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Iranian Society of
Mining Engineering
(IRSE)

Evaluation of Geochemical and Geophysical Methods for Separation of Copper Oxide and Sulfide Zones in Chogan, Markazi Province

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Article Info

Received 7 June 2024

Received in Revised form 18 August 2024

Accepted 25 August 2024

Published online 25 August 2024

DOI: [10.22044/jme.2024.14645.2766](https://doi.org/10.22044/jme.2024.14645.2766)

Keywords

Sulfide and oxide zones

Copper exploration

Factor and cluster analysis

Geochemical and geophysical indices

Chogan in Markazi Province

Abstract

Chogan region is located in the west of the Urmia-Dokhtar volcanic belt and northwest of the Markazi province in Komijan City. Copper mineralization has a vein type with a length of 260 meters and an average thickness of 4 meters. Mineralization was taken in a sheared silica vein. Eighty-three samples were taken from the surface ground, in the trenches and it determined the concentration of 10 elements such as Fe, Al, Ca, Ba, S, Mn, As, Pb, Zn, and Cu. It was determined, that S, Ba, Mn, Fe, and Cu are secondary elements in the tuffs by the method of factor and cluster analysis. The constituent mineral such as barite and malachite are vein-shaped, but iron oxides such as hematite and goethite in the form of iron gossan. Geochemical, mineralogical, and geophysical (IP/RS) indices were investigated to separate copper oxide and copper sulfide zones. Sulfur and Ba were used in barite and excess S was chosen as sulfide index (Is). Chalcopyrite and metal factor were chosen as separating oxide and sulfide zones. By combining the geochemical and metal factor, it was approximated the apparent sulfide zone depth and confirmed with actual depth in borehole and error was less than 12%.

1. Introduction

It is necessary to identify and separate the different areas of these deposits and how they are formed. Determining oxide and sulfide zones is one of the most important stages of exploration. Using different methods, including geochemistry and geophysics, are effective in separating the two oxide and sulfide zones [1-5]. Exploration operations are risky and its success depends on choosing the correct exploration methods for each specific type of mineralization and in any given environment [6-8]. Geochemistry and geophysics, together with geology are considered among the most important criteria for identifying the mineralization and separating of copper oxide and sulfide zones [9-10]. Element distribution maps along with primary type geochemical halos and hypogene alterations and using elemental geochemical indices are important geochemical tools to explore hidden deposits [11-15]. Many

deposits have a high sulfide and oxide mineralization and indirect methods such as geochemical and geophysical method can show these deposits and save time and money before drilling method [16]. According to the extensive discoveries that have been made in relation to sulfide deposits, it has increased the importance of investigating and exploring oxide deposits [17-19]. The only study to separating the oxide zone from the sulfide zone was by factor analysis and fractal model [19]. In connection with the copper deposit, it is also important to pay attention to the geological and structural features, the type of alterations, primary halos, the mineralization environment, host rock lithology and the relationship of each with the mineralization of the region [20]. The identification of these deposits is very important by considering the extent and diversity of these types of deposits [21].

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Due to the fluctuations of the water table and according to the existing fractures, the surface precipitation did not reach the lower part and sulfur minerals such as chalcopyrite remain intact under the oxide zone. The sulfide areas are also affected by weathering and are oxidized to the oxide zone on the surface [22-23]. Fluctuations in water level cause a transition zone to be created where oxide and sulfur minerals are placed together. For example, copper oxide is present in the form of malachite and azurite in the oxide zone, and copper sulfide is often present in the form of chalcopyrite in the sulfide zone. Mineralogical evidences shows the presence of chalcopyrite in the oxide zone as a diagnostic criterion of the sulfide zone [22]. Copper oxide minerals include malachite, azurite, and tenorite can show its sulfide minerals such as chalcopyrite, chalcocite, covellite, bornite, and dignite.

Determining the approximate boundary and separating the oxide and sulfide zones of Chogan copper by various geochemical and geophysical methods is one of the aims of this manuscript to reduce time and cost spent in drilling.

2. Geology of the region

Chogan copper area is located in the Urmia-Dokhtar belt. Urmia-Dokhtar belt is the most important place for the formation of copper deposits (Figure1). This belt has a length of 1500 km from the northwest to the southeast of the area and is caused by the subduction phenomena of the calc-alkaline series [23]. Different types of copper mineralization such as porphyry, mantos and epithermal can be seen in this belt, examples of which are Sarcheshme, Midok, Songon, Chah Musa, Kohang and Mari mines [24]. In the central part of Urmia-Dokhtar belt and the plate of central Iran, copper mineralization and its related deposits have been seen in many places, and the copper deposits are in the form of mantos or veins. Along the main fault line in the Saveh region, there are intrusive masses with a large copper deposits. The main faults of the region, such as Khalkhab and Kushk Nusrat, in the central Iranian plate, have created a suitable environment for the accumulation of copper deposits in the middle Eocene [25].

