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"TOROUD", THE LATE MOTION FOR As-Sb BEARING Cu PRODUCTION FROM 2ND MILLENNIUM BC IN IRAN: AN ARCHAEOMETALLURGICAL APPROACH

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ABSTRACT

The interest in arsenic copper and its use in antiquity is on a speedy rise. The potential values of such commodity have drawn significant attention. According to many literatures that will be presented throughout this paper, there is great evidence. that real tin bronze replaced arsenic bronze during 2350-2200 B.C. in the central plateau of Iran. "Chah-Messi" copper mine could be a key point of such investigations. Indeed, multi-melange metallic outcrops made this region to a great metallogenic zone. Archaeometallurgical investigations based on geological survey in "Chah-Messi" copper mine in northern part of the central Iranian desert indicate that during the 2nd millennium BC ancient mining and metallurgy were carried out because of outcropping of hydrothermal copper mineralization. The main point of this work focuses on the characterization of the extractive slags with respect to the Cu-As-Sb bearing minerals.

Mineralogical-petrochemical studies have been carried out via reflected- and transmitted light microscopy including electron probe microanalyser (EPMA) to perform the analysis of the chemical composition of phases. Based on the results, the material proved to have high amount of Cu, CaO and iron oxide and low in MgO, MnO. Furthermore the result of this study indicated that the Chalcosite and covellite were the processed ore. Lauzonite (Cu-As-Sb) and domeykite (Cu-As) were the dominant Cu-As-Sb bearing minerals which could have the primary influence on the smelting processes and composition of extracted metal. Such characteristics are the hall mark of this region.

KEYWORDS: Archaeometallurgy, Copper, Slag Petrology, As-Sb Mineralization, Electron Probe Microanalysis, Chah-Messi, Toroud

1. INTRODUCTION

Investigations on the ancient mining and smelting of sulphide ores from the area between east Anatolia and north Mesopotamia-including Iranian plateau- demonstrated early historical evidences of metallurgy and pyro-technology in this region (Wertime, 1964). Accordingly, copper and copper alloys were prominent subjects for archaeometallurgical studies. The main impulse for this study is based on the suggestions was reported by Keesmann & Moreno Onorato (1999), De Ryck et al (2005) and Thornton & Rehren (2009).

Production and use of copper and copper alloys in Iranian plateau might have had their beginnings in the Neolithic site of "Ali Kosh" in the south west of Iran, where a rolled bead of native copper was found (Moorey, 1969; Pigott 1999; Thornton, 2009). The bead from "Ali Kosh" has been dated back to a period between the 8th and 7th millennium BC (Hole, 2000; Thornton, 2009). It was further specified that on the Iranian Plateau copper extracted technology had a local development and reported consecutive from beginnings of Bronze Age for each local (Dyson and Voigt 1989; Oudbashi et al., 2012). Ultimately, this brought to the emergence of industrial peripheries, disseminated in different parts of west and central Iran (Thornton, 2009). Archaeometallurgical investigations about copper in Iran have been reported for the most part with focus on mining and smelting technologies in different areas such as Lurestan, Kerman, Yazd, Khouzestan, Sistan and northern part of the central Iranian desert (Pigott et al., 1982; Hezarkhani and Keesmann 1996; Emami, 2005; Keesmann 2005; Thornton, 2009; Roustaei, 2012). Technological development of metallurgy may have happened by crossing the central desert from the west and southwest of the Zagros Range (in some part of today's Iraq) to the north and northeast of Iran, for instance the use and extraction of metals found in "Yarim Tappeh"(Mueller Karpe, 1990). This route might be identified as the copper path, that still exist in a large part of the south and central Iranian plateau with production remains and heaps of slags (Emami 2005; Frame, 2010). The association of the mines to archaeological settlements will be of great interest. It is an important criterion for the identification of ancient metallurgical activities and might also be a main clue for interpretation of analytical results. For instance, the presence of lead in the bronze objects from "Malian" (Pigott et al., 2003) or arsenic bearing copper from "Teppeh Yahya" and the arsenical coppers from "Talmessi" and "Messkani", close to "Anarak" - that might be related to "Arisman" area (Pigott 1999; Chegini, 2004) - are cases for linking the technical periphery to a settlement. Analytical studies of several cupreous objects belonging to the middle Bronze Age (3000 – 2000 BC) revealed that the main element is copper with variable amounts of Zn, Pb, As and Sn (Thornton et al 2002; Thornton and Ehlers, 2003). This diversity in elemental constituents reflects dissimilarity in the metallurgical process and in the fabrication of the objects, and raises the question of the source of economic ores. Recently investigations at Arisman proved that most of the slags from this site are copper smelting slags, which produced arsenical copper (Rehren et al., 2012). Indeed, Arisman is located closed to the important site of Sialk (3th millennium BC), but this site cannot be the main claim for metallurgical evidences in northeast of Iranian desert. Based on the previous literatures, arsenical copper had an important role on the Iranian plateau during 3th millennium BC (De Ryck et al 2005). Taking into account that arsenical copper had also been produced by adding arsenical iron (i.e. Speiss) to the copper matte (Marechal, 1985), so called roasting-reduction reaction. Does exist a sharp boundaries between accidental and experimental metallurgy in antiquity?

Recent publication about appearance of tin bronze in Eurasia deal with the question, concerning on the existence of different copper alloy as accidental metallurgy or even more experimental metallurgy (Radivojevic et al., 2013). The disappearance of the arsenic-copper alloy in some part of the Iranian plateau at the end of second millennium BC suggest that this alloy was a cultural alloy and their production must have an old tradition that preference these objects and was not haphazardly. Indeed, the beginning of metallurgy for making well known dictated arsenical alloy was accidental, but till end of the second millennium BC this made a tradition in some part of Iranian plateau. The know-how about co-smelting and direct reduction of metals is a consequence based on experimental metallurgy.

The precocious technologies of melting and smelting copper in Iran were definitely established during the Chalcolithic period in Tal-e Iblis (5500 – 3200 BC), as crucibles and slags have been excavated (Pigott, 1999; Frame, 2012). At this time, the smelting of copper ores could be identified through the appearance of impurities in the extracted metal, such as, for example, arsenic, and this gives early evidence of the use of arsenical copper (Frame, 2012). Due to the archaeometallurgical point of view, there are a few scientific reports from the metallurgical interest of the south central Iranian desert (Hezarkhani and Keesmann 1996; Matthews and Fazeli 2004; Momenzadeh 2004; Pernicka, 2004; Pigott, 1999a, 2004b; Schreiner et al., 2003). Furthermore, different researchers carried out with respect to the geoarchaeological surveys on the north Iranian Plateau, but some of the ancient mines located in the middle of the desert are still unknown. Their importance is also supposable due to the accessible route to some of the important archaeological sites and to the ancient mines in the northern part of the central desert (Thornton et al ., 2009; Roustaei, 2012).

The central zone of the Iranian desert is approximately 170,000 km^2, and it consists of sand and salt. There are diversified deposits of economic minerals, such as high amounts of copper, gold, silver, lead, antimony, zinc, nickel and chromites in this region. Toroud is the nearest and largest copper mine to “Tappeh Hissar” (4th millennium BC) that is located 120 km southeast of this site. As the recent surveying and expedition that reported by Roustaei (2012), the dates of the mining activities in the district Toroud-Moaleman-Damghan goes back to the Late Bronze/Iron age. But, his results and interpretations are based on comparative geoarchaeological clues. Publications with informative data concern on metallurgy and smelting of copper leave no doubt that by the Late Bronze Age, copper, lead and silver were locally produced in the central Iranian plateau (Wertime, 1964). The orogenic district of “Anarak” and “Nakhlak”, are known as the places with the earliest traces of metallurgy in Iran, as well as, in the Middle East. Many kinds of ore paragenesis come together as a regional polymetallic ore mineralization (Pigott, 1999). In the mineralization zone of Messkani – Talmessi – Anarak – Nakhlak, copper contains high amounts of arsenic and the main minerals are domeykite (Cu_3As) and algodonite ($Cu_{6\text{-}7}As$). Through the 5th and 4th millennium BC the indigenous copper metallurgy consisted of hammering, annealing, melting and reduction of oxide or carbonate ores to the metallic state, with the addition of several kinds of fluxes and additives such as hematite (Fe_2O_3) or calcite ($CaCO_3$). In the 4th millennium BC the technology of copper extraction had a spontaneous development that can be distinguished in four main methods (Pigott 1999; Thornton et al., 2002).

1) Knowing about sulphide ores
2) Addition of different metallic ores to the molten copper.
3) Reduction of antimony-bearing copper arsenics.
4) Reduction of sulpho-arsenides.
5) Arsenical sulphide and oxide ores are smelted together to produce arsenical copper so called "co-smelting process" (Lechtman and Klein 1999).

More that 96% of the active copper mines in Iran have an older use before starts to be economically exploited nowadays. All important Copper ore outcrops with ancient traces of exploitation occur in most parts of the Iranian plateau as illustrated in Fig. 1.

These copper outcrops tend to show that the organization of copper production and metallurgy has well developed manner along the different social and technological context in Iranian plateau.

