chlorite, epidote, albite, calcite, anhydrite, and pyrite [22].

The Reko Diq deposit shows this zone around the quartz sericitic alteration zone, mainly associated with andesitic flows and characterized by the presence of chlorite, epidote, and calcite [25, 26]. At Humai propylitic alteration zone is marked by chlorite, epidote, and calcite [5]. The propylitic alteration at Durbanchah is represented by the extensive development of chlorite, epidote, and calcite. At the contact zone, the andesite is completely replaced by epidote and thus is a good indicator of mineralized zone in the vicinity [27]. At Ziarat Pir Sultan, this alteration is characterized by chlorite, epidote and pyrite. At Missi prospect, the propylitic alteration was identified by the presence of chlorite, epidote and calcite.

Propylitic alteration at Dashte Kain is restricted in the pre-ore dioritic and andesitic rocks and is represented by epidote, chlorite, calcite, and pyrite. Epidote generally occurs in the ground mass replacing the plagioclase and ferromagnesian minerals and chlorite have developed after hornblende and biotite. Calcite generally occurs as open space fillings. At places, intense epidotization is observed replacing the whole rock [23]. The propylitic alteration zones are the most widespread alteration footprints that commonly surround phyllic alteration zones in the porphyry deposits of western Chagai Arc [24, 31].

4. Discussion

All the porphyry copper prospects of Chagai Arc are associated with tonalitic to dacitic porphyritic rocks except Missi prospect, which is associated with granodioritic rocks. Hydrothermal alteration has been developed in concentric zonal patterns. The intensity of alteration generally decreased from the center in each case as proposed by Lowell and Guilbert [2].

The presence of porphyritic texture in the host rocks of all the porphyry Cu settings suggests that they have gone through two different physico-chemical environments during their course of emplacement. In deeper environments and at high P, T conditions, larger crystals formed and when the partially crystallized magma further rose up and reached relatively in the shallower environments having low T, P conditions, smaller crystals of the groundmass were formed and consequently a porphyritic texture was developed contemporaneously due to decrease in confining pressure over the magma, a vapor phase was released as hydrothermal solution, which is responsible for hydrothermal alteration in the porphyry systems.

The Rose [32] proposed that hydrothermal alteration is generally controlled by the temperature and HCl/KCl ratio in the brines. The alteration in the porphyry copper system is mainly metasomatic/hydrothermal in nature and is in accordance with the mesothermal zone of Lindgren [33] but more recent studies report a wide range of fluid-inclusion homogenization temperatures (200°–760°C) from porphyry copper deposits [34, 35]. Bodnar [36] has reported magmatic fluid inclusions of high-salinity and halite bearing, which homogenized at a relatively high temperature (> 500°–600°C). Therefore, it is suggested that the alteration at the central zones might have been caused by primary magmatic, highly saline, Na, K, Ca, Cl, brines at about 500-750°C, while the alteration in the outer zone may be produced by the circulation of less saline meteoric water at about 250°C [37, 38]. Cooke et al. [39, 40], Richards [41], Sinclair [42], Sillitoe [43]; Sillitoe and Perello [44] have suggested magmatic-hydrothermal fluids generated from subduction-related calc-alkaline igneous rocks for the formation of porphyry copper deposits. The source of metals in porphyry deposits is magmatic as evidenced by magmatic fluid inclusions found in the early quartz in veins [36].

The source of metal of porphyry copper setting of the Chagai belt may be the upper basaltic part of the subducted oceanic lithosphere in which massive copper sulphide mineralization, was emplaced during oceanic spreading along Mid-Tethyan ridge and subsequently partial melting of the above
basalt along with massive copper sulphides, later on during the subduction under the southern margin of Afghan microcontinent produced calc-alkaline magmatism and associated porphyry copper mineralization in the Chagai belt [45]. Small quantities of both copper and molybdenum might have been derived from the wedge of mantle overlying the Benioff zone [46, 47]. Richards et al. [48], and Richards [41] revealed a compositional distinction between productive intrusions of porphyry deposits with fractionated REE patterns and depletions of manganese, thorium, yttrium, and the heavy-REE compared to barren intrusions in the Andes arc. Similarly, Siddiqui et al. [15, 19], have noted enrichment of large ion lithophile elements (LILE) and light REE in the pre-ore host volcanic rocks associated with porphyry copper bearing plutons of the Chagai Arc. This reflects that larger amount of subduction-related fluids (enriched in LILE and LREE) had contributed to the sub-arc mantle source of porphyry copper bearing magmatic rocks.

5. Conclusion
Description of hydrothermal alteration in the foregoing pages reveals that almost all the prospects exhibit a similar pattern of hydrothermal alteration which is quite comparable with the model proposed by Lowell and Guilbert [2]. Out of the above porphyry copper settings, only Saindak, Reko Diq and to some extent Dasht-e-Kain have been explored and evaluated so far.

At Saindak, the proved copper ore reserves are about 412 million tons, at Reko Diq 2,200 million tons and at Dasht-e-Kain estimated reserves are about 350 million tons. Other porphyry copper prospects of the Chagai Belt have smaller alteration areas than Saindak.

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