Economic Geology, Mining Archaeological and Archaeometric Investigations at the Veshnaveh Ancient Copper Mine, Central Iran

Nima Nezafati and Thomas Stöllner

Keywords

Archaeometallurgy, Copper Ore, Mineralogy, Mining Archaeology, Provenance Studies

Abstract

The Veshnaveh ancient copper mine is located in the middle of the Orumieh-Dokhtar volcanic belt in north central Iran and is hosted by middle-upper Eocene volcanic and sedimentary rocks. The focus of this paper is the investigation of ore and rock samples from Veshnaveh using diverse geochemical and mineralogical methods including ore microscopy, scanning electron microscopy, inductively coupled plasma mass spectrometry and lead isotope analysis in order to better understand the nature of mineralization. The results were then compared with the results from the ancient metallurgical relics from some key sites in central Iran including Tappeh Sialk, Arismān, Tappeh Sarm and Jamkarān. The results show the Veshnaveh deposit is a Manto type mineralization whose ore has been possibly used from the Middle Bronze Age until the early Iron Age by surrounding communities.

Introduction

The Veshnaveh ancient copper mining area with the general coordinates of 51° 51' 00" to 51° 52' 30" and 34°12' 30" to 34° 14' 30" is located in north central Iran, 60 km south of Qom and ca. 50 km northwest of ancient Tappeh Sialk of Kāshān (Figure 1). Based on the geological subdivisions of Iran, the Veshnaveh mine is situated in the western part of the central Iran domain and in the middle of Orumieh-Dokhtar volcanic belt. According to Ghalamghash (1995) and Fonoudi (1996), middle-upper Eocene volcanic and sedimentary rocks comprise the major geological outcrops of the area.

More than 60 large and small ancient diggings and holes have been so far recognized and partly documented at Veshnaveh by Holzer and Momenzadeh (1971), Holzer (1974), Berthoud and colleagues (Berthoud et al. 1976), Weisgerber (1976, 1978, unpublished), and Stöllner and colleagues (2000-2005; Stöllner, et al., 2004; Stöllner, Mireskandari and Roustaei, 2011) (Figure 2). The mine consists of the three main mining sites, Mazrayeh (1.5 km southwest of the village), Lāghe Morād (ca 4.5 km south of village), and Chāle Ghār (4 km southeast of the village) (Figure 3). The Mazrayeh ore-deposit was reworked in 1960s by the Puyesh Mining Company, during which time ancient mines were destroyed. The presence of grooved hammer stones, traces of fire-setting for exploitation of the ore, and recent archaeological and radiocarbon dating data show that there has been active for copper production from the late 3rd millennium until the mid and late 2nd millennium BC (see discussion: Stöllner, Mireskandari, and Roustaei, 2011) (Figure 2). Later finds dating to the Iron Age and Islamic periods do not provide evidence for subsequent copper mining activity but rather are related with agro-pastoral and ritual activities in and nearby the mines (Stöllner, 2012).

This paper summarizes the recent mineralogical, geochemical, and archaeometric research on the Veshnaveh ancient mine which was conducted at the Deutsches Bergbau-Museum within the framework of a three month Heinrich-Winkelmann fellowship to the first author combining with the long-standing archaeological study of the Veshnaveh project by the second author.

Objectives and aims

The Veshnaveh ancient mine was archaeologically investigated and excavated by the Iranian-German joint team for five seasons from 2000 to 2005 (Chegini, et al., 2001; Stöllner, et al., 2004; Stöllner, Mireskandari and Roustaei, 2011). This was the first systematic mining archae-



Figure 1. a) Location of the study area showing the geological subdivisions of central and west Iran, b) The access roads of the study area.

ological excavation in Iran that especially focused on the chronological, technical and social aspects of prehistoric copper ore extraction. One of the main results was the establishment of a systematic dating sequence that established a chronology for a series of mining sites: the mines were operated repeatedly over a rather long time span between the beginning of the 3rd and the mid and 2nd half of the 2nd millennia BC (Stöllner, Mireskandari and Roustaei, 2011). Although the mines had been well documented archaeologically, the possible influence of the ore mineralogy and geochemistry on the ancient exploitation (and possibly extraction) methods and also the possible connection of the ore with metal objects found in neighboring ancient sites have yet to be investigated. First estimates made in regard to the general net production of prehistoric copper exploitation indicate a rather moderate copper ore yield, which certainly can be explained by the method of the prehistoric exploitation (Stöllner, Mireskandari and Roustaei, 2011). Because of the lack of contemporary smelting remains, it is assumed that most of the ore concentrates had been processed elsewhere outside the mountainous areas of the Kuhestān-e Qom. As 3rd and 2nd millennia BC settlement sites are still unknown at the 2000 m sea-level areas around the modern village of Veshnaveh (Stöllner, 2012, pp.26-27 Fig. 20) and there is no evidence for on-site smelting and permanent settling on any scale, it can be assumed that a seasonal and diffuse exploitation strategy was practiced by pastoral people.

