

# Characteristics Of Supergene Copper Oxides Mineralization In The Binamar Area, Ardabil, NW Iran

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**Abstract—** Binamar area located in the northwest of Iran in the Alborz-Azerbaijan structural zone and completely is covered by a series of Eocene volcanic and volcanoclastic rocks, including mainly porphyritic and megaporphyritic andesite, basaltic andesite, basalt and accompanying agglomerates and andesitic tuffs. The volcanic rocks host copper mineralization, including malachite, azurite, brochantite and native copper as fracture filling in the oxidized zone. By noticing the type of minerals and their forms in the study zone, it is supposed that copper mineralization is the result of the oxidation and leaching primary hypogene minerals and reprecipitation of releasing copper as new secondary minerals at the surface.

**Keywords—** mineralogy; supergene; copper oxides mineralization; Binamar; Iran

## I. INTRODUCTION

Weathering and erosion are the Earth's primary natural mechanisms for redistributing mass on its surface, and these processes are driven by natural agents such as climate, animals, plants and surface and ground waters. When rocks that were formed at high temperatures and high pressures are exposed at the Earth's surface (average  $T_{\text{atm}} \sim 15^{\circ}\text{C}$ ;  $P_{\text{atm}} \sim 1$  bar; and  $p\text{O}_2 \sim 0.2$  bar), their equilibrium is disturbed. This causes their mineral constituents to react and undergo transformations so as to adjust to the new lower temperatures, pressures, and higher oxygen concentrations and moisture conditions. Near-surface oxidation and leaching of originally deeply formed rocks and ore deposits are major ore-enriching (or ore-forming) processes.

Weathering and erosion are combinations of geological, chemical, physical, and biological processes operate together on preexisting metal-bearing rocks to form secondary supergene minerals. The formation of supergene zone involves dissolution of rock material, transport of soluble elements, and precipitation of new ore minerals. The phenomenon known as supergene mineralization refers to the secondary, in situ, accumulation of metals (e.g. Cu, Zn, Ag, Au, Ni, or U) as a result of three essential processes: (1) the electrochemical oxidation of

primary sulfides, oxides or native metals (e.g. native copper Cu(0) to Cu(II)) (2) the transport of the released metals as soluble metal species (e.g.  $\text{CuSO}_4^0$ ,  $\text{AuCl}_4^-$ ); and (3) the reprecipitation of the metals by reduction (e.g. Cu(II) to native copper Cu(0)), by supersaturation (e.g.  $\text{Mg}^{2+}$  in magnesite deposits), or by cation-exchange (e.g.  $\text{Ni}^{2+}$  exchange for  $\text{Mg}^{2+}$  in smectite- or serpentine-group minerals) [1]. Oxidation processes are active in the surficial vadose zone and the capillary fringe above the water table. Leaching processes also respond to changes in physicochemical properties, such as the partial pressure of oxygen ( $p\text{O}_2$ )—and its effect on the redox potential (Eh)—and the activity of  $\text{H}^+$  of descending aqueous solutions [2].

Copper oxides represent an attractive exploration target because even low-grade prospects have the potential to produce low-cost copper in an environmentally friendly fashion. Derived from hypogene and/or supergene sulfides, copper oxides comprise a series of distinct assemblages that characterize a variable pH, oxidizing geochemical environment known as “the oxide zone.” Development of oxide copper minerals is a function of source-rock and host-rock mineralogy, pyrite and other sulfide abundance and distribution, fracture density and distribution, phreatic and/or vadose zone occurrence and stability, and maturity of the weathering profile.

When sulfide ore deposits are exposed to the oxidation zone, they are weathered and altered with the country rocks. The oxidation of sulfide minerals, especially pyrite, is critical in determining the geochemical environment that characterizes a weathering sulfide-bearing rock volume. The oxidation of sulfides other than those of iron produces only modest quantities of acid sulfate-bearing solutions, a factor which is significant in determining the types and distribution of oxide minerals developed within a zone of weathering. Therefore, pyrite oxidation is generally the most important source of the acidic solutions responsible for mineral destruction during the weathering of a rock volume. This means that pyrite quantity is critical in determining oxide zone mineralogy. Sulfide destruction creates solutions containing hydrogen ions, metal ions, and sulfate. The combination of sulfate as a complexing anion,

hydrogen ions (i.e., acid conditions), and atmospheric oxygen to enhance and maintain an oxidizing environment results in destruction of sulfides, oxides, and silicate minerals. These solutions must be at least partially neutralized if the metals of economic significance are to be redeposited. One of the most important factors influencing the generation of the acid sulfate bearing solutions is the ratio of reduced sulfur to metal in sulfide minerals before oxidation. Well-developed copper oxide zones appear to form through two distinct mechanisms: (1) via substantial copper addition to a volume being oxidized, including the formation of exotic copper deposits, and (2) through in situ oxidation of a copper-bearing sulfide resource. Importantly, the first type of copper oxide system requires copper transportation from a source region, but the protore does not need to have high copper content if leaching and precipitation are efficient. Conversely, the second type requires substantial protolith copper content if the copper oxide zone developed is to be of potential ore grade, and requires also that removal of copper be minimal [3].

Supergene processes are important because the reactions between primary sulfide minerals and surface waters produce secondary sulfides with metal contents higher than those of the primary ore. These processes may result in a two- to ten-fold increase in metal grades for such commodities as Cu, Al, Fe, Ni, Mn, U, Au and Zn [4].

In the traditional view, supergene alterations are the products of reactions between hypogene sulfide minerals and descending, acidic meteoric waters with other silicate minerals. These processes take place at or near the ground surface in subaerial environments and change compositions of host rocks and primary minerals [5]. In the present contribution the mineralogy and interactions leading to the formation of secondary copper mineralization associated with weathering of primary minerals in the volcanic host rocks in the Binamar area are examined.

## II. GEOLOGY OF THE STUDY AREA

Binamar area is located in the northwest of Iran in the Ardabil province. Based on classification of structural units of Iran [6], Binamar area is situated in the western Alborz-Azerbaijan zone (Fig. 1), which is part of the Alpine-Himalayan fold belt. Studied area situated in the Taram-Hashtjin metallogenic province (THMP). Structurally, THMP is located in merge between western Alborz Magmatic Belt and Sanandaj-Sirjan Zone and have several mineralizations of epithermal-porphyry and other type of hydrothermal ore deposits [7]. The geological setting of the studied area is Cenozoic volcano-tectonic zone, which contains Eocene porphyritic and megaporphyritic andesite, basaltic andesite, basalt, accompanying agglomerates and andesitic tuffs [8].

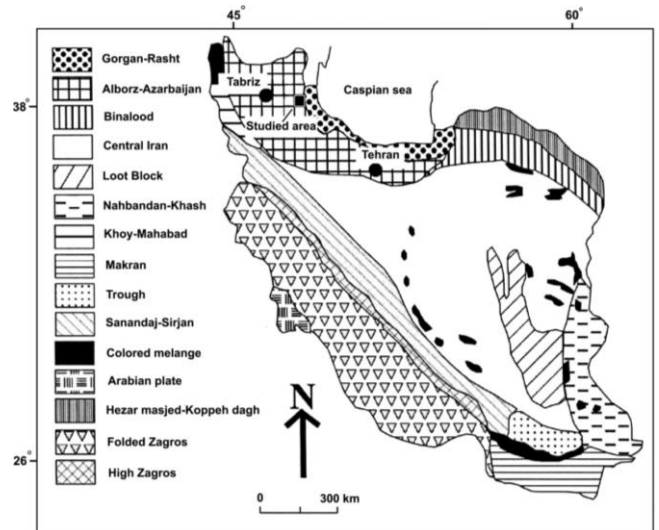


Figure 1: Major structural zones of Iran and the location of the studied area in the western Alborz-Azerbaijan zone.

## III. MATERIALS AND METHODS

A large number of samples were collected from altered volcanic rocks and mineralized body. Mineralogy was studied in polished sections using a reflected light microscope. Bulk mineral composition, in order to identify unknown minerals was determined by X-ray diffraction (XRD) using a Siemens D500 diffractometer, with Cu-K $\alpha$  radiation and a graphite monochromator. Chemical analyses of whole rock were carried out with wavelength dispersive X-ray fluorescence (WD-XRF) using a Siemens SRS 303 XRF spectrometer.

Fig. 2 shows chemical composition of Binamar volcanic rocks according to Winchester & Floyd diagram [9]. This diagram is more accurate than others since Zr and Ti are not mobile elements. According to this diagram most of the samples fall in the andesite region.

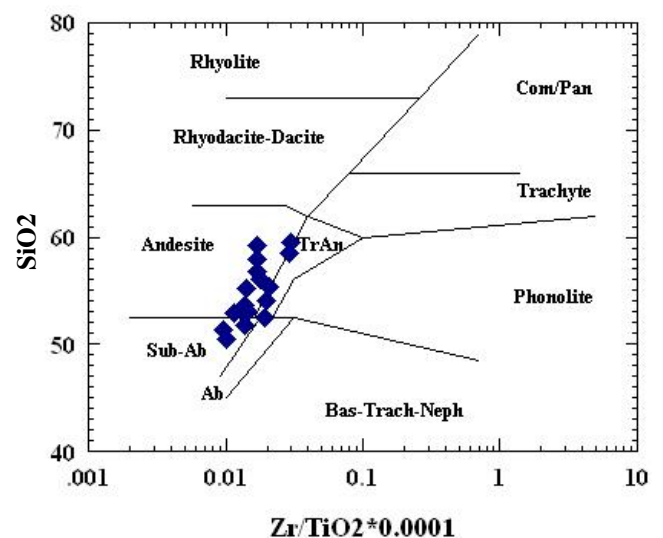


Figure 2: Classification of the investigated volcanic rocks

#### IV. SUPERGENE COPPER OXIDES MINERALIZATION

The "oxide zone" consists of the rock volume in which copper oxide minerals are stable and are the dominant copper minerals. Eh-pH diagram of the stability fields of common supergene sulfide and oxide minerals in the system Cu-O-S-H<sub>2</sub>O at 25°C (fig.3) shows possible paths followed by solution descending from the oxidized zone, generating enrichment, and infiltrating into hypogene ore or protore. The facies are defined by hydrologic regimes in the vadose zone, in the zone of capillary fringes and in the saturated zone. Fields within the diagram illustrate which copper mineral, aqueous species, or ion is stable.

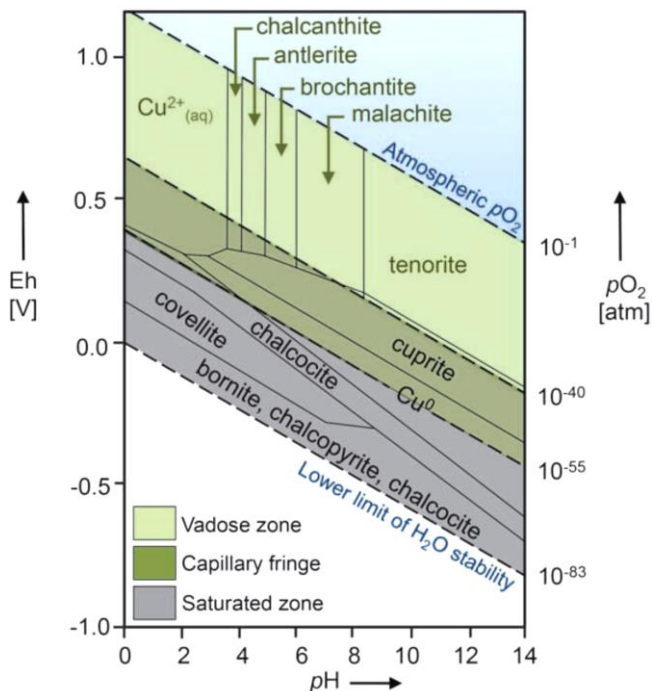


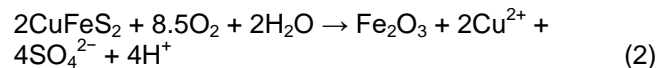
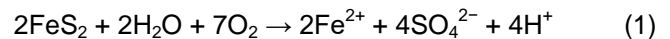
Figure 3: Graph of redox (Eh) and partial oxygen pressure ( $pO_2$ ) versus pH showing the stability of dissolved copper species and copper minerals in the supergene environment. The diagram maps out possible occurrence of stable phases under particular redox and pH conditions along a supergene profile. Conditions shift vertically from the more reducing, saturated zone in grey at the bottom (below the water table), to the more oxidizing conditions towards the top of the profile (vadose zone, where the soil and rock pores contains air as well as water) [10].

Copper minerals in the oxidized zone of study area are mainly secondary, including native copper along with sulfate (brochantite) and carbonates (malachite and azurite) (fig. 4).

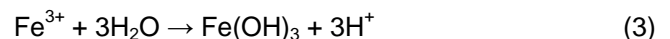
#### V. DISCUSSION

The paragenetic sequence of copper oxide minerals observed from many oxidized copper-bearing orebodies reveals that a specific series of progressive mineralogic changes takes place during supergene oxidation, transport, and precipitation. During weathering, Cu was completely leached from the upper parts of the profile and only partially concentrated as a complex assemblage of secondary