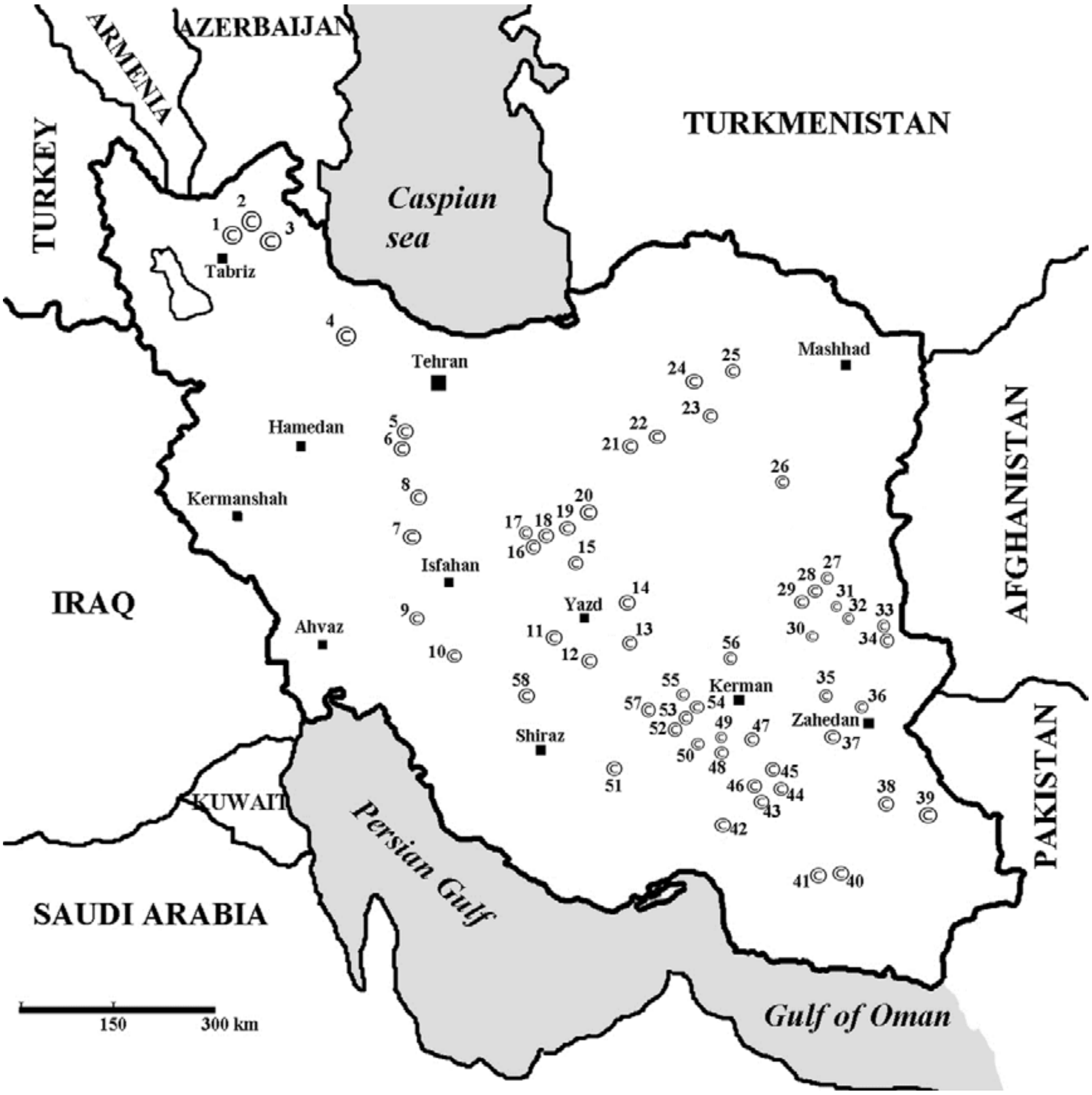

Figure 1. A map of ancient copper ore distribution and local name of the mines.

1. Sungun, 2. Anjert, 3. Mazraeh, 4. Dizejin, 5. Abbas abad, 6. Takht-e Chaman, 7. Ghamssar, 8. Veshnaveh, 9. Deh Madan, 10 Chanegah, 11. Kuht, 12. Tang-e Chenar, 13.Narigan, 14. Khoshumi, 15. Chah Palang, 16. Messkani, 17. Talmessi, 18. Talkhe, 19. Nakhlak, 20. Bagh Ghorogh, 21. Chah Messi, 22. Baghalu, 23. Rugero, 24. Biarjomand, 25. Damanjala, 26. Cheshmeh Gaz, 27. Kalat-e Ahani, 28. Kach, 29. Gazu, 30. Hoz-e Rias, 31. Mir-e Chash, 32. Shikast-e Sabz, 33. Darmian, 34. Lotfabad, 35. Chehel Kureh, 36. Haji Koshte, 37. Sian Gekul, 38. ChahDoost, 39. Sheikh Ahmad, 40. Mehjulu, 41. Ishpash, 42. Sheikh Aali, 43. Gerdukulu, 44. Kamadurn, 45. Tal-e Madan, 46. Baghara, 47. Chehel Narp, 48. Chahar Gonbad, 49. Deh Siahan, 50. Sarcheshmeh, 51. Kune Mess, 52. Chah Messi, 53. Lachah, 54. Darabidu, 55. Tezerg, 56. Chanuk, 57. Meydook 58. Jian

"Toroud" is also located near some important archaeological settlements: Sialk (3th millennium B.C.), Abbas-Abad (3th millennium B.C.) and Teppeh Hissar (4th Millennium B.C.). Ancient extractive metallurgy in this area can be clarified with a systematic investigation on the slag assemblage from this region. The scope of this study may be summarized as follow:

1. An experimental investigation of the extracted ores used for metallurgy in Chah-Messi which is also located in an archaeologically important triangle area in the northern part of the Iranian desert.

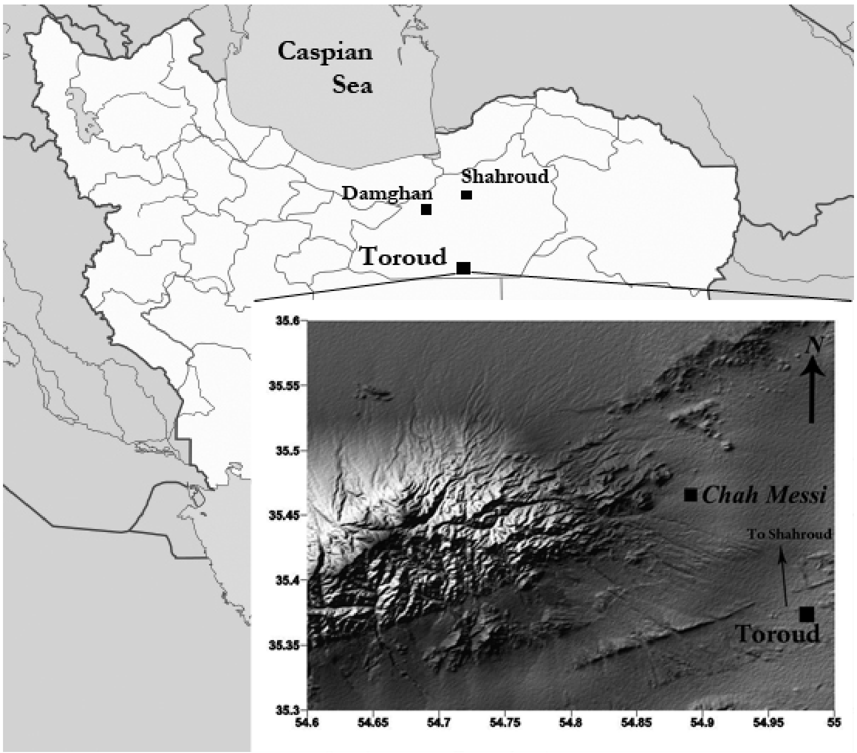

Figure 2. Geomorphological location of Toroud and Chah-Messi copper mine

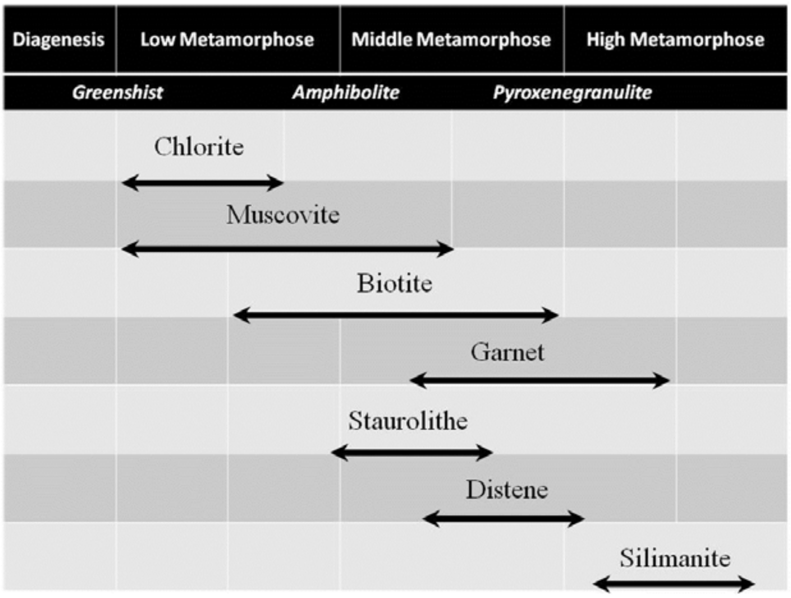

Figure 3. Mineralization sequence in Toroud area, according to geological field surveying

2. A possible connection between the high As-Sb technological residues (slags) and the provenance of the ores. The chemical composition of the ore from this region is more similar to the earlier related metallurgical evidences reported by De Ryck (De Ryck et al., 2005).

This is a preliminary report on an ongoing project and no archaeological studies have been carried out yet on the site. Archaeological studies are planned for the near future, but in this paper only the possible correlation of the mining area with the smelting residues has been investigated. This investigation could report some in-formations based on the chemical composition of the finds in this region for discovering a connection between north part of the Iranian plateau and Tarus-Antitarus orogeny in the western part.

V. Gordon Childe who placed metallurgical technology at the forefront, arguing on the roles of "itinerant metal smiths" and bronze production in the rise of social elites and complex societies. Childe was also one of the first to systematically argue for the diffusion of metallurgy from the Near East to the rest of Eurasia (Thornton and Roberts, 2009). The Investigations of the earliest known copper smelting evidences in the site of Belovode reviewed the question on the origins of metallurgy in this region. The recent archaeometallurgical investigation in Eurasia" describe the evolution, organization as well as the know-how of pyrometallurgical activities on early metals in the Balkan region (Radivojevic and Roberts, 2013).

According to this report four sites Jarmovac, Belovode, Gornja Tuzla and Plocnik have demonstrated the pyrometallurgical activities in east mediteranean region. On the other side Polychromic decoration on the broze objects such as Enkomi cup which is found in syprus is a significant objects from 1425 BC. As Giumlia Mair described, Enkomi cup describes clear Aegaen und Mycaenean conection (Giumlia Mair, 2012).