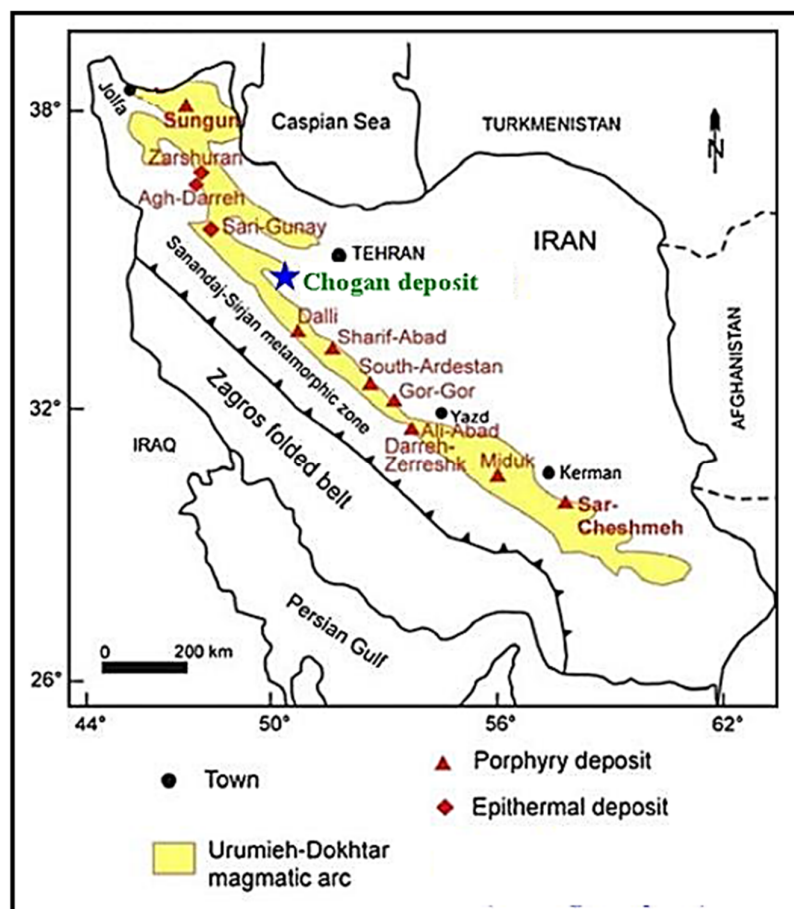


Figure1. Location of epithermal and porphyry deposits in Urmia Dokhtar magmatic arc and the location of Chogan copper deposit in its middle part [26].

The main rocks of this belt are mainly andesitic volcanic rocks and intrusive masses with a combination of diorite and granite [24]. Volcanic rocks in this belt are lavas, pyroclastic deposits, and ignimbrite, which range from basalt to rhyolite. Along with volcanic rocks, sedimentary rocks are mainly clastic-biochemical [27]. The rock stratigraphic units of Chogan region are divided

into three groups (Figure 2): Limestones with brown and gray colors intermittent with sandstones and marls; Medium-layered calcareous sandstones with interlayers of greenish tuff; Grayish-green marls intermittent with shale and green tuff. The main faults of the region mainly have a northwest-southeast direction.

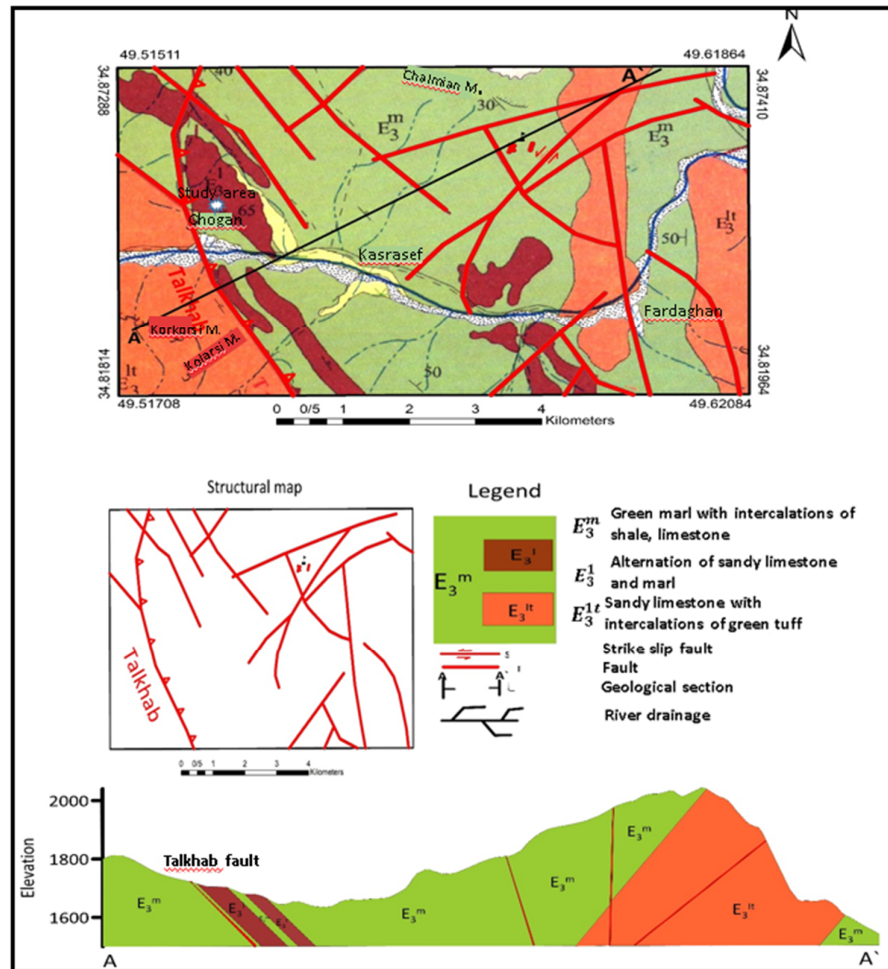


Figure 2. Geology of Chogan copper area.

Chogan copper mineralization can be seen in tuffs and in sheared siliceous and barite veins. Iron oxides with a thickness of approximately one meter were found in one of the tunnels, which include malachite, barite along with hematite and goethite (Figure 3).

3. Materials and methods

Eighty-three samples were taken from profiles A to E perpendicular to the mineralization trend (Figure 4). Fifty surface and 33 samples from the trenches were sent to the ICP-MS studies and were determined the concentration of 10 elements such

as Fe, Al, Ca, Ba, S, Mn, As, Pb, Zn and Cu. Statistical correction, normalization of the data, then multivariate analysis such as correlation matrix, factor analysis, and cluster analysis were used to evaluate and identify the effective methods for separating the oxide and sulfide zones in the Chogan copper deposit. Apparent specific resistivity data in geoelectric method was used by inversion method to confirm the results of the data. Polished sections were used to identify sulfide and oxide copper mineral and the results of geophysical and geochemical investigations were combined to identify the sulfide zone and separate it from the oxide zone.