copper oxide minerals and native copper. "Copper oxides" are defined as those copper minerals containing oxidized anions, especially copper oxides, sulfates, phosphates, carbonates, and arsenates. In the study area copper minerals occur dominantly along fractures at the surface, implying that they are secondary minerals deposited by percolating groundwater. Malachite is the most common copper mineral in the study area. Azurite has been observed in contact with malachite and is less common than it. Malachite and azurite commonly occur at shallow depths in the oxide copper zone. The absence of primary copper sulfides (e.g., chalcopyrite and bornite) at the surface of area suggests that all of them were oxidized to secondary supergene copper minerals. In most copper ore deposits, the stepwise hydrolysis and oxidation of primary pyrite-bearing assemblages leads to a decrease in the pH of descending groundwater and the liberation of oxidized sulfur as  $SO_4^{2-}$  anions (1). There is a simultaneous breakdown of chalcopyrite ( $CuFeS_2$ ), which produces soluble  $Cu^{2+}$  ions that are transported downwards, encountering progressively greater reducing conditions deep into the profile (2). This process is accompanied by "capping," the precipitation of iron oxyhydroxides in the leached zone from which Cu is removed. The abundance of iron oxide minerals decreases with depth. The thickness of the leached cap is highly variable but can reach several hundred meters in porphyry Cu deposits, particularly when the water table was deep enough during the supergene oxidation and enrichment phase.



Other sources of acidic solutions, albeit generally minor compared to sulfides, include magnetite and Fe-bearing silicates. Silicate minerals that contain  $Fe^{2+}$  are susceptible to oxidation, and minerals such as biotite, Fe amphiboles, Fe pyroxenes, and Fe-bearing garnets (e.g., the La Democrata skarn system in the Cananea district, México) may contribute to the generation of acid solutions during weathering. This is because ferric iron, produced during mafic mineral oxidation, generates goethite plus hydrogen ions via reactions such as (3):



Acidity, providing by the oxidation of primary sulfide minerals, like pyrite and chalcopyrite results in sulfuric acid being produced in large quantities which is mixed with water and makes it very corrosive. Acidic water attacks the ore deposit and liberates copper from it. With high concentration of  $SO_4^{2-}$  and presence of  $Cu^{2+}$ , brochantite ( $Cu_4(SO_4)(OH)_6$ ) is one of the first product of reaction between them in moderately low to near-neutral pH values. Brochantite is a sulfate mineral, one of a number of cupric sulfates.



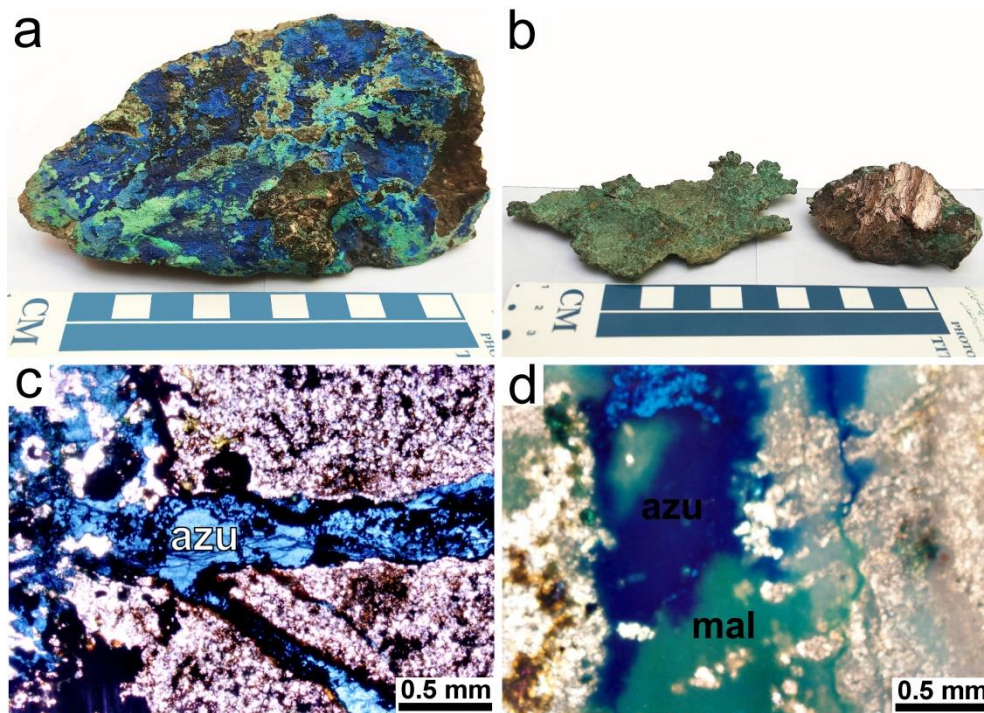


Figure 4: Hand specimens and polished sections of supergene copper mineralization in the oxidized zone of Binamar area. a) malachite (green) and azurite (blue); b) native copper coated with malachite; c and d) malachite and azurite in the polished section under microscope.

Brochantite is formed in arid climates or in rapidly oxidizing copper sulfide deposits (4). It is very rare and has been detected by XRD analysis (fig. 5). As oxidation continues, brochantite also is developed at the expense of the native copper in the topographic middle of an oxide column.

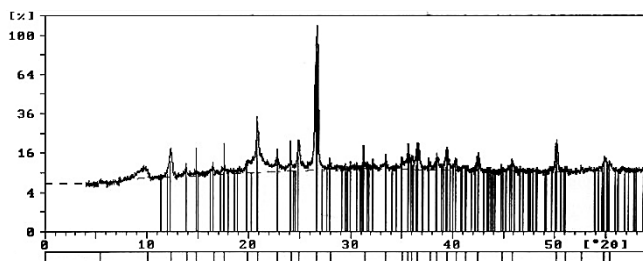
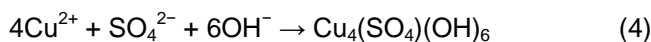
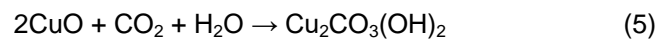


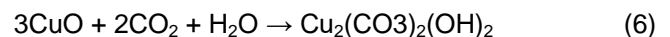
Figure 5: XRD graph of sample from oxide zone

Copper is mobile at low pH and copper-bearing meteoric water is moving away from weathered ore and copper starts to precipitate as carbonates when carbonate is available from sedimentary sources, atmospheric sources, and/or indigenous bacteria cells [11]. When the acidic water encounters a neutralizer like limestone country rock or calcite vein its pH increases. Malachite ( $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ) is a green and azurite ( $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ ) is a blue copper-bearing hydrated carbonate mineral. Malachite and azurite are common constituents of copper oxide zones. Malachite found at the top and fringes of the oxide

copper zone and is the most stable copper mineral in environments in contact with the atmosphere and hydrosphere. Carbon is present in the atmosphere and biosphere and so malachite needs no particular source to form (5).



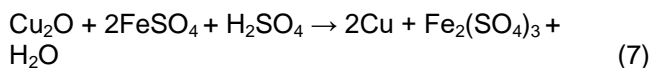
Azurite formed in groundwater environments, through in situ recombination of carbonate ions originating from dissolving host-rock carbonates and downward percolating  $\text{Cu}^{2+}$  (leached from copper sulfides) (6).



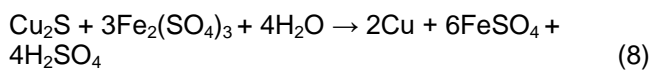
Malachite and azurite precipitation takes place at pH values between 6 to 8, depending  $\text{CO}_2$  partial pressure. Azurite is only stable under relatively acid condition and elevated partial pressures of carbon dioxide ( $\text{pCO}_2$ ) greater than atmospheric levels, a condition fulfilled only in mineral assemblages containing calcareous gangue. Since high carbonate activities imply mostly basic conditions, this explains why malachite is the more common and stable form of copper carbonate and that azurite can be formed only under rather unusual conditions. It also explains the frequent alteration of azurite into malachite [12].

Native copper is observed as shiny, dendritic copper leaf or massive along fractures particularly at margins and deeper within the copper zone. Native copper typically occurs in lower and peripheral parts of the oxidized zone. Native copper is a common minor constituent of the oxidized zone, and it occurs

directly above the zone of secondary chalcocite enrichment. The native copper stability field, dependent primarily on the oxidation-reduction potential, lies between the field of cuprite and that of chalcocite (fig. 3). Accordingly, as the environment changes from oxidizing at the surface to reducing at depth, native copper should and, in fact, commonly does occur most abundantly near the base of the zone of oxidation and just above the zone of secondary chalcocite enrichment. In regard to the manner in which native copper is formed in weathering zones, in the oxidation of chalcocite deposits, native copper is developed from cuprite by the action of ferrous sulfate as follows (7).



Also, native copper may be formed directly from chalcocite by the action of ferric sulfate (8).



## VI. CONCLUSION

Copper oxide zones are the product of sulfide destruction produced by weathering under oxidizing conditions that takes place above the water table. Indigenous copper oxide zones, generated via in situ oxidation of a sulfide-bearing rock, are usually developed so that the most reduced copper oxides (native copper) are formed in the lower portions of the oxide column. According to the position of secondary copper minerals in Eh-pH diagram, it is supposed that enriched zone including chalcocite and covellite in the Binamar area located below the zone in which native copper was found.

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