The importance of archaeometallurgical background between east mediteranean toward to Middle East is described based on the surveying projects that carried out by some of the most legendary twentieth century researchers of ancient technology (Cyril Stanley Smith, Ronald Tylecote, Frederick Matson, Radomir Pleiner, Beno Rothenberg, Robert Brill, and Theodore Wertime). Based on their investigations it suggests that the beginning of metallurgy can be reported along the district from Turkey to Iran and Afghanistan with respect to the evidence of ancient mining and metal production (Thornton, 2009). It is included that the beginnings of Old World metallurgy must have occurred in the ore-rich Taurus–Zagros highlands, and to understand the development of early metallurgy in this district, first of all it is necessary to understand the development of metallurgy in Turkey, Transcaucasian and Iran (Wertime 1973). Most important ancient centers of copper mining stretch from western Anatolia (Beycesultan 5th Millennium BC) to the metal-production center in Sialk central Iran (4500-4000 Millennium BC). The possible source of native copper were deposited in the copper belt district from Toroud in syprus (the same name as discussed in this paper) to Ergani Maaden (5th millennium BC) in anatolia toward to Nachlak-Anarak in central Iran. The place of mining was not accidental because copper ores appeared in a clear assortment on the earth based on their color. The huge outcrops of gray chalcosite and green malachite in Toroud-Iran had an appreciate sign of metallogeny in north part of Iran.

With an understanding of the possible connection between north and western part of Iranian plateau based on the chemical composition of the ores as well as slags, one can appreciate the possible breakthrough pyrotechnical developments.

2. GEOLOGICAL SETTING ON THE FIELD

Toroud is located in the middle of an important zone of metallurgical orogeny in central Iran. The geographical coordinates of this area are 35-36°N and 54-55.30°W (Fig.2). This site is closed to "Anarak" and "Nakhlak" Cu-Pb mineralization zone in the southern part (Hezarkhani and Keesmann, 1996; Keesmann, 2005; Stöllner ,2004) and in the northern part it is connected to the porphyry, Au, Zn and turquoise mineralization zone called "Baghu". The impregnation deposit in "Baghu" still has a high amount of Cu, based on its high quality turquoise in the hydrothermal mineralization zone (Hooshmandzadeh et al 1978). The important orogenies around this field are "Chah-Shirin", "Soukhte", "Toroud" and "Sahl", placed in east - west direction. Among them, "Chah-Shirin" is the highest peak with about 2350 m altitude from the sea level (Burnol 1968). Ancient metallurgical slags are disseminated across the mineralogical zone of "Toroud" – "Chah-Jam".

In the southern part of "Toroud" and "Chah-Shirin", the geological regime is restricted to a lower faulting system from tertiary sedimentation. Magmatic segregation is observed from the southern part to the northeast of this field. The earliest paragenesis in this field goes back to Precambrian while geological formations close to "Toroud" mainly belong to the eocean-oligocean (Foerster 1978). The main magmatic rocks on the basis of paleontological investigation are;

1. Trachyandesite/Andesite from Silurian.
2. Diorite/Granite/Granodiorite from Precambrian.
3. Andesite and Dacite from Eocen-Oligocean.

The major rock formations are Basalt/Andesite/Trachyandesite and Dacite which among them Andesite is the common rock in this field (Emami 2002). The metamorphosis grade is characterized from low to middle grade, based on the mineralogical paragenesis (Fig.3). The primary ore mineralization is chalcosite, covellite and secondary chalcopyrite. They occur as veins that formed lenses and disseminations. Copper, molybdenum, lead and zinc were also formed in association with porphyry magmatite as hydrothermal ore deposition.

3. ARCHAEOLOGICAL FINDS

The investigated area estimates a 30 x 30 km^2. Montan-archaeological evidences take account of 20 mines as well as residual smelting activities were practiced in 4 areas. The mining activities were not concentrated on a specific point and several separated locations were exploited in this region. It seems that the miners were challenged by the environmental conditions during their high days (Wesgerber and Hauptmann, 1988; Stöllner, 2004). The depth of the tunnels and the art of quarrying methods prove that the miners left the unit after definite time. Archaeometallurgical activities not only consist of smelting slags, but also relevant metallurgical accessories such as furnaces, crucibles, hammer stones and anvils.

3.1 Mining specifications

One of the most noticeable characteristics of this region is the azure blue color of the desert, due to the copper sulphate enrichment on the surface as vitriol. This effect was also an important indication for prospectors' economic reservoir in the past. The exploitation tunnels are in various directions and depths, which follow the ore body. The tunnels were dug parallel to the ore body (Figure 4a) or within the ore body (Figure 4b). Consequently, some of the tunnels were dug perpendicularly to the hydrothermal veins. Environmental conditions influenced the mining methods in this region. Topography, type of overburden, irrigation water, drainage, lighting and climate are important factors for an industrialized periphery in the past. In general, ancient mining methods had conventional developments in each region, andcan be logically used for classification of the mining techniques (Hauptmann et al., 2003; Stöllner, 2003). Water drainage and lighting were the main dilemmas the miners were confronted within this region. To solve the lighting problem, the miners decreased the depth of the tunnels to have enough natural light for working. Interestingly, the direction of the tunnels was oriented to the sun movements in this area (i.e. they were placed in inverse direction to the day light). Thedrainage of water in "Chah-Messi" was represented a great problem and the miners were often forced to abandon the shaft. The tunnels mainly quarried at the foot of the mountain. No places were mined on the top.

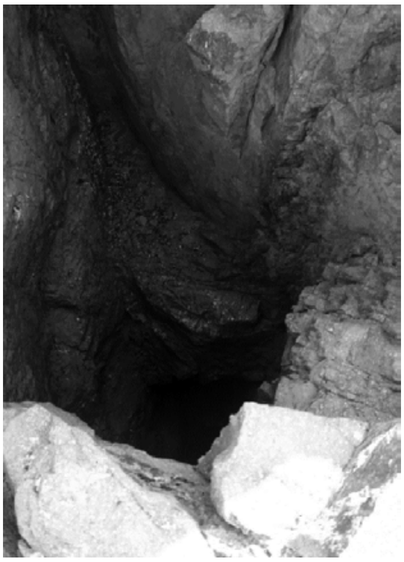

Figure 4a. The tunnels dug perpendicular to the ore body

Figure 4b. The tunnels dug parallel to the ore body

3.2 *Metallworking tools*

Hammer stones (Fig. 5), grinder and crucibles belong to the archaeometallurgical signs that should be considered for the reconstruction of the mining technology in this site. The methods used in exploitation of the ore from the source rock and the gangue in antiquity depended both on the texture and the hardness of the stones (Weisgerber 1990). These tools show typical shapes, designed to achieve the best results. The tools found in Chah-Messi have various sizes and shapes. They are approximately 5-11 cm long and ca. 6-15 cm in diameter with a spherical, globular head. These stone tools are made of diorite and gabbro. The sides of these stones are concave, perhaps because of long time usage.

Figure 5. Some examples of hammer stones that excavated from the Toroud closed to Chah-Messi copper mine

3.3 *Slag's typology and research strategy*

The slags from Chah-Messi are classified with respect to their external (color, weight and texture) and internal characteristics (Hauptmann 1985). The slag also contained remains of coal, ore or even furnace wall. According to their external characteristic the slags are classified as follows (Figure 6a & b):

- ✓ Fluid slags with macroscopic signs of flow on the surface and dense structure;
- ✓ Flat slag with macroscopic remains of coal in the texture
- ✓ Porous slag.

The color of the slags from Chah-Messi varies from black to dark brown and brown to grey. Internal characteristics of the slags were interpreted by petrochemical- microscopical investigation (Keesmann et al., 1983; Hauptmann 1985; Hauptmann 2007).

Mineralogical- chemical investigation on the slags was carried out by optical microscopy, using both transmitted andreflected light, as well as utilizing the electron probe micro analyser on the crystalline phases to determine major, minor and trace elemental constituents (Ströbele 2010). To achieve more complete results, a piece of ore collected on the site was also examined. The samples descriptions are given in the table1 which is mentioned in I, II, III, IV (Table 1). The weights of the slags are between 1100 – 3700 g.

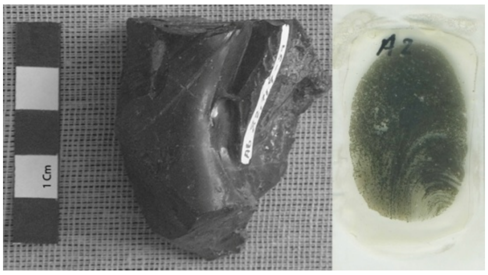

Figure 6a. Typical Vitreous slag from Toroud, bright brown to dark green, low porosity

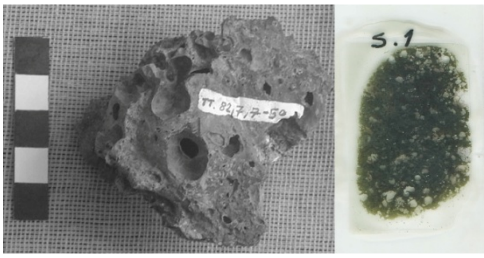

Figure 6b. Typical slags Non vitreous, light green, with holes (right)

Table 1 Sample description from investigated site

Sample Number	Location	Date	External Typology
I. Compact, dense slags with no macroscopically fluid texture			
2865	Chah-Messi Peak	ca 1150 BC	Vitreous, bright brown to dark green, low porosity
2888, 2889, 2868, 2867, 2864	Chah-Messi Mine	ca 1150 BC	Vitreous, dark brown to light brown
1873	Mazrae	ca 1100 BC	Non vitreous, light green, with holes
II. Compact, dense slags with macroscopically fluid structure			
2868, 2589, 2860, 2861	Chah-Sukhte Peak	ca 1170 BC	Vitreous, many stone fragments, dark grey to reddish
2872	Mazrae	ca 1100 BC	Low porosity, brown, with metallic droplets within the texture
III. Porous slags			
2871, 2862, 2863	Chah-Sukhte Peak	ca 1170 BC	Furnace wall, clayey pipes, dark brown to reddish, porous, with gang stone and another accessories
IV. Ore			
2892	Chah-Messi Mine		Chalcosite & covelline (observed microscopically)

4. RESULTS

4.1 Chemical analysis of material

It has not been possible to date all materials and objects, because many of them have been collected from surface surveying. As main point of this investigation, only the slags from around Chah-Messi mine have been sampled. Dating of the materials has not been carried out but the sampling zones are dated back to ca 110-1170 BC based on the archaeological interpretation on and around this region (Tosi, 1989; Maurer Thrinkhaus, 1686a, 1989b; Roustaei, 2012). Consequently, mining activity in this periphery must have been a common tradition in the late Bronze Age and in the early Iron Age (Roustaei, 2012). According to the microchemistry of the slags, the common phases are silicate- oxide- sulphide and metallic phases; include metals and metal-arsenide and metal-antimonite (Table 2). The major elements in the slag texture are SiO_2, Al_2O_3, FeO, MgO and CaO. The minor elements are As, Sn, Na and K. Mn, Ti and Zn were detected as trace elements responsible for the type of orogeny and the formation sequence of deposits. Through the chemical analyses, it has been proved that with an increasing content of CaO and MgO, the sum of $SiO_2+Al_2O_3$ also increased. On the other hand the amount of FeO depends largely on the sum of $SiO_2+Al_2O_3$ and with the increase of SiO_2, FeO amount decreases. The chemical analysis led to the classification of the finds on the bases of their major components into four thermodynamic systems (Craddock 1986);

1. $CaO – Al_2O_3 – FeO$
2. $SiO_2 – Al_2O_3 – FeO$
3. $SiO_2 – Al_2O_3 – CaO$

4. SiO_2 – CaO – FeO

According to the correlation between some of their related components, the oxides will add together (Kessmann et al.,1982). According to this diagram four different groups of slag were clustered, based on their main chemical components (Fig. 7).

<u>Groups I:</u> pyroxene rich slag(sample 2888 & 2889). The chemical composition of pyroxene shows high amounts of SiO_2- and (FeO+ MgO+ MnO). Pyroxenes show a variable composition with different weight proportion of elements that their ranges are about 27.73 – 50.54 wt% for FeO; 11.24 – 22.76 wt% for MgO and < 1 wt% for MnO.

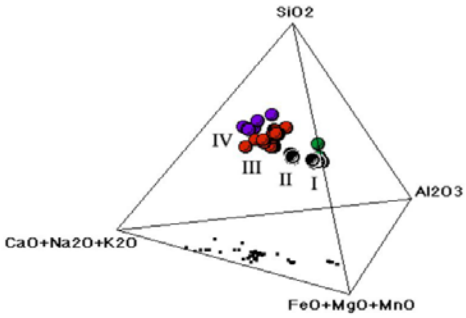

Figure 7. Chemical composition of the slag in system SiO2-Al2O3-CaO-FeO. Amount in mole %
Black point analyses are the samples from Mazraee area. Green point analyses are the samples from Peak Tschah-Suchteh. Blue point analyses are the samples from peak Tschah-Messi. Red point analyses are from Chah-Messi Mine

Table 2. Chemical analysis of silicates in the samples

Sample 2888 in w %

Anal. No:	Na_2O	SiO_2	K_2O	MnO	P_2O_5	Al_2O_3	MgO	CaO	FeO	S	TiO_2	CuO	SnO_2	BaO	ZnO	∑
1111	0,60	32,86	0,83	0,03	0,15	6,78	0,92	15,96	13,23	0,02	0,94	0,05	0,02	25,92	0,41	98,70
1112	0,85	33,14	1,58	0,03	0,10	6,55	0,67	11,28	14,63	0,16	1,31	0,02	0,00	27,11	0,36	97,79
1113	0,67	30,36	0,73	0,10	0,10	7,16	0,78	15,07	13,27	0,01	1,11	0,00	0,00	28,79	0,40	98,53
1114	0,89	32,84	1,51	0,10	0,13	7,15	0,63	11,08	14,10	0,15	1,24	0,17	0,01	27,54	0,41	97,94
1115	0,77	33,11	1,33	0,02	0,12	7,38	0,64	11,11	13,89	0,15	1,31	0,16	0,00	27,88	0,33	98,20
1116	0,85	32,03	1,58	0,05	0,14	7,19	0,64	11,54	14,41	0,26	1,10	0,31	0,00	27,68	0,16	97,96
1117	0,32	33,17	0,79	0,01	0,06	7,60	0,71	11,54	13,04	0,03	1,30	0,13	0,00	30,27	0,44	99,41
1118	0,82	32,32	1,62	0,00	0,14	6,95	0,60	11,28	13,65	0,10	1,22	0,11	0,00	28,03	0,29	97,13
1119	0,85	31,99	1,56	0,04	0,18	6,86	0,67	11,18	14,31	0,11	1,34	0,01	0,00	27,85	0,29	97,23
1120	1,11	37,10	0,63	0,00	0,05	3,04	2,03	24,38	13,87	0,01	0,49	0,00	0,02	10,92	0,72	94,37
1121	0,89	35,79	0,60	0,10	0,06	3,71	1,57	18,71	13,48	0,01	0,84	0,03	0,03	20,69	0,52	97,01
1122	0,80	33,45	1,16	0,15	0,13	7,34	0,57	10,50	14,22	0,10	1,35	0,00	0,00	28,15	0,46	98,37
1123	0,78	0,60	1,43	0,00	0,13	6,98	0,65	10,69	14,11	0,14	1,32	0,11	0,00	27,97	0,36	97,76
1124	0,57	0,85	2,20	0,02	0,15	6,08	0,51	10,44	15,10	0,03	1,42	0,08	0,00	30,40	0,33	99,25
1125	0,40	0,67	0,77	0,02	0,13	6,70	0,68	11,56	13,36	0,03	1,41	0,00	0,02	29,51	0,33	97,92
1126	0,74	0,89	1,30	0,13	0,14	6,10	0,66	10,90	15,68	0,17	1,30	0,08	0,00	27,56	0,21	97,43
1127	0,98	0,77	0,87	0,00	0,09	2,25	0,21	10,23	14,61	0,17	2,03	0,23	0,00	36,45	0,22	99,59
1128	0,85	0,85	1,45	0,08	0,12	7,11	0,65	10,64	14,65	0,15	1,37	0,07	0,02	27,71	0,24	97,94
1129	0,31	0,32	0,66	0,03	0,05	15,07	0,49	6,87	8,25	0,03	1,40	0,14	0,00	32,16	0,14	98,83
1130	0,50	0,82	0,67	0,00	0,08	5,30	0,91	15,23	13,47	0,02	1,22	0,00	0,00	25,27	0,46	96,87
1131	0,80	0,85	1,40	0,04	0,13	7,06	0,65	10,64	14,99	0,12	1,28	0,00	0,00	27,64	0,36	97,05
1132	0,37	0,00	0,71	0,13	0,17	5,07	0,60	10,00	14,80	0,02	1,57	0,00	0,00	29,14	0,52	96,71
1133	0,44	1,11	0,91	0,02	0,15	7,14	0,63	11,17	14,16	0,00	1,38	0,01	0,00	28,17	0,23	97,24
1134	0,74	0,89	1,43	0,08	0,12	7,09	0,68	10,91	14,59	0,16	1,34	0,34	0,02	26,98	0,27	97,56
1135	0,75	0,77	1,39	0,03	0,16	7,06	0,67	10,44	14,04	0,13	1,45	0,00	0,00	27,38	0,33	97,19

Sample 2889 in w %

Anal. No:	Na_2O	SiO_2	K_2O	MnO	P_2O_5	Al_2O_3	MgO	CaO	FeO	S	TiO_2	CuO	SnO_2	BaO	ZnO	∑
1136	0,19	33,05	0,78	0,09	0,00	20,13	0,19	2,80	7,05	0,12	1,45	0,52	0,02	35,39	0,02	101,81
1137	0,12	35,61	1,19	0,00	0,00	24,59	0,10	0,50	2,95	0,01	1,39	0,09	0,02	36,70	0,02	103,30
1138	0,72	33,46	1,27	0,10	0,16	5,10	0,75	11,90	15,54	0,20	1,42	0,10	0,00	26,05	0,41	97,17
1139	0,62	33,09	1,16	0,01	0,13	2,47	0,95	12,99	20,09	0,09	1,24	0,20	0,04	24,09	0,40	97,58
1140	0,10	33,96	0,41	0,06	0,01	27,23	0,06	0,16	1,27	0,07	1,55	0,39	0,04	38,67	0,00	104,00
1141	0,78	33,23	1,59	0,11	0,08	7,14	0,62	10,02	15,12	0,09	1,40	0,05	0,00	27,01	0,29	97,52
1142	0,81	33,04	1,88	0,00	0,13	7,26	0,65	10,38	14,14	0,08	1,36	0,01	0,02	27,66	0,32	97,74
1143	0,83	33,01	1,46	0,05	0,16	7,16	0,62	10,34	15,15	0,07	1,33	0,00	0,00	26,71	0,34	97,23
1144	0,38	34,05	0,89	0,02	0,11	7,31	0,71	11,70	13,27	0,01	1,46	0,00	0,00	27,89	0,19	97,99
1145	0,44	34,78	1,15	0,07	0,13	8,78	0,67	8,52	14,34	0,06	1,46	0,04	0,00	27,81	0,49	98,74
1146	0,79	33,43	1,34	0,00	0,12	7,10	0,64	9,93	14,49	0,06	1,42	0,10	0,03	27,02	0,32	96,79
1147	0,75	33,84	1,27	0,02	0,18	2,72	0,84	12,90	17,10	0,08	1,39	0,04	0,00	24,81	0,31	96,25
1148	0,75	33,72	1,48	0,06	0,15	7,23	0,66	10,29	14,21	0,06	1,36	0,05	0,03	27,43	0,31	97,77
1149	0,81	33,89	1,48	0,07	0,15	7,30	0,67	9,49	14,24	0,07	1,35	0,04	0,01	27,02	0,26	96,85
1150	0,64	33,45	1,19	0,00	0,16	6,97	0,64	10,45	14,77	0,13	1,34	0,00	0,00	27,69	0,42	97,85

1151	0,15	33,73	0,88	0,06	0,05	22,28	0,17	1,99	4,69	0,03	1,50	0,05	0,00	36,06	0,21	101,83
1152	0,76	33,90	1,34	0,05	0,12	5,00	0,74	11,42	15,26	0,10	1,50	0,05	0,02	26,46	0,18	96,90
1153	1,02	33,51	1,57	0,02	0,13	3,78	0,66	11,64	17,01	0,16	1,37	0,03	0,00	25,94	0,15	97,00
1154	0,98	33,22	1,69	0,00	0,09	5,10	0,71	11,09	15,67	0,15	1,40	0,01	0,04	26,00	0,34	96,48
1155	0,72	33,22	1,00	0,06	0,13	4,05	0,81	12,76	17,32	0,12	1,49	0,17	0,00	24,48	0,47	96,80
1156	0,18	6,99	0,06	0,01	0,00	0,35	0,03	0,30	60,46	0,84	0,00	6,99	0,00	0,06	0,94	77,21
1157	0,79	32,78	1,38	0,06	0,11	7,21	0,71	10,24	14,44	0,12	1,42	0,20	0,01	27,63	0,30	97,39
1158	5,13	49,60	0,51	0,07	0,44	1,03	3,07	3,34	8,43	0,54	0,22	0,00	0,00	2,45	0,22	75,04
1159	0,95	25,07	1,76	0,00	0,04	8,26	0,38	8,63	10,77	0,07	1,65	0,00	0,00	29,58	0,32	87,47
1160	0,78	33,18	1,65	0,02	0,12	7,18	0,63	10,62	13,37	0,05	1,48	0,01	0,00	26,90	0,36	96,33

Sample 2865 in w %

Anal. No:	Na_2O	SiO_2	K_2O	MnO	P_2O_5	Al_2O_3	MgO	CaO	FeO	S	TiO_2	CuO	SnO_2	BaO	ZnO	∑
1161	0,35	42,58	0,02	0,25	0,02	6,65	0,87	18,49	25,10	0,00	0,46	0,02	0,00	0,00	0,22	95,02
1162	0,30	42,47	0,00	0,14	0,15	7,36	2,55	18,35	22,33	0,01	0,45	0,07	0,03	0,00	0,25	94,45
1163	0,32	41,37	0,04	0,30	0,22	7,59	1,19	17,88	23,45	0,00	0,71	0,51	0,00	0,04	0,12	93,74
1164	4,11	47,32	3,23	0,30	0,27	10,32	0,02	17,74	9,81	0,00	0,36	0,20	0,01	0,42	0,67	94,79
1165	1,14	44,83	1,14	0,30	0,19	8,30	1,64	16,31	19,87	0,00	0,45	0,19	0,01	0,11	0,19	94,67
1166	2,54	49,82	2,38	0,30	0,21	11,48	0,12	13,37	11,94	0,00	0,30	0,12	0,00	0,33	0,28	93,18
1167	0,17	86,79	0,02	0,00	0,00	0,69	0,01	0,28	0,33	0,02	0,01	10,15	0,00	0,00	0,00	98,48
1168	0,21	44,55	0,01	0,22	0,20	6,73	4,95	18,84	17,93	0,00	0,64	0,09	0,01	0,00	0,08	94,47
1169	0,68	48,39	0,56	0,39	0,06	2,21	1,65	24,95	12,91	0,01	0,10	0,21	0,00	0,00	0,14	92,26
1170	1,09	49,15	1,06	0,31	0,07	3,62	2,23	22,55	12,40	0,01	0,15	0,33	0,01	0,07	0,20	93,26
1171	0,05	50,34	0,04	0,34	0,02	0,17	2,52	26,85	12,39	0,00	0,05	0,38	0,00	0,05	0,00	93,19
1172	11,37	65,87	0,02	0,06	0,00	20,68	0,02	0,87	0,04	0,00	0,00	0,00	0,01	0,05	0,02	99,00
1173	0,37	49,29	0,51	0,28	0,09	1,64	1,48	27,55	10,61	0,00	0,13	0,10	0,00	0,00	0,23	92,27
1174	0,24	12,18	0,07	0,41	0,13	1,63	2,19	11,41	31,46	0,06	0,00	11,19	0,04	0,24	0,07	71,32
1175	0,31	43,36	0,02	0,25	0,04	5,96	3,50	17,94	21,39	0,00	0,45	0,17	0,00	0,00	0,18	93,57
1176	0,09	97,96	0,04	0,03	0,03	0,20	0,01	0,02	0,00	0,00	0,10	0,00	0,00	0,00	0,09	98,56
1177	0,41	30,14	0,11	0,21	0,15	5,33	1,70	13,86	16,25	0,00	0,41	0,39	0,01	0,03	0,05	69,04
1178	1,92	46,78	1,44	0,23	0,20	8,96	1,49	14,27	17,35	0,00	0,41	0,21	0,01	0,07	0,33	93,68

Sample 2868 in w %

Analyse No.	Na2O	SiO2	K2O	FeO	Cl	F	MgO	CaO	MnO	TiO2	Al2O3	Cr2O3	BaO	∑
1179	0,01	38,91	0,03	26,20	0,01	0,00	5,71	7,73	1,21	0,03	21,81	0,09	0,15	101,89
1180	0,00	38,96	0,00	26,32	0,00	0,05	5,50	7,54	1,48	0,04	21,60	0,06	0,04	101,59
1181	1,65	40,54	1,88	17,38	0,97	0,00	9,77	10,76	0,09	1,25	12,15	0,13	0,20	96,77
1182	1,78	40,73	2,02	17,52	1,02	0,18	9,85	11,13	0,11	1,08	12,82	0,00	0,05	98,28
1183	8,13	61,55	0,33	0,27	0,00	0,12	0,00	5,49	0,06	0,00	23,90	0,03	0,26	100,14
1184	0,02	38,87	0,01	27,36	0,02	0,00	6,39	6,00	1,38	0,01	21,37	0,09	0,00	101,51
1185	0,03	38,99	0,03	26,85	0,02	0,00	6,17	5,64	1,62	0,01	21,34	0,09	0,00	100,78
1186	0,00	36,22	9,17	18,04	0,80	0,46	12,96	0,03	0,08	3,59	13,97	0,01	0,94	96,27
1187	0,01	36,24	9,39	18,89	0,98	0,72	12,53	0,00	0,00	3,38	14,14	0,08	1,12	97,48
1188	0,01	36,50	9,47	18,65	1,01	0,52	12,81	0,09	0,04	3,33	14,33	0,00	0,20	96,95
1189	8,34	61,18	0,24	0,05	0,01	0,11	0,01	5,05	0,00	0,03	23,00	0,00	0,07	98,09
1190	0,02	36,09	9,33	18,67	0,77	0,55	12,94	0,00	0,08	3,51	14,21	0,10	1,06	97,32
1191	0,01	36,30	9,26	18,73	0,79	0,51	12,66	0,01	0,08	3,62	14,03	0,00	1,14	97,14
1192	8,43	61,06	0,27	0,36	0,01	0,00	0,20	5,38	0,01	0,01	23,15	0,00	0,00	98,88
1193	0,10	35,77	8,41	17,72	0,78	0,37	13,12	0,23	0,09	3,59	14,36	0,07	0,79	95,39
1194	1,67	39,61	1,90	18,65	1,11	0,25	9,08	11,19	0,05	1,28	12,93	0,00	0,08	97,80
1195	1,64	40,45	2,01	18,84	1,07	0,17	9,46	11,16	0,04	1,36	12,26	0,06	0,00	98,52
1196	1,04	32,21	1,65	14,54	1,05	0,12	6,13	9,07	0,14	0,94	10,09	0,12	0,22	77,32
1197	8,25	60,26	0,38	0,03	0,01	0,05	0,00	4,79	0,00	0,04	22,98	0,02	0,00	96,82
1198	8,68	62,32	0,35	0,02	0,01	0,02	0,00	4,37	0,02	0,01	23,20	0,03	0,12	99,14
1199	8,67	63,41	0,37	0,12	0,00	0,00	0,00	4,11	0,02	0,02	22,98	0,00	0,00	99,69
1200	1,58	37,04	1,54	15,83	0,87	0,34	8,41	9,79	0,09	1,22	11,53	0,04	0,04	88,31
1201	1,74	40,39	1,91	18,04	1,05	0,27	9,58	11,17	0,14	1,42	12,18	0,07	0,03	97,99
1202	1,14	62,38	13,88	0,15	0,01	0,00	0,02	0,02	0,00	0,00	18,68	0,10	2,75	99,13
1203	0,26	29,18	0,16	27,73	0,13	0,06	13,17	0,44	0,05	0,03	14,10	0,02	0,01	85,33
1204	4,63	45,23	0,57	3,68	1,02	0,13	1,34	10,52	0,02	0,01	20,65	0,08	0,12	87,99
1205	5,76	49,98	0,58	0,17	1,16	0,00	0,03	12,98	0,05	0,00	24,17	0,03	0,12	95,02
1206	1,52	40,73	1,93	16,05	1,05	0,20	10,31	11,17	0,04	1,35	12,25	0,00	0,16	96,76
1207	5,82	50,22	0,47	0,27	1,25	0,00	0,02	12,52	0,05	0,02	23,05	0,01	0,04	93,74
1208	5,66	49,43	0,61	0,16	1,41	0,00	0,05	11,99	0,05	0,01	22,92	0,02	0,00	92,30
1209	1,69	41,64	1,92	16,49	0,96	0,40	10,76	11,07	0,20	1,56	11,67	0,09	0,01	98,46
1210	1,68	41,13	1,82	16,33	0,74	0,21	10,84	11,36	0,14	1,20	12,00	0,14	0,03	97,61

Sample 2872 in w%

Analyse No.	Na2O	SiO2	K2O	FeO	Cl	F	MgO	CaO	MnO	TiO2	Al2O3	Cr2O3	BaO	∑
1211	1,56	41,53	1,76	16,21	0,67	0,20	11,34	11,40	0,13	1,11	11,87	0,09	0,00	97,87
1212	1,80	41,08	1,97	16,14	0,76	0,31	10,65	11,40	0,11	1,37	12,69	0,14	0,00	98,42
1213	0,00	38,96	0,01	25,53	0,00	0,00	6,41	6,82	1,45	0,02	22,14	0,05	0,00	101,39
1214	5,22	54,61	0,19	0,27	0,00	0,00	0,00	10,86	0,03	0,03	27,85	0,03	0,00	99,09

1215	0,01	38,94	0,00	26,15	0,00	0,13	6,16	7,25	1,37	0,08	21,72	0,03	0,14	101,99
1216	0,00	0,06	0,00	50,54	0,00	0,00	1,04	0,27	0,08	43,55	0,13	0,43	0,00	96,10
1217	0,00	37,91	0,01	26,48	0,00	0,00	6,32	7,12	1,42	0,10	21,60	0,01	0,07	101,04
1218	0,00	0,00	0,00	49,62	0,00	0,00	1,26	0,00	0,15	48,67	0,05	0,13	0,00	99,88
1219	0,02	39,17	0,00	25,80	0,00	0,00	6,11	7,93	1,55	0,04	21,82	0,05	0,00	102,48
1220	0,04	52,50	0,02	24,01	0,00	0,16	22,76	0,29	0,48	0,05	1,59	0,00	0,00	101,89
1221	0,51	47,24	0,03	7,48	0,00	0,00	13,00	19,99	0,16	0,16	1,86	0,00	0,00	90,43
1222	5,82	55,81	0,19	0,02	0,00	0,00	0,00	10,17	0,02	0,01	27,75	0,01	0,02	99,82
1223	0,55	64,16	15,69	0,00	0,00	0,00	0,00	0,05	0,00	0,00	19,03	0,04	0,78	100,30
1224	6,39	56,94	0,24	0,08	0,00	0,09	0,02	9,25	0,02	0,00	26,95	0,00	0,00	99,98
1225	0,60	63,98	15,69	0,06	0,00	0,00	0,00	0,10	0,00	0,00	18,86	0,00	0,69	99,98
1226	6,57	57,40	0,32	0,04	0,00	0,00	0,00	8,73	0,00	0,01	26,52	0,06	0,07	99,72
1227	0,67	63,69	15,59	0,05	0,00	0,00	0,00	0,03	0,00	0,00	18,75	0,03	0,85	99,66
1228	6,53	57,61	0,37	0,11	0,01	0,00	0,03	8,47	0,00	0,00	26,27	0,00	0,00	99,40
1229	0,47	64,54	15,70	0,02	0,00	0,13	0,00	0,02	0,06	0,01	18,55	0,08	0,83	100,41
1230	6,13	56,88	0,27	0,20	0,00	0,00	0,20	9,24	0,00	0,02	26,53	0,06	0,00	99,54
1231	0,53	64,09	15,81	0,01	0,00	0,00	0,01	0,00	0,00	0,01	18,86	0,06	0,65	100,03
1232	6,40	56,42	0,19	0,07	0,00	0,05	0,01	9,33	0,03	0,01	26,99	0,00	0,00	99,50
1233	0,51	63,77	15,95	0,00	0,00	0,27	0,00	0,03	0,01	0,00	18,91	0,08	0,52	100,05
1234	6,31	56,88	0,29	0,05	0,01	0,00	0,00	9,08	0,01	0,02	27,04	0,04	0,00	99,75
1235	0,68	64,34	15,63	0,00	0,00	0,05	0,02	0,04	0,04	0,00	18,67	0,00	0,73	100,19
1236	0,01	53,14	0,01	23,32	0,00	0,02	22,90	0,29	0,69	0,02	1,05	0,06	0,00	101,51
1237	0,02	52,55	0,00	23,78	0,00	0,00	22,29	0,31	0,69	0,05	1,39	0,06	0,13	101,27
1238	5,40	54,34	0,24	0,11	0,00	0,00	0,01	11,26	0,04	0,04	28,69	0,05	0,03	100,22
1239	0,00	52,28	0,00	23,63	0,00	0,06	22,45	0,35	0,60	0,02	1,66	0,02	0,00	101,08
1240	0,00	51,26	0,01	29,63	0,01	0,00	18,24	0,47	0,53	0,06	1,21	0,11	0,05	101,56
1241	0,03	51,04	0,01	28,46	0,00	0,03	18,53	0,40	0,41	0,05	1,22	0,00	0,11	100,29
1242	0,00	51,39	0,00	28,75	0,00	0,00	18,87	0,65	0,65	0,08	0,84	0,00	0,00	101,22
1243	0,01	51,61	0,00	29,27	0,01	0,00	18,77	0,48	0,54	0,09	0,78	0,05	0,00	101,62
1244	0,03	48,31	0,00	27,34	0,01	0,10	17,03	0,49	0,56	0,07	1,64	0,08	0,00	95,66
1245	1,12	40,16	1,88	16,80	0,34	0,50	9,42	11,50	0,08	1,82	13,09	0,13	0,00	96,83

The Fe/Mg ratio leads to the formation of ferossilite rich orthopyroxene. As it is illustrated in Fig. 8, the CaO contents are not so high in this case.

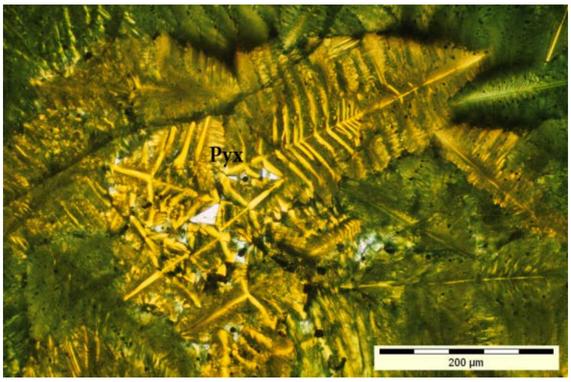

Figure 8. Diopside // to c axes in the glassy matrix. Sample 2867, x20-2.pol-reflected light-dark field

Group II: this group is characterized by CaO content more than group I (sample 2872, 2868 and 2871). The chemical-mineralogical composition induces the formation of pigeonite and augite. The samples show 5.66-27.38 wt% FeO; 6.17-13.12 wt% MgO, and 0.1-1.2 wt% MnO.

Group III: CaO content is also high enough to form hedenbergite-pyroxene in this group (samples 2888 and 2889). Due to the increasing amount of CaO, the first mineral produced is clinopyroxene. Clinopyroxene is rounded and with extended surface. The chemical analyses of pyroxenes show the composition ca. 7.05-60.46 wt% FeO, < 3.07 wt%MgO and 11.09-24.38 wt% CaO. In this group the increasing CaO is responsible for the melilite formation.

Group IV: this group is characterised by a high amount of CaO. The CaO content is high enough to form melilite, and this phase is optically observed in a few samples. The CaO constituent varies between 14.27-26.85 wt%, and the FeO content is very low compared to other samples. In all cases the amounts of FeO were high enough for clinopyroxene, feldspar and spinelle formation.

4.2 *Petro-chemical investigations of the slag*

Mineralogical investigation on the slag textures was revealed many crystalline phases in different thermodynamically stability within the matrixin different mineralogical conditions. Clinopyroxene is a mineral commonly detected in the samples. The crystals show varieties of habits and structures. Normally they are prismatic and stretched out parallel to the [001] (Fig. 8). According to the petrographic observation, it is lucid that in all areas where clinopyroxene was crystallized, quartz and melilite (Åkermanite) mostly formed as relict of tiny fragmentations (Fig. 9).

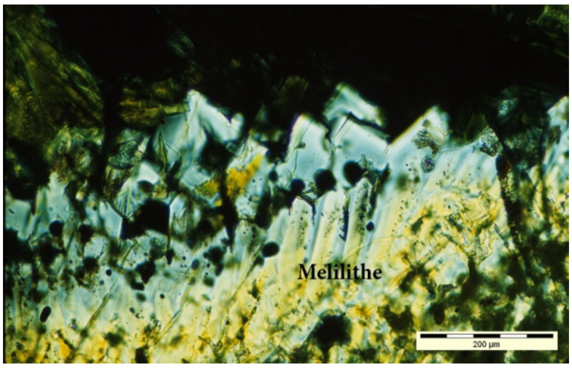

Figure 9. Melilite with hypidiomorph structure. Sample 2865, x20-2.pol-transmitted light

Under these conditions melilite demonstrates zoning effect on the boundaries resulting from high Ca re-deposition in its crystal structure. Melilite is the most important phase, formed as hypidiomorphic crystals in a melt with high amount of Ca and SiO_2 (mainly Åkermanite) that interrupted the formation of olivine. Slant extinction on pyroxene is followed by Mg/Fe ratio in the crystal structure. In contrast to the fayalitic slags from central Iran (Hezarkhani and Keesmann 1996), olivine is not observed in thin sections.

The examination with electron probe micro analyser showed that three kinds of pyroxene are present (Fig. 10 and Table 2). The first (*I*) includes pyroxene with a low amount of CaO and FeO that tends to form diopsidic pyroxene. In this category MgO is responsible for the zoning effect around the mineral interface. The chemical composition of second group (IIa,b) controlled by CaO/FeO+MnO ratio. Increasing of SiO_2 and Al_2O_3 followed by fast decrease in temperature, as discussed by Kronz (1997) is a reason for the early formation of pyroxenes in the glass (Figure 11).

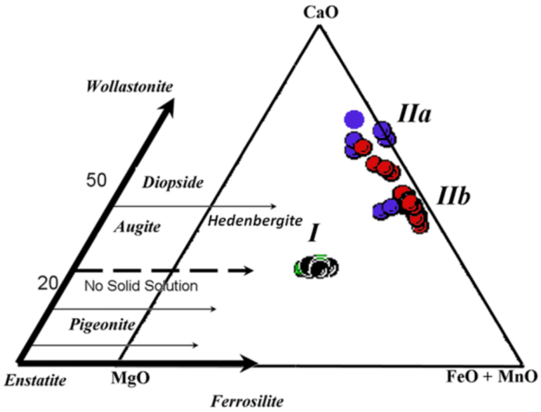

Figure 10. Chemical composition of pyroxene in the slag in system CaO – MgO – Feo+MnO

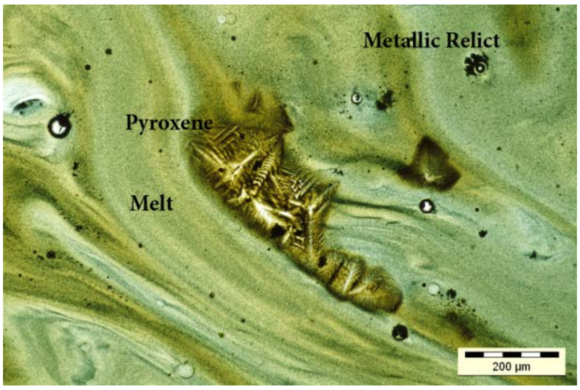

Figure 11. Forming of dendritic clinopyroxene within the melt. The tiny darck points are metallic copper. Sample 2869 x10-1.pol-transmited light

In addition to the silicates, other important phases in the slag matrix are oxides and sulphides. The common oxides detected in the slag are magnetite (Fe_3O_4), hercinite ($FeAl_2O_4$), cuprite (Cu_2O) and delafossite ($CuFeO_2$). The existence of these phases depends on the oxygen fugacity in the environment and expands our know-how about the technological quality via metallurgy. According to the amount of FeO and inconstant amount of Al_2O_3, the chemical composition tends to form more magnetite than hercinite in the texture. Cuprite can be produced in two ways. Firstly as primary oxidation product after metallic copper by high oxygen fugacity; and secondly as secondary phase from metallic copper (Hauptmann 1985). Cuprite and chalcocite cannot be simultaneously present due to their thermodynamically zone of stability. Therefore in high oxygen fugacity the reaction has a tendency to form cuprite from metallic copper followed by reactions bellow (Marechal, 1985).

i) $Cu_2S + 2O_2 \rightarrow 2CuO + SO_2\uparrow$
(Partial Roasting)

ii) $2FeS + 3O_2 \rightarrow 2FeO + 2SO_2\uparrow$
(Partial Roasting)
$FeO + CuO \rightarrow CuFeO_2$
(Rapid Oxidation in the Slag)

iii) $Cu_2S + 2CuO \rightarrow 4Cu + SO_2\uparrow$
(Primary Extraction)

iv) $CuO + CO \rightarrow Cu_{(metal)} + CO_2\uparrow$
(Reduction Extraction)

v) $2FeO + SiO_2 \rightarrow 2FeO{\cdot}SiO_2$
(Slag Formation)

This reaction would be accomplished with high SO_2 fugacity in the melt during roasting reduction reaction, emitting from sulphidic ores such as chalcosite (Su_2S) and covelline (CuS). As a matter of fact, in this case cuprite is observed in the smelt as a thin layeras primary oxidizing product after metallic copper (Figure 12).

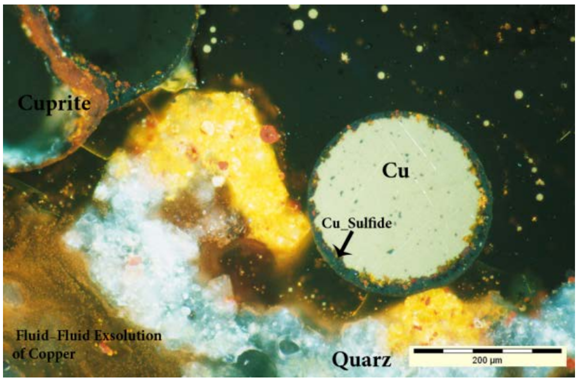

Figure 12. Sample 2868/C, Cuprite as rim around metallic copper. x20, 1 Pol., reflected light-dark field

Sulphides are the most important phases for the interpretation of the metallurgical technique as well as the smelting temperature. The main sulphide bearing ore paragenesis in this region is covellite-bornite-calcopyrite (Figs 13 and 14 and Table 3).

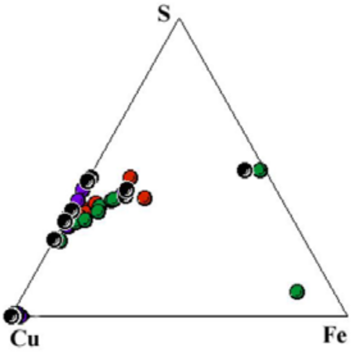

Figure 13. Distribution of chemical composition of sulfidic phases in the slag in system Fe-Cu-S

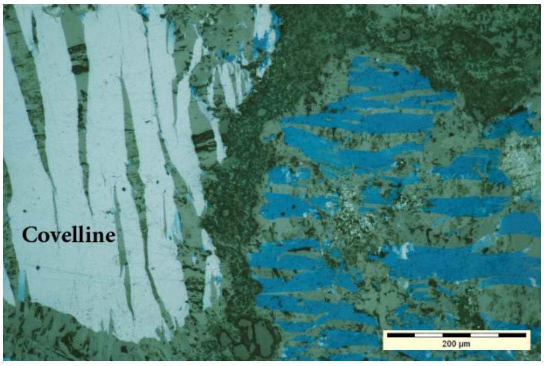

Figure 14. Covelline – chalcosite paragenese as the main extracted ore. X20, 1Pol., reflected light-bright field.

Thermodynamically the eutecticum stays by 925°C and bornite forms as exsolution from bornite-chalcopyrite through cooling (Fig. 15). With a high amount of iron, bornite tends to yellowish furthermore with a high amount of copper the color tends to bluish. In these samples the color tends to blue, and consequently the copper must be very pure. Due to the above mentioned eutecticum, the smelting temperature can be between 925-1000°C.

Exsolution of secondary chalcopyrite in bornite is present as a result of rapid cooling consequently. Domeykite (Cu_3As) is a common phase in all sample slags. It was identified with its typical anisotropic effect, appearing as a bright blue color under crossed polarized light. The interference color varies from bright blue to blue-pink.

In these slags domeykite was identified as coexisted within the metallic copper. Copper droplets contain 2.3 w% arsenide. Based on the calculated arsenic contents from chemical analyses of metallic copper, it was noticed that domeykite formed from sulfidic ores such as bornite or digenite. Domeykite is formed in a Cu-rich slag in the crystallization temperature at eutecticum by 610°C.

Table 3. Chemical analysis of metallic droplets and sulphide in the samples

Sample. Nr. 2872 in W%

Anal No	As	Fe	P	Ni	Cu	S	Co	Mn	Ti	V	Zn	Sn	Sb	∑
1111	0,48	0,25	0,01	0,02	77,94	18,58	0,02	0,01	0,00	0,00	0,00	0,00	0,00	97,29
1112	0,62	0,20	0,01	0,06	74,80	21,00	0,00	0,02	0,02	0,00	0,00	0,00	0,01	96,74
1113	0,18	14,58	0,00	0,04	54,94	26,47	0,04	0,06	0,01	0,01	0,00	0,00	0,02	96,35
1114	0,21	53,33	0,00	0,39	8,06	33,20	0,12	0,09	0,01	0,00	0,00	0,00	0,03	95,43
1115	0,78	0,02	0,00	0,03	99,08	0,00	0,00	0,01	0,02	0,00	0,00	0,00	0,00	99,94
1116	0,77	0,02	0,00	0,03	98,23	0,07	0,03	0,01	0,01	0,00	0,00	0,00	0,00	99,15
1117	0,09	0,11	0,00	0,00	79,83	13,92	0,02	0,02	0,01	0,00	0,00	0,03	0,01	94,03
1118	0,74	0,03	0,00	0,03	99,19	0,00	0,00	0,00	0,02	0,00	0,00	0,00	0,00	100,01
1119	0,05	0,10	0,00	0,00	62,00	26,22	0,01	0,02	0,00	0,00	0,00	0,01	0,03	88,42
1120	3,82	0,33	0,01	0,08	94,11	0,04	0,02	0,01	0,00	0,00	0,00	0,04	0,02	98,48
1121	0,12	0,40	0,01	0,01	77,54	18,79	0,01	0,01	0,02	0,01	0,00	0,00	0,00	96,91
1122	0,01	0,60	0,01	0,00	61,25	27,30	0,02	0,02	0,01	0,00	0,00	0,00	0,02	89,23
1123	0,16	14,68	0,00	0,01	54,95	24,51	0,02	0,04	0,01	0,00	0,00	0,01	0,00	94,39

Sample Nr. 2868 in W%

1138	0,04	0,39	0,01	0,00	84,21	0,02	0,02	0,01	0,03	0,00	0,00	0,00	0,05	84,78
1139	0,17	0,22	0,01	0,00	77,22	0,02	0,01	0,02	0,02	0,00	0,00	0,00	0,03	77,71
1140	0,25	0,42	0,03	0,02	71,49	17,09	0,00	0,01	0,00	0,00	0,00	0,00	0,01	89,31
1141	2,74	1,35	0,00	0,00	91,44	0,02	0,01	0,04	0,01	0,03	0,00	0,00	0,01	95,65
1142	3,23	0,02	0,00	0,00	95,98	0,01	0,01	0,00	0,02	0,00	0,00	0,03	0,04	99,34
1143	0,01	0,05	0,01	0,00	76,79	18,14	0,01	0,01	0,01	0,00	0,00	0,01	0,01	95,06
1144	3,40	0,02	0,00	0,00	95,44	0,02	0,00	0,01	0,00	0,00	0,00	0,00	0,03	98,91

Sample Nr. 2865 in W%

1145	4,14	1,46	0,00	0,02	93,49	0,31	0,01	0,02	0,02	0,02	0,00	0,00	0,05	99,54
1146	4,84	1,23	0,00	0,01	94,49	0,01	0,00	0,03	0,01	0,01	0,00	0,00	0,02	100,65
1147	0,06	1,06	0,01	0,00	84,58	0,01	0,01	0,02	0,02	0,01	0,00	0,02	0,00	85,81
1148	7,41	1,06	0,00	0,01	92,44	0,01	0,02	0,02	0,00	0,02	0,00	0,00	0,00	100,99
1149	0,42	1,57	0,00	0,01	76,76	17,05	0,02	0,03	0,00	0,00	0,00	0,00	0,03	95,87
1150	6,44	0,50	0,00	0,00	93,08	0,02	0,02	0,02	0,02	0,00	0,00	0,01	0,00	100,10
1151	1,94	2,10	0,01	0,01	82,34	0,04	0,01	0,03	0,01	0,01	0,00	0,00	0,02	86,52
1152	0,02	1,55	0,00	0,00	82,68	0,01	0,01	0,03	0,02	0,00	0,00	0,01	0,00	84,33
1153	0,09	0,07	0,00	0,00	97,96	0,11	0,00	0,01	0,01	0,01	0,00	0,00	0,00	98,27
1154	3,34	2,54	0,00	0,02	93,75	0,01	0,02	0,02	0,03	0,00	0,00	0,01	0,05	99,79
1155	0,33	0,79	0,00	0,00	77,64	19,52	0,02	0,02	0,00	0,01	0,00	0,00	0,00	98,31
1156	4,78	0,26	0,01	0,01	95,00	0,00	0,00	0,01	0,01	0,00	0,00	0,01	0,02	100,11
1157	22,90	1,06	0,00	0,01	71,77	0,08	0,02	0,02	0,00	0,00	0,00	0,00	0,21	96,08
1158	0,24	0,77	0,00	0,00	77,62	19,54	0,00	0,00	0,02	0,00	0,00	0,02	0,00	98,20
1159	15,64	0,08	0,01	0,00	44,81	0,13	0,01	0,02	0,01	0,00	0,00	0,00	0,03	60,74
1160	0,56	0,57	0,00	0,00	70,18	22,65	0,01	0,03	0,00	0,02	0,00	0,01	0,03	94,06
1161	0,19	13,84	0,00	0,02	56,46	25,42	0,03	0,02	0,02	0,00	0,00	0,00	0,04	96,02
1162	0,11	0,29	0,00	0,00	74,39	19,11	0,01	0,02	0,02	0,00	0,00	0,00	0,01	93,96
1163	0,28	0,19	0,00	0,03	69,12	25,92	0,02	0,03	0,00	0,02	0,00	0,02	0,06	95,69

Sample Nr. 2889 in W%

1164	0,09	6,67	0,00	0,05	67,99	23,17	0,01	0,01	0,01	0,00	0,00	0,01	0,04	98,05
1165	0,27	2,66	0,00	0,05	57,05	15,43	0,02	0,01	0,01	0,00	0,00	0,00	0,00	75,49
1166	31,28	18,49	0,00	15,76	23,51	0,10	0,28	0,00	0,00	0,00	0,00	0,07	10,80	100,29
1167	0,57	4,72	0,01	0,12	71,24	20,73	0,03	0,01	0,03	0,02	0,00	0,00	0,04	97,52
1168	0,57	13,21	0,01	0,04	50,57	28,70	0,04	0,02	0,01	0,00	0,00	0,00	0,06	93,21
1169	0,68	6,95	0,01	0,00	67,46	21,24	0,02	0,01	0,01	0,00	0,00	0,02	0,01	96,40
1170	1,04	0,99	0,00	0,14	76,21	17,32	0,03	0,01	0,00	0,02	0,00	0,02	0,08	95,86
1171	3,04	2,09	0,00	0,20	74,36	16,77	0,02	0,01	0,01	0,00	0,00	0,02	0,58	97,10
1172	23,40	0,04	0,00	9,26	55,55	0,04	0,12	0,03	0,00	0,00	0,00	0,09	13,51	102,02
1173	10,30	0,02	0,00	0,64	86,86	0,02	0,03	0,01	0,00	0,00	0,00	0,00	2,26	100,14
1174	24,61	0,03	0,01	0,58	67,49	0,09	0,02	0,01	0,00	0,00	0,00	0,05	8,39	101,27
1175	22,89	13,79	0,00	8,47	32,19	15,92	0,82	0,00	0,14	0,00	0,00	0,02	3,95	98,19
1176	0,36	7,72	0,00	0,06	65,90	21,83	0,01	0,02	0,00	0,02	0,00	0,01	0,04	95,95
1177	0,38	6,22	0,00	0,08	67,92	20,98	0,03	0,00	0,00	0,00	0,00	0,02	0,04	95,69
1178	0,47	4,92	0,00	0,00	70,15	21,42	0,01	0,01	0,00	0,00	0,00	0,00	0,00	97,00

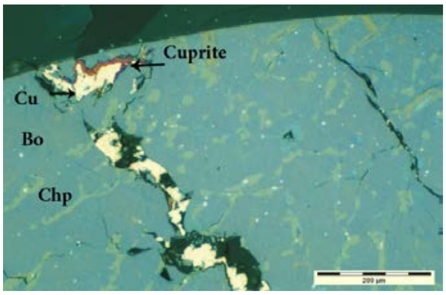

Figure 15. Sample 2888, Bornite (dark grey), Chalkopyrite as exsolution lamella (bright grey) on the bornite with metallic copper which is decomposed to Cuprit. All of these phases are in a tiny droplet of sulphide. X20, 1Pol., reflected light-bright field.

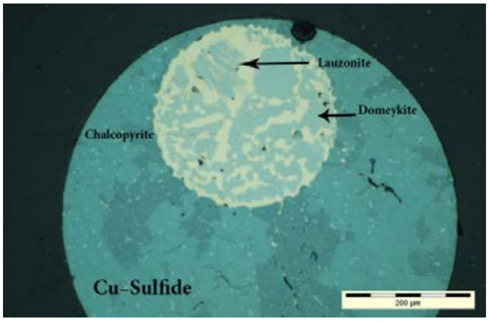

Figure 16. Sample 2889, Domeykite (bright grey) in eutecticum to Fe-rich metallic copper (bright white) in the centre of sulphide droplet. The big droplet consists of bornite (blue) associated with domeykite. x20, 1Pol., reflected light

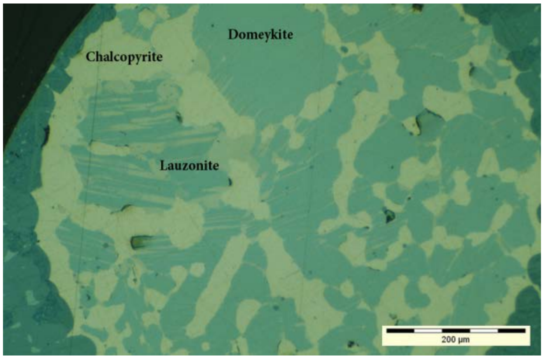

Figure 17. Sample 2889, Luzonite (bright grey) with lamellar structure with As-rich metallic copper and domeykite (bright blue). X20, 1. Pol., reflected light

One of the most interesting phases in the slag was luzonite $Cu_3 As_{0.685} Sb_{0.315} S_4$, a rare copper arsenide sulphide bearing mineral that has not been yet reported in the archaeometallurgy of Iran. Luzonite was discovered in the slag along within metallic copper and domeykite and it is a reason for syngenetical formation of this mineral. Based on literature review luzonite decompose continuously to Stibioluzonite (Cu_3SbS_4) (Baumann and Leeder, 1991), and was detected by bright pink to violet colorwith cross polarized light and weak twinning structure which is detectable by highest magnification and in low brightness (Fig. 16). Luzonite could be an important fingerprint of these samples because it observed in all samples including well identified anisotropic effect (Fig. 17).

5. CONCLUSION

The interpretation of ancient metallurgical processes based on archaeometallurgical evidences lead to determine the kind of technology practiced "Toroud" district in northern part of Iranian desert. For a scientific approach all aspects influencing the metalworking process, such as mining methods, smelting conditions, furnaces, slag and geography of the archaeological settlements in this region must be considered.

"Chah-Messi" is located near the "Toroud" village in the northern part of the central desert in Iran that is one of the places that motivated the investigation on ancient metallurgy of copper in the late second millennium BC. The study of the slags from the "Chah-Messi" copper mine proved that the miners used the exploited local ore paragenesis (chalcosite–covelline) for smelting. After the mineralogical-chemical observations and the interpretation of results, the main components were determined as silicate, oxide, sulphide, arsenide and metallic phases (Cu). The primary crystallization and the cotectic structure and stability of phases in eutecticum are the most important points. The main oxide constituents were SiO_2, Al_2O_3, CaO and FeO. The variations in chemical composition of phases were produced by different amounts of FeO, MnO and MgO in their structures. As a matter of fact, the presence of CaO in the chemical composition of the slags indicates that CaO was intentionally used. The metal extracted in "Chah-Messi" was copper and copper-arsenic with a high amount of As-Sb.

According to the chemical composition of the investigated samples, the slags are classified mainly based on their CaO content to clinopyroxene- and clinopyroxene-melilite Slag.

The presence of pyroxene in the slags is the main reason for occurrences of high oxidation reaction in the reducing condition of the furnace, where magnetite and metallic copper can be thermodynamically observed together. Metallic copper is mainly concentrated in the sulphide rich part of the slag. The most important elements in the ore are Cu, Fe, As, Sb and S. Different phases were detected within copper rich zones in the slag texture by electron probe micro-analyser. These phases are as follows:

1) Copper – Bornite – Domeykite
2) Copper – Chalcosite/Digenite – Bornite
3) Copper – Chalcosine/Digenite – Chalcopyrite
4) Copper – Chalcosine/Digenite – Covelline

The use of chalcopyrite in the melt brought to the addition of iron oxide as a flux. Chalcopyrite was mainly observed as secondary crystal structure after bornite. Sulphides mostly include Chalkosine/Digenite (Cu_2S), Covelline (CuS) and Domeykite (Cu_3As). The metallic copper present in the slag is mostly enriched with arsenide and low amount of sulphide. The enriched metallic copper resulted from oxidizing Cu_2S. This process is feasible when the extraction takes place at the equilibrium condition in presence of iron oxide and sulphide phases in a non-silicate smelt. In this condition iron oxide (magnetite) appears in the form of dendritic structure through oxidation reaction. Luzonite is the important well known phase in the slag which can be the prominent hallmark of this ore. According to the archaeometallurgical studies, As-Sb bearing minerals are also useful for the recent metallurgical activities for extraction of Sb.

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As his last student in mineralogy and archaeometallurgy at the Johannes Gutenberg Universitaet Mainz-Germany, I would like to dedicate this paper to him.

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