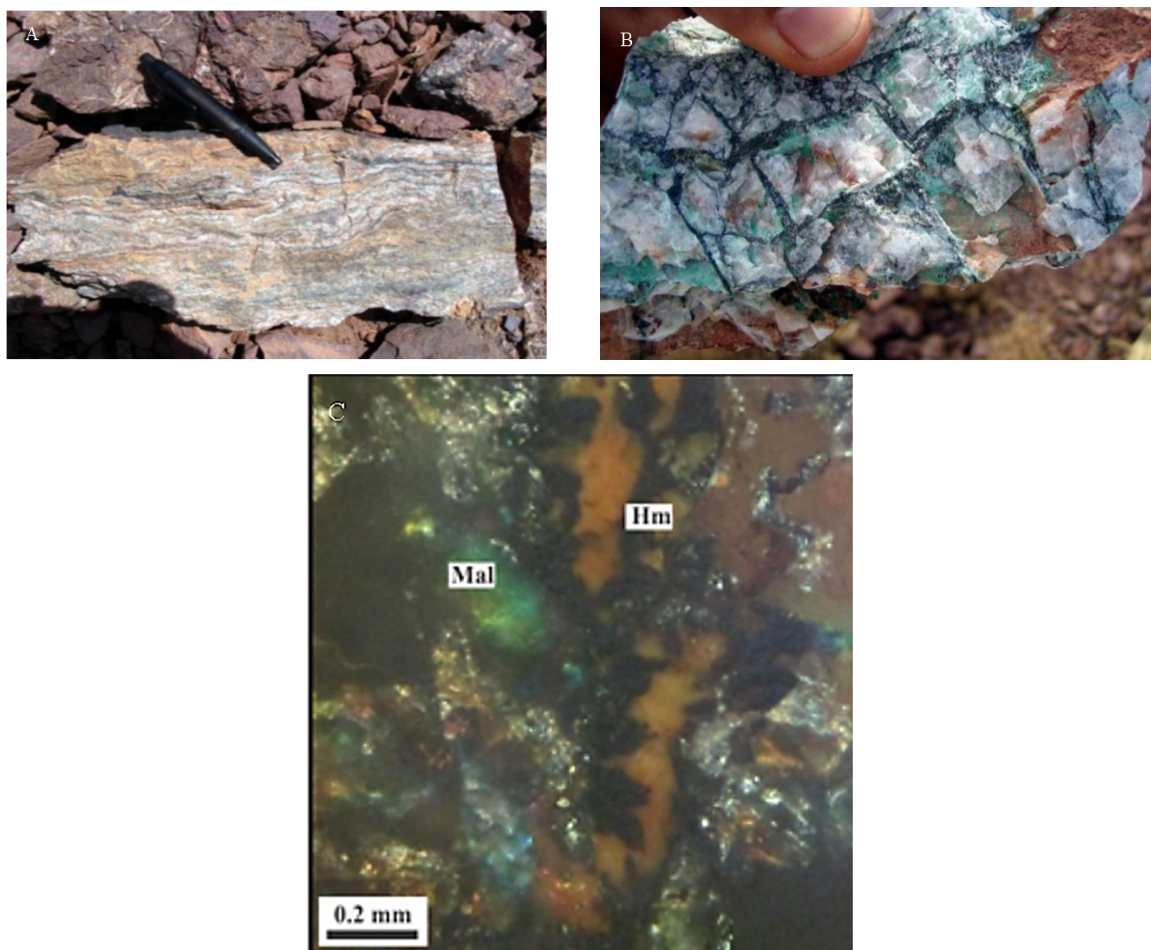


Figure 3A) Mineral veins including silica, barite and iron oxides; B) Hydrothermal breccia containing malachite and barite; C) Polishing section containing malachite (Mal) and hematite (Hem).

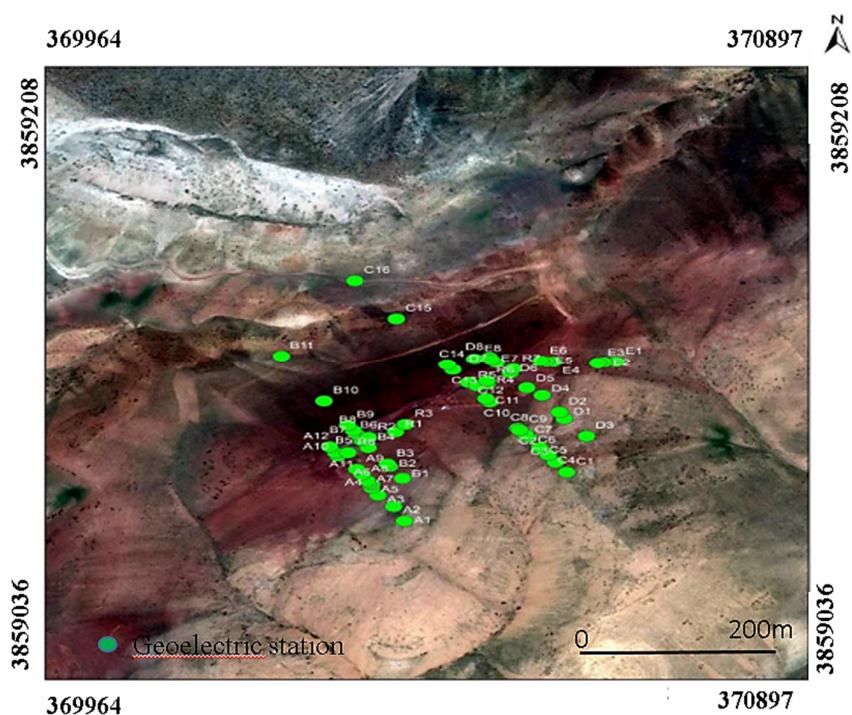


Figure 4. The location of the samples taken from the area in the satellite photo [28].

4. Results and discussion

4.1. Factor Analysis

The main aims of this analysis are to find the minimum number of variables with maximum variability among geochemical data and to reduce the number of data dimensions by determining the relative impact of each variable in relation to the changes in the distribution of elements [29]. The factors should be able to justify the major part of the changes and be independent in statistics version 12 software. Four factors includes 78.20% cumulative variance value based on table1. The

eigenvalue of the first factor showed the highest value and 25.09% of highest variance, and then the second, third, and fourth factors included 21.26%, 17.73%, and 14.11% variance, respectively. The first factor has a negative effect on 7 elements, and shows a high and positive correlation with S and Ba. The presence of S can indicate the oxide and sulfide region. The second factor with elements such as Al, Ca and Mn indicates rock-forming elements. The third factor also has the highest values for Cu, Fe As, and the fourth factor is related to Pb and Zn [28].

Table 1. Effect of geochemical variables from factor analysis in Chogan region.

	Factor1	Factor2	Factor3	Factor4
Fe	0.14	0.12	-0.60	0.39
Al	-0.44	0.62	0.36	0.10
Ca	-0.40	-0.60	-0.17	0.56
Ba	0.79	-0.33	0.44	-0.05
S	0.80	-0.34	0.44	-0.06
Mn	-0.54	-0.63	-0.17	-0.31
As	0.25	-0.23	-0.56	0.47
Pb	-0.41	-0.51	0.39	0.53
Zn	-0.43	-0.49	0.37	0.54
Cu	0.35	0.41	-0.45	0.08
Eigenvalues	2.50	2.12	1.77	1.41
Cumulative Eigenvalues	2.50	4.63	6.40	7.82
Variance%	20.09	21.26	17.73	14.11
Cumulative variance%	25.09	46.35	64.08	78.20

4.2. Cluster analysis

In cluster analysis, the aim is to achieve a criterion for the best possible classification of variables or samples based on the greatest similarity within the class and the greatest difference between the classes. Similarity or dissimilarity can be measured by distance measures such as Euclidean distance or correlation coefficients. The algorithm used in this study was Ward's method, Pearson's distance and perform hierarchical clustering process.

According to Figure 5, if the linkage distance is considered 1.5, the cluster analysis divides the data into four main clusters. The first cluster includes Ba and S, the second cluster includes As, Fe and Cu, the third cluster includes Pb, Zn and Al, and the fourth cluster includes Ca and Mn. Obviously, the first and third clusters correspond to the factor analysis. Sulfur and Ba in the first cluster have a high correlation and indicates a similar origin. These two elements also have a high correlation in the factor analysis, which indicates the presence of S as an indicator of the oxide and sulfide region.

4.3. Sulfide/ oxide mineralization ratio

Seven polished sections were used to identify sulfide minerals (Figure 6A). The area of oxide and sulfide minerals was calculated in the desired parts. Then, the ratio of each oxide and sulfide part was determined to the entire polished section and finally calculated the ratio of sulfide to oxide for each part (Figure 6B and Table 2). Two samples 3 and 5 with 2.74% and 2.01% chalcopyrite showed the highest percentage compared to copper oxide (malachite) in the entire polished section. Copper sulfide percentages indicate the sulfide zone relative to the oxide zone in polished sections [28].

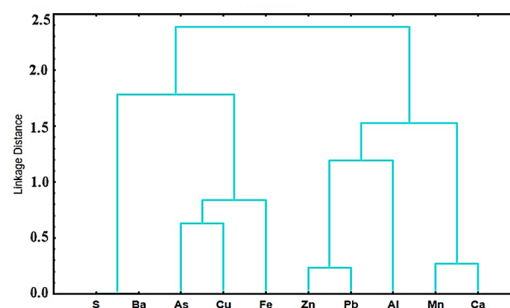


Figure 5. Dendrogram of 10 elements in the cluster analysis.

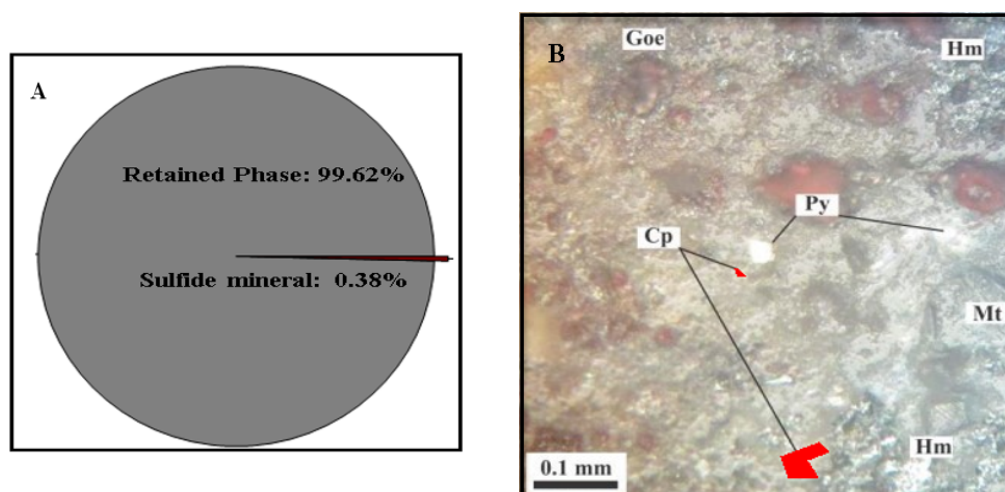


Figure 6A) Mineralization of chalcopyrite (Cp), pyrite (Py), magnetite (Mt), hematite (Hm), goethite (Geo); B) The proportion of copper sulfide mineralization (chalcopyrite) to the entire polished section.

Table 2. Proportion of sulfide to copper oxide minerals to the entire polished section.

Sample No.	Cu sulfide%	Cu oxide	Cu sulfide/ Cu oxide	Cu sulfide/ Cu oxide*100
1	0.69	0.00	0.0069	0.69
2	0.38	0.00	0.0038	0.38
3	2.67	0.00	0.0274	2.74
4	0.31	0.00	0.0031	0.31
5	1.98	0.00	0.0201	2.01
6	1.98	0.00	0.0201	2.01
7	0.20	0.00	0.0020	0.20
8	0.00	9.74	0.0000	0.00
9	0.00	3.78	0.0000	0.00
10	0.11	0.00	0.0000	0.11
11	0.00	1.90	0.0000	0.00
12	0.24	0.00	0.0024	0.24

4.4. Geochemical index of sulfur (I_s)

The excavated trenches on the mineralization vein were used in order to investigate the copper sulfur zone and the copper oxide zone (Figure 7). According to study of 7 polished sections, the total amount of S was related to chalcopyrite and barite minerals. Therefore, an index was defined for copper that can be used to separate the oxide and sulfide zones. On the other hand, according to the results of ICP analysis, barite was the dominant and major mineral that consumed sulfur, so it was removed from the equation. Sulfur concentration was selected for copper sulfide after removing the excess S related to barite and was chosen as a possible amount of copper sulfide minerals.

Based on the molecular masses of sulfur, barite and copper, two geochemical indices were defined to separate the sulfide and oxide zones (Eq. 1 and 2).

$$I_{S1} = S_{ICP} - 0.2327Ba \quad (1)$$

$$I_{S2} = \frac{S_{ICP} - 0.2327Ba}{Cu_{ICP}} \quad (2)$$

In equation 1 and 2, S_{ICP} is the amount of total sulfur in the sample obtained from the results of chemical analysis by ICP method, Ba is the value of barite value, Cu_{ICP} is the amount of copper value of the samples and I_{S2} is the geochemical index resulting from the ratio of the amount of remaining sulfur related to copper after S removal. Barite was obtained based on the amount of Cu concentration for each sample and was used as a geochemical index to separate oxide and sulfide zones. The calculation steps are as follows:

- The average S concentration was obtained in 83 samples by ICP method.

- The S concentration in one mole of $BaSO_4$ (Barite) was calculated and multiplied by the average S concentration in all samples. In this way, used S concentration in barite was calculated.

- The ICP sulfur concentration was separated from the S consumed in barite, so the excess S was calculated (I_{S1}) (Eq. 1).

- It considered the concentration of excess S in the construction of chalcopyrite ($CuFeS_2$), supposedly.

- The ratio of excess S in barite (I_{S1}) and added S to Cu average was defined in all samples as geochemical

index chalcopyrite (I_{S_2}) (Eq. 2). This index was used to distinguish the oxide zone from the sulfide zone.

- The I_{S_2} index is calculated for each sample based on ICP data and given index has no unit and its value is variable between 0 and 22. The higher I_{S_2} value, the stronger S conditions in the environment.

As mentioned, trenches were used to check sulfur index (I_s). The first trench is located at zero, the second trench is at a distance of 40 meters, the third trench is at a distance of 140 meters, and the fourth trench is at a distance of 206 meters from the first trench. In Figure 8, the Cu concentration

shows the maximum concentration 12000 mg/kg at the distance of 130 to 190 meters. This concentration is located at a distance of 140 meters and a depth of approximately 4 meters.

The calculation of the I_{S_2} geochemical index shows that an anomaly was observed with an index value higher than 12 at a distance of 40 meters and at a depth of 2.6 meters from the surface ground (Figure 9). This anomaly indicates the presence of sulphide zone. At distance of 140 meters from the origin of the trenches and at a depth of less than 2 meters, there is another observed sulphide area with an index greater than 13.

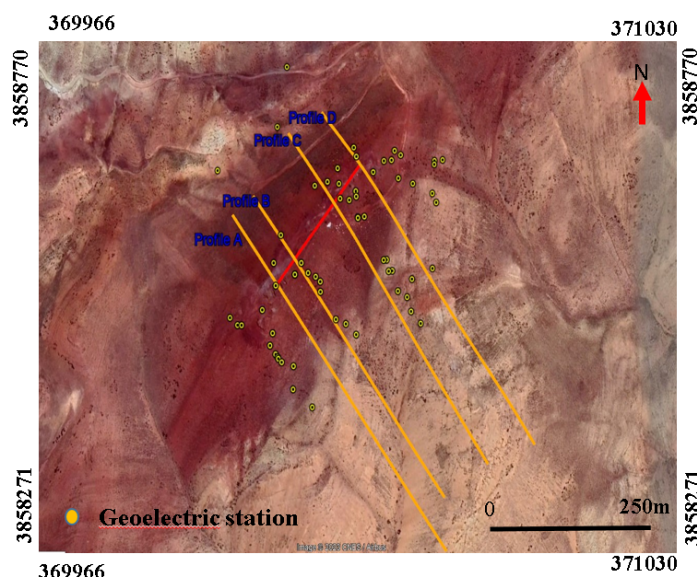


Figure 7. Showing the trend of trenches (red color) perpendicular to 4 geophysical profiles (orange color) along with the location of surface samples (yellow dots).

4.5. Geoelectric criterion

Four geoelectric cross-sections were drawn perpendicular to the mineralization and it was selected profile B in this manuscript. Profile B has a length equal to 250 meters and northwest-southeast trend (Figure 10A and B). In Figure 10A (specific resistivity), the lowest specific resistivity

and the highest conductivity are colored blue, and indicates mineralization, while the lowest conductivity and the highest specific resistivity values are colored red and without mineralization. High chargeable values are shown in red and low chargeable values in blue colors (Figure 9B). High amounts of chargeability and specific resistivity can be caused by Fe and Mn hydroxides [30].

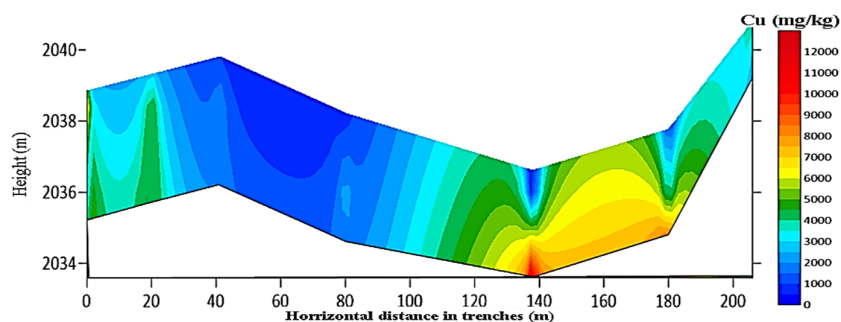


Figure 8. Changes of Cu concentration in the trenches.

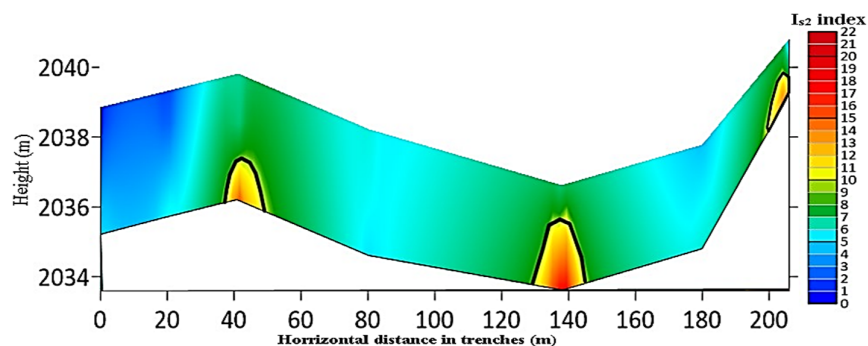
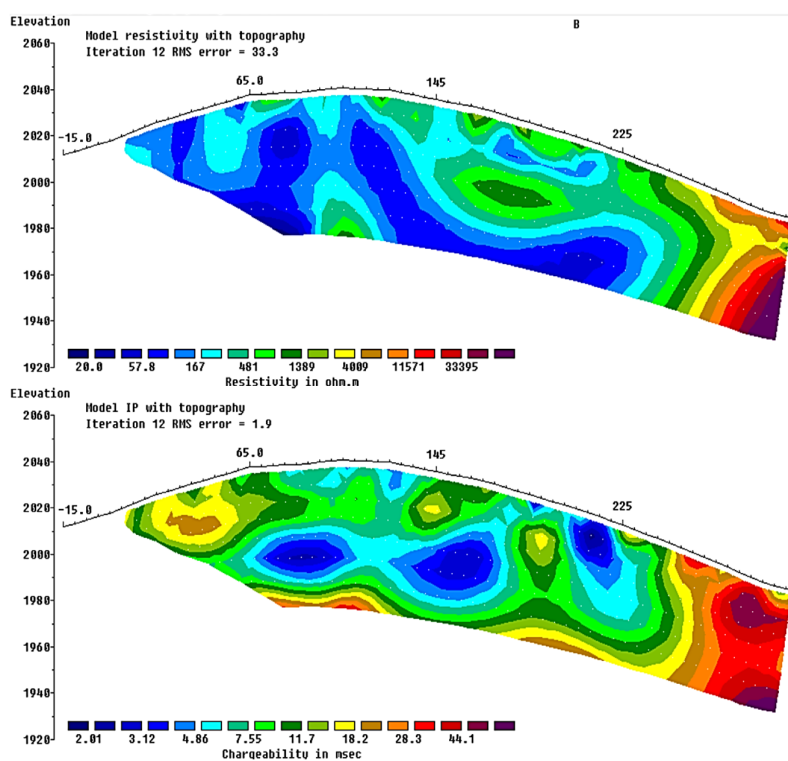
Figure 9. Cross-section of I_{s2} index in trenches

Figure 10A) RS; B) IP sections in profile B.

An anomaly is observed in the IP cross-section at a depth of about 50 meters and distance of 70 to 120 meters from the ground surface (Figure 11A). At distance of 130 to 150 meters was observed a relatively high chargeability and is associated with gossan on the ground surface. At a distance of about 180 meters to 205 meters, there was a barite vein that extends towards the end of the profile with a slope of 85 degrees. In the RS section is observed a vein with Cu mineralization in the form of oxide at distance of about 90 to 120 meters, near the ground surface and extends towards the end of the profile with a slope of approximately 80 degrees (Figure 11B). The specific resistivity is

low in the northwestern part. A high anomaly has been observed in the southeastern part, which has shown high chargeability and specific resistivity. An anomaly can be seen in the initial part of the profile B and in the depth with a relatively high intensity in the metal factor section (Figure 11C). The border of this anomaly is marked with a dashed dot at depth of 40 meters from the trench site, at distance of 45 to 90 meters and at depth of less than 40 meters. This anomaly extends to a depth of about 65 meters with slope of about 80 degrees towards the southeast. This anomaly includes copper sulfide mineralization at the surface ground.

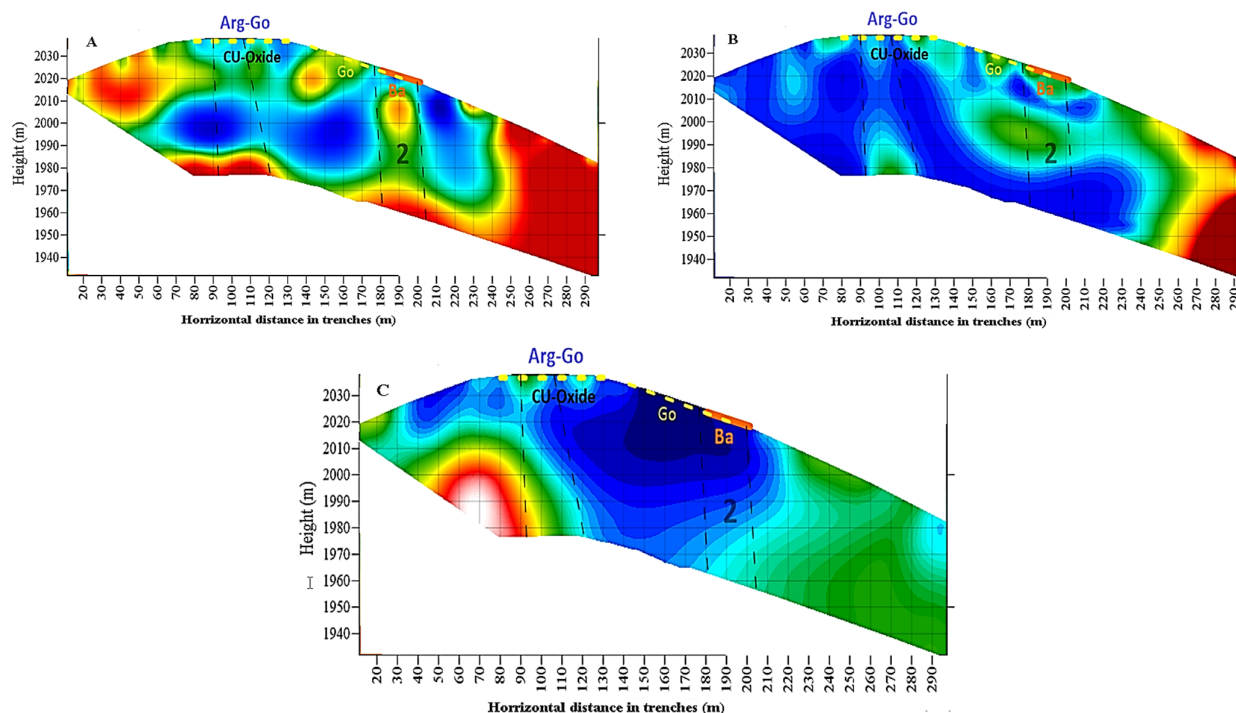


Figure 11A) IP section (Arg-Go: Argilite-Goethite; Go: Goethite; Ba: Barite; 2: The area corresponding to the surface trench on it); B) RS section; C) metal factor section in profile B.

The I_{S2} geochemical index and metal factor section were used along the trenches to determine the oxide and sulfide boundary and to suggest drilling points. At distance of 0 to 206 meters from the metallic factor section, there is a strong anomaly at depth of 0 to 40 meters (Figure 12). This anomaly is probably due to sulfide mineralization (electrode polarization) and indicates the beginning of the boundary of the sulfide zone [4, 16 and 31]. The three-dimensional model of induced polarization (IP), ordinary kriging technique and comparing those with drilling data showed that the

three-dimensional model (IP) is suitable in separating these two regions. The sulfide zone can be seen at a depth of less than 30 meters in the first part of the geophysical cross section in the Chogan area (confirmation is needed to drilling). There is also the possibility of water between the clay and marl particles (membrane potential) or bedrock with high electrode polarization. Therefore, it was used to the metal factor for integration due to clay and marl [32]. Surface anomalies are observed at distances of 40, 140 and more than 200 meters, as well as depth at all distances (0 to 206 meters).

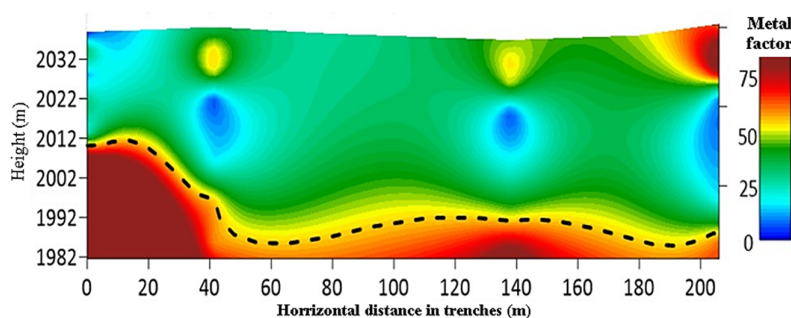


Figure 12. Cross-section of metal factor in the trenches path.

In Figure 13, the information of geochemical section of I_{S2} index (number1) and metal factor section (number2) is presented in the direction of trenches simultaneously. Anomaly is shown in the

deep part of the trenches and at distances of 40, 140 and 206 meters from the section of geochemical index I_{S2} . The resulting anomaly coincides with the anomalies observed at depth of less than 10 meters

in the metal factor section. In other words, increasing the value of I_{S2} index (more than 12) coincides with increasing value of metallic factor (more than 50) at depths less than 10 meters and at distances of 40, 140 and 206 meters.

There is a direct relationship between the Cu concentration data in the trenches (Figure 8) and geoelectrical data in the desired depth. The anomaly areas indicate the presence of mineralization. Absence of anomaly in the surface areas in the geoelectrical sections indicates oxide mineralization along the trenches and toward the depths indicates a sulfide zone. According to the similar behavior, there is a possibility of sulfide mineralization (electrode polarization) in the distance from 0 to 206 meters in depths. Therefore, the nearest possible sulfide zone is at distance of 15 meters and in the depth of about 27 meters in the geoelectric section in BH1. The possible separation boundary is shown by the dashed line and the suggested drilling named BH1 to BH4 in Figure 13.

The sulfide zone is located in borehole BH1 with a (depth of 120 meters) at a depth of 25 meters (Figure 14). The depths of sulfide zone in other drillings are shown in Table 3 and the average estimation error for the boundary of the oxide zone is 11%.

It determined the sulfur index in each trench, the graph of this index was placed on the profile of the geoelectric metal factor in the trench location, and the anomaly was identified based on these two methods in the trench location, and the assumed oxide and sulfide zone boundary was separated (Figure 13). Drilling was carried out at the location of the desired trenches according to Figure 13. The oxide (malachite) and sulfide (chalcopyrite) zones were separated in the core of drilling (Figure 14). This boundary was found to conform to the proposed geoelectric boundary (metal factor, Figure 13) and the error percentage was determined (Table 3).

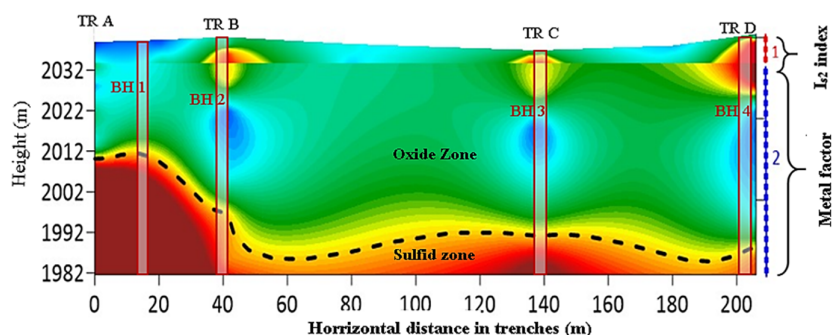


Figure 13. Combination of sulfur index section (I_{S2}) and metal factor section (Tr: Trench)

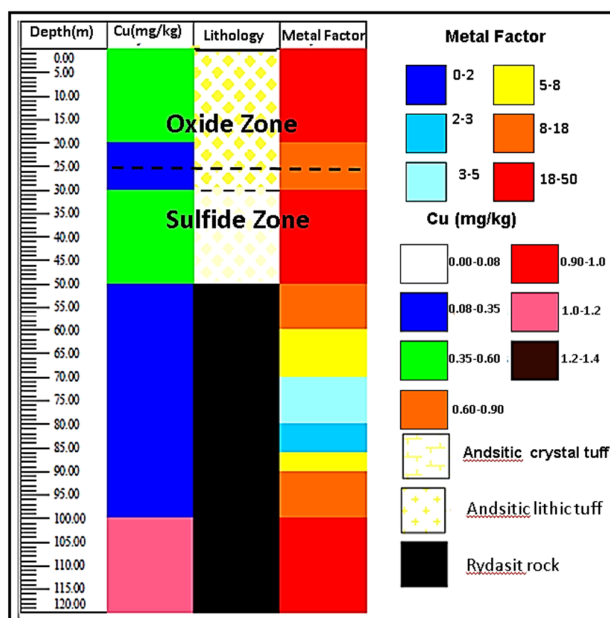


Figure 14. Boundary of oxide and sulfide zones in borehole BH1

Table 3. Suggested and actual oxide and sulfide boundary table and error percentage

Borehole	Depth (m)	Suggested depth(m)	True depth(m)	Error%
BH1	120	27	25	7.5
BH2	140	32	36	11
BH3	160	43	38	12
BH4	120	45	39	13

5. Conclusions

There are more than hundreds of vein copper mines in the north and northwest of the Markazi province and in cities such as Saveh, Tafarsh, Ashtian, Zarandiye and Delijan. Copper is extracted in the form of oxide (malachite). The maximum copper oxide depth of extraction is 50 meters. It is abandoned after the extraction of malachite. There are traces of chalcopyrite inside the copper oxides indicating a sulfide zone in the region. On the other hand, due to the limited thickness of copper veins and the high cost of drilling, miners are less likely to drill deeper than 50 meters.

In order to solve the above problems, an attempt has been made by using geochemical indicators (sulfur index), mineralogy index (chalcopyrite) and geophysical index (metal factor) which can confirm the presence of sulfide zone. The boundary of the oxide and sulfide zone is determined by combining the maps driven from the sulfur index and the metal factor and suggested drilling depth. Error was determined less than 12% based on the ratio of suggested depth by geochemical and metal factor method and actual sulfide zone depth in borehole,

Chogan copper oxide area was selected from Komijan city in the northwest of Markazi Province. However, drilling has been done to verify the validity of the determined model. We hope that the above subject will help other miners in the region and in general in the total Urmia-Dokhtar belt (including a large part of Iran) which, they do not neglect the extraction of copper sulfide in the depths.

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ارزیابی روش های ژئوشیمیایی و ژئوفیزیکی جهت تفکیک زون های اکسیدی و سولفیدی

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ارسال ۲۰۲۴/۰۶/۰۷، پذیرش ۲۰۲۴/۰۸/۲۵

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چکیده:

منطقه چوگان در غرب کمربند آتشفشانی ارومیه-دختر و قسمت توفی آن در شمال غرب استان مرکزی در شهر کمیجان واقع شده است. کانی‌زایی مس دارای تیپ رگه‌ای با طول ۲۶۰ متر و ضخامت متوسط ۴ متر و کانی‌زایی در رگه سیلیسی برشی شده صورت گرفته است. تعداد ۸۳ نمونه از سطح و ترانشه‌ها برای تعیین عیار ۱۰ عنصر آهن، آلومینیوم، کلسیم، باریم، گوگرد، منگنز، آرسنیک، سرب، روی و مس از منطقه برداشت گردید. به روش تحلیل عاملی و تأیید آن به روش خوشه‌ای مشخص شد که گوگرد، باریم، منگنز، آهن و مس عناصر ثانویه در توف‌های منطقه محسوب می‌شوند. کانی‌های تشکیل دهنده باریت و مالاکیت به شکل رگه‌ای و اکسیدهای آهن نظیر هماتیت و گوتیت به شکل گوسان هستند. معیارهای مختلف ژئوشیمیایی، مینرالوگرافی و ژئوالکتریکی با هدف تفکیک مناطق اکسیدی و سولفیدی و با تمرکز بر کانسار مس بررسی شد. در روش‌های ژئوشیمیایی به طریق تحلیل عاملی گوگرد و باریم عناصر بارز انتخاب و به روش جرم ملکولی گوگرد مازاد بر باریت جدا و شاخص گوگردی تعریف گردید. به روش مینرالوگرافی کانی کالکوپیریت و به روش ژئوفیزیکی Ip/RS شاخص فلزی تعیین شد. با تلفیق معیارها و شاخص‌های ذکر شده، عمق تقریبی جدایش زون اکسیدی از زون سولفیدی تعیین و نتایج حفاری، عمق‌های پیشنهادی را تأیید نمود.

کلمات کلیدی: زون های سولفیدی و اکسیدی، اکتشاف مس، تحلیل عاملی و خوشه ای، شاخص های ژئوشیمیایی و ژئوفیزیکی، چوگان استان مرکزی.