Recent archaeological surveys have provided no evidence for the establishment of permanent settlements before the beginning of the 1st millennium BC. It is obvious that this later occupation of the highlands was not connected at all with the copper deposits metals but was rather based on an agro-pastoral subsistence strategy that was concentrated around the modern village of Veshnaveh (Stöllner 2012, pp. 25-27).

It is most likely that prehistoric pastoral groups reached the ore-deposits from the northern or eastern plains and likewise also transported the ore-concentrate to prehistoric settlements there. So, it was therefore an important question to explore such connections as it would allow further statements regarding possible consumption patterns that were typical and traditional on the Iranian Central plateau. Such presumptions certainly need to be proven by an accurate investigation of the ore from mineralogical and geochemical points of view. In light of the lack of analytical research on the Veshnaveh copper mines, the authors aimed to demonstrate the exact composition of trace elements and mineralogy of the



Figure 2. a) Overview of part of the ancient diggings at Mazrayeh, b) ancient diggings with traces of fire setting (Mazrayeh location, mines 2, 3 and 4), c) a one-man diggings with traces of fire setting, a copper vein is visible on the wall of the diggings (Sourakh-e Palang – Chāle Ghār mine 10), d) another one-man diggings with fire setting traces (Chāle Ghār, mine 21), e & f) Hammer stones (Lāghe Morād), g) an anvil stone at the entrance of mine 1 in Lāghe Morād (Stöllner, Mireskandari and Roustaei, 2011, p.574), h) slag pieces found at Karnovoon, Photos: Nima Nezafati, Islamic Azad University Tehran

ore together with the lead isotope signature of the ore and host rocks. Such a study should help not only to understand the total amount of copper once produced but also the consumption pattern in which this ore exploitation once was embedded. To answer where and in which social contexts the Veshnaveh copper ore were used during the latter 3rd and 2nd millennia BC, analyses of contemporary metal artifacts from surrounding regions were compared to the ore samples.

Background to the research

First reported as "Weshnave" copper seam - a very small copper mine for local use - by *von Stahl* in 1894-1895, Veshnaveh and its ancient mining relics were later described in detail by Holzer and Momenzadeh (1971). Later Berthoud (1976-1984) and Weisgerber (1976, 1979) visited the site and presented archaeological descriptions on the ancient mining relics. There was a



Figure 3. Geological map of the Veshnäveh ancient mining area (redrawn and modified after Momenzadeh and Haghnazar, 2008).

break in archaeological and archaeometric investigations of the site until 2000 when the joint Iranian-German project of Arisman for ancient mining and metallurgy in west central Iran commenced. During the Arismān project, systematic archaeological excavations were carried out on some of the ancient mining together with archaeometric investigations (Stöllner, Mireskandari and Roustaei, 2011; Pernicka, et al., 2011). Surveys and excavations were carried out at 12 prehistoric mines; two mines (Chāle Ghār 1 and 21), of which one was used as an offering place for cultic practices from the later Iron Age onwards, were completely excavated. Recent archaeological investigations evidenced a near-surface exploitation of a copper mineralization at the beginning of the 3rd millennium BC, thus indicating that the earliest traces of copper extraction are contemporary with and could have contributed to the eminent ancient metallurgical sites of Tappeh Sialk and Arisman. A larger part of the exploitation certainly took place during the 1st half of the 2nd millennium BC, in principle the Middle to Late Bronze Age using the Central plateau chronological sequence (14C-dates and ceramic chronology). Some of the dates indicate continuity in copper exploitation up to the beginning of the early Iron Age at the end of the 2nd millennium BC (Stöllner, Mireskandari and Roustaei, 2011, pp.601-603).

Selection of archaeological artifacts and metallurgical samples

In order to perform a study on the economic and historical background of the Veshnaveh mining activities during the 3rd and 2nd millennia BC we selected samples from ore-bodies, particularly from ore-veinlets and mineralized host-rocks (see Table 1) from various ore deposits and from archaeological sites in the surroundings. Samples of slag, ore and metal objects were obtained from two recent regional important excavations (Table 1). One is the key site of Qolī Darvish south of Qom (Azarnoush and Helwing, 2005, pp.207-208; Sarlak, 2011; Pollard, et al., 2015). The site provided an outstanding stratigraphic sequence that comprised layers from the Late Chalcolithic to the Early Bronze Age as well as those from the 2nd millennium BC. The latter are most exceptional as they count among the very rare settlement sites at the Central Plateau where a Middle and Late Bronze Age stratigraphic sequence can be shown and studied. As Qolī Darvish is contemporary with most of the exploitation periods in Veshnaveh it was an important candidate for the question of where its ore-concentrates had been processed. During the excavation metallurgical workshops have been discovered that may support a possible connection to copper mining at Veshnaveh. Some of the metallurgical evidence of a furnace found in a workshop at trench 1 (excavation 2004 by ICHTO under direction of S. Sarlak) has been investigated during this study. Samples were obtained from copper rich slag, furnace lining as well as a metal fragment.

Further samples were gained from an Iron Age II/ III cemetery near Kahak called Tappeh Sarm, a site situated north of the Kuhestān-e Qom and therefore might have been also related to the ore-exploitation processes in Veshnaveh. At Veshnaveh dates might indicate a continuity of mining until this age (Stöllner, Mireskandari and Roustaei, 2011, p.602 Fig. 92). Sarm is located on a natural hill immediately to the east of the road from Qom to Kahak, about 1 km from the Iron Age hilltop site of Shamshirgah (Kleiss, 1983). The dating is slightly younger than the site of Qolī Darvish. The cemetery obviously once was of regional importance as the funerary structures and the range of grave goods indicate. 85 inhumations have been discovered between 2001 and 2003, from which we could sample metal objects from features 206-208 and 213 (Azarnoush and Helwing, 2005, pp.224-225). These objects allowed a further discussion about the contemporary metal consumption.¹

Materials and methods

A total of 22 samples of ore and host rocks of the mineralization were investigated during this study. The samples were collected either during the field work that was performed by the first author in June 2014 or from the archaeological excavation of Veshnaveh (2000-2005, stored at the Deutsches Bergbau-Museum, henceforth DBM).

The samples were prepared as polished-thin sections for polarized light microscopy (PLM) and scanning electron microscopy (SEM) investigations. The same samples were also prepared and measured for X-ray diffraction (XRD) and inductively coupled plasma mass spectrometry (ICP-MS) analysis at the research laboratories of the DBM. The lead isotope measurements of the ore and rock samples were performed at the Goethe-University Frankfurt, Institute of Mineralogy, while the ancient artifacts were measured at the Curt-Engelhorn-Zentrum Archaeometrie, Mannheim by help of X-ray fluorescence (XRF) and ICP-MS. The list of artifacts and slag investigated by the Curt-Engelhorn Centre is presented in Table 1,² and the list of the geological samples and their characteristics together with their XRD results is presented in Table 2.

Table 1. List of samples investigated by ICP-MS for Pb-isotope ratios and X-ray fluorescence analysis at the CEZ Mannheim in 2008.

Sample	Archaeological site/context	Object	Mannheim sample numbers
1	Tappeh Sarm, trench 8, grave 206, objekt 49	bracelet	FG-071504; MA-071504 (LIA, RFA)
2	Tappeh Sarm, trench 8, grave 207, objekt 47	bracelet with overlapping ends	FG-071505; MA-071505 (LIA; RFA)
3	Tappeh Sarm, trench 8, grave 213, object 35	bracelet with overlapping ends	FG-071506; MA-071506 (LIA, RFA)
5	Tappeh Sarm, trench 7, grave 208, object 51	spiral bracelet	FG-071507; MA-071507 (LIA; RFA)
6	Tappeh Sarm, trench 7, grave 208, object?	arrow head	FG-071508; MA-071508 (LIA, RFA
7	Tappeh Sarm, trench 7, grave 208, object?	arrow head	MA-071509 (RFA)
8	Tappeh Sarm, trench 7, grave 208, object?	arrow head	FG-071510; MA-071510 (LIA, RFA)
9	Tappeh Sarm, trench 7, grave 208, object?	metal hilted dagger	MA-071511 (RFA)
10	Tappeh Sarm, trench 7, object 17	arrow head	MA-071512 (RFA)
11	Jamkarān, Qolī Darvish, excavation 2004, trench 2, feature 102, furnace	metal handle	MA-071513 (RFA)
12	Jamkarān, Qolī Darvish, excavation 2004, trench 2, feature 102, furnace	non-ferrous metal fragment, scorched	MA-071514 (RFA)
14	Jamkarān, Qolī Darvish, excavation 2004, trench 2, feature 102, furnace	casting droplet; non-ferrous metal fragment, scorched	MA-071515 (RFA)
15	Jamkarān, Qolī Darvish, excavation 2004, trench 2, feature 102, furnace	metal fragment	FG-071516; MA-071516 (LIA, RFA)
16	Jamkarān, Qolī Darvish, excavation 2004, trench 1, feature 100/1, area BA 41	slagged furnace lining	FG-071517?? (LIA)
18	Jamkarān, Qolī Darvish, excavation 2007, area Z 20, feature 402/1 (furnace)	smelting slag	FG-071518 (LIA)
19	Jamkarān, Qolī Darvish, excavation 2007, area Z 20, feature 401-2 (furnace)	copper-rich slag	FG-071519 (LIA)
21	Tappeh Sarm, trench 7, grave 208, object?	tongue-shaped spearhead/ dagger,	MA-071520 (RFA)
22	Tappeh Sarm, trench 7, grave 208, object?	spearhead with tang	MA-071521 (RFA)
23	Tappeh Sarm, trench 7, grave 208, object?	spearhead with tang	MA-071522 (RFA)
24	Tappeh Sarm, trench 7, grave 208, object?	spearhead with tang	MA-071523 (RFA)
26	Veshnaveh, Chāle Ghār, mine 3, find 7764/2005	ore sample	FG-071524 (LIA
27	Veshnaveh, Mazrayeh, installation, feature 20211c; from the mine	ore sample	FG-071525 (LIA)
28	Veshnaveh, Lāghe Morād, mine 1, excavation 2002, see also Table 2, 4709/14 and 4710/14	ore sample	FG-071478 (LIA)

Table 2. List of the geological samples of Veshnäveh deposit together with their XRD result.

Lab No.	Sample No.	Location	Sample type	XRD results
4686/14	NVSM-2	Mazrayeh	Ore (+ Host rock)	Quartz, calcite, hematite, oligoclase, ankerite, clinochlore, pumpellyite, prehnite
4687/14	NVSM-3	Mazrayeh	Ore	Albite, hematite, ankerite, clinochlore, quartz, chalcocite, malachite
4689/14	NVSM-5	Mazrayeh	Andesite porphyry	Albite, greenalite, pyroxene
4690/14	NVSM-6	Mazrayeh	Andesite-Basalt	Quartz, hematite, oligoclase, clinochlore, ankerite, calcite, orthoclase
4691/14	NVSM-7	Mazrayeh	Amygdaloidal andesite	Oligoclase, clinochlore (ferroan), calcite, orthoclase
4692/14	NVSM-8	Mazrayeh	Red amygdaloidal andesite	Oligoclase, quartz, hematite, ankerite, calcite, clinochlore, orthoclase
4693/14	NVSM-9	Mazrayeh	Host rock + Fe-Oxide	Quartz, hematite, oligoclase, ankerite, orthoclase, clinochlore
4694/14	NVSM-10	Mazrayeh	Ore+Host rock	Quartz, calcite, prehnite, muscovite, ankerite
4695/14	NVSC-1	Chāle Ghār	Host rock	Albite, hematite, calcite, pumpellyite, augite (aluminian)
4696/14	NVSC-2	Chāle Ghār	Host rock (+ore)	Quartz, calcite, albite, pumpellyite
4698/14	NVSC-4	Chāle Ghār	Host rock (+ore)	Prehnite, calcite, hematite, oligoclase
4699/14	NVSC-5	Chāle Ghār	Ore (+ Host rock)	Calcite, quartz, oligoclase, hematite, muscovite, kaolinite, haycockite
4701/14	NVSL-3	Lāghe Morād	Host rock	Calcite, albite, hematite, ankerite, diopside
4702/14	NVSL-4	Lāghe Morād	Ore	Hematite, oligoclase, clinochlore
4703/14	NVSL-5	Lāghe Morād	Ore+Qz+Cc	Calcite, albite, muscovite, malachite, microcline, clinochlore, chalcocite
4704/14	NVSL-6	Lāghe Morād	Host rock	Oligoclase, calcite, orthoclase, hematite, clinochlore, muscovite
4705/14	NVSL-7	Lāghe Morād	Ore+Qz+Cc	Calcite, albite, hematite, microcline, malachite, chalcocite
4707/14	Vesh-1	Sample Weisgerber 1978	Ore	Hematite, chalcocite, ankerite, oligoclase, greena- lite, prehnite, digenite
4708/14	Vesh-2	Lāghe Morād, sampling 2002	Amigdaloidal Andesite-Basalt	Oligoclase, ankerite, hematite, muscovite, clinochlore, prehnite, orthoclase
4709/14	Vesh-3	Lāghe Morād, mine 1, excavation 2002	Ore	Quartz, hematite, albite, ankerite, prehnite, digenite, clinochlore, malachite, chrysocola, bornite
4710/14	Vesh-3A	Lāghe Morād, mine 1, excavation 2002	Ore	Hematite, chalcocite, quartz, brochantite, prehnite
4711/14	Vesh-4	Lāghe Morād, mine 6, sampling Weisgerber 1978	Ore	Oligoclase, calcite, microcline, muscovite, chalcocite

The XRD analyses were performed with a PANalytical X'Pert instrument (PRO MPD) and X'Celerator detector and interpreted with the High Score Plus-software.

For chemical analysis, the samples were first digested in a three acid solution using a µPREP-A microwave (MLS GmbH). For samples with low lead content (below 1 %) about 100 mg of pulverized sample was digested in PTFE pressure vessels with 6 ml HCl, 1.75 ml HF and 4.8 ml HNO₃ for 40 minutes, at 250 °C. The solutions were then diluted to 100 ml with ultrapure water. The chemical analyses were performed using an ICP-SFMS Thermo Scientific ELEMENT XR. For major elemental analysis, the sample solutions were diluted 1:100, while for trace elements a 1:10 proportion with 5 % HNO₃ was applied. For gold measurement, the sample solutions were separately diluted with 2 % HCl. The analyses were carried out with FAST SC-system, ST 5532 PFA µ-FLOW nebulizer, Peltier-cooled PFA spray chamber and 1.8 mm sapphire injector in triple detector mode at all three different mass resolutions $(m/\Delta m)$ depending on the elements of interest. Measurements had been controlled with standards FER-2 (Canadian Certified Reference Materials Project), GBW 07107 and NCS DC 7001 (MC Certified Reference Material).

For lead isotope analyses, the sample preparation was performed at the clean laboratory of the research laboratories of the Deutsches Bergbau-Museum, while the measurements were conducted at Institute of Earth Sciences, Goethe-University Frankfurt am Main. In this regards, the samples with trace amounts of lead (Pb) underwent column-chromatography with anion-exchange resin (BIO-RAD Laboratories, AG®1-X8 Resin). About 80 mg of each sample (with about 100 ppm Pb) was dissolved in 5 ml concentrated hydrofluoric acid/ nitric acid (HF / HNO₃) (5:1) in Teflon beakers at 100° C. The solutions were then evaporated at 105 °C, taken up with 1 ml 7 N hydrogen bromide (HBr) and 6 ml ultrapure water and centrifuged for 10 minutes. The resin was placed in 1 ml-Qtz-columns, cleaned, by turns, with several runs of 1.5 resin volumes (RV) 6 N HCl and 3 RV ultrapure water and then conditioned with 3 RV 1 N HBr before addition of the sample solutions. Before elution of Pb with 4.5 RV 6 N HCl into Teflon beakers and evaporation, resin was again conditioned with 2 RV 1 N HBr and cleaned with 2 RV 2 N HCl. Prior to lead isotope analysis, the collected Pb was diluted in a 2 % HNO₃ solution to yield a concentration of 500 ppb Pb, and spiked with 100 ppb thallium (Tl)-standard NIST SRM-997. The measurements were performed with a MC-ICP-MS Thermo Scientific NEPTUNE (for details, see e.g. Klein, et al., 2009).

Geologic setting

The Veshnaveh area is located in the middle of the Urumieh-Dokhtar magmatic belt which, with a NW-SE trend, is characterized by its extensive volcano-sedimentary activity especially during Eocene. This belt hosts several copper, gold, iron, manganese, lead and zinc, and polymetallic deposits. At Veshnaveh, a sequence of volcano-sedimentary rocks is exposed. The volcanic rocks are mainly basic to intermediate in composition. Intrusive bodies are not common near the study area (Figures 1 and 3).

According to Emami (1981), the main rock units of the Veshnaveh area are composed of (from older to younger units) (1) Megaporphyric andesite, (2) Breccia tuff, (3) conglomerate and sandstone, and (4) andesite-basalt. These units which are all (Middle-Upper) Eocene in age have been cut by Plio-Quaternary andesite dykes and are, in some cases, covered with Plio-Quaternary basaltic lava flows (Figure 4a).

Geology of the host rock

The (amygdaloidal) and esite-basalt unit is the most abundantly exposed unit at Veshnaveh and hosts the mineralization. This unit shows variations in composition and texture from olivine basalt to olivine dolerite and to andesite-basalt. The main texture of the and esite-basalt unit is porphyritic within a microlithic-glassy matrix. In some cases a trachytic texture is also observable.

The rock shows an amygdaloidal texture in hand specimen (Figure 4b, 4c, and 4d). Amygdales are vesicles filled with secondary minerals, either deuteric (precipitated from hydrothermal solutions derived from the magma) or metamorphic (Vernon, 2004). Vesicles in the andesite-basalt unit of Veshnaveh, which are observed in both spherical and ellipsoidal forms, have been filled with chlorite, prehnite, pumpellyite, quartz, (actinolite, pistasite and malachite), sulfide grains and in some cases with residual melt (segregation vesicles). These are sometimes (especially in ellipsoidal form) aligned within the trachytic-textured groundmass (Figure 4d). Concerning the formation of the amygdales as Vernon (2004) explains, exsolution of gas from magma occurs when the melt becomes supersaturated with a volatile component, especially water, in response to crystallization of non-volatile minerals and/or a decrease in pressure. Bubble shapes can be preserved, if the magma becomes viscous enough to preserve them before they collapse as the gas escapes. Many vesicles are spherical. Others are ellipsoidal, owing to flow of the magma. Aqueous solution circulating through cracks may dissolve chemical



Figure 4. a) an overview of the three major rock units of the area (I) Brecciated tuff, (II) conglomerate, and (III) andesite-basalt, b) Different views of the major host rock of the mineralization i.e. amygdaloidal andesite (basalt), c) amygdaloidal andesite, d) amygdaloidal andesite with ellipsoidal amygdales, e) propylitic alteration of the host rock, f) propylitic alteration cut by mineralized calcite veins.

components from buried sequences of volcanic rocks and deposit secondary minerals in vesicles, forming amygdales (Vernon 2004). Presence of prehnite in the burial metamorphism assemblage of Veshnaveh may imply the formation temperatures between 200 and 280 °C and the pressures between 1 to 4 kb assuming a geothermal gradient of less than 30 °C / km (Turner, 1981; Frey and Robinson, 1999).

The major phenocrysts of the andesite-basalt unit of Veshnaveh are plagioclase (labradorite). The other

phenocrysts are of clinopyroxene. The microlites are of plagioclase and clinopyroxene whose pores have been filled with oxidized glass. Albitization and some sericitization are the main types of plagioclase alteration. A frequent accessory mineral in the rock is a Cr-(Zn-V)spinel (possibly a Cr-Zn-V-bearing hercynite) together with magnetite (Figure 5b) which occurs in hypidiomorphic as well as skeletal (dendritic) forms (Figure 5a). According to Vernon (2004), skeletal crystals are incomplete polyhedral single crystals with interval cavities



Figure 5. a) Hypidiomorphic crystals of a Cr-(Zn-V)-spinel (possibly hercynite), b) Skeletal (dendritic) magnetite.

that are commonly crystallographically controlled and were formed in response to rapid cooling of the lava. The skeletal, dendritic, and spiky crystals of magnetite (and also olivine, plagioclase, pyroxene, and chromite) occur in quenched volcanic rocks including submarine basalts (Vernon, 2004).

The crosscutting Plio-Quaternary dykes are often andesitic in composition with a porphyritic texture and a fluidal microlithic matrix. Plagioclase and to some extent brown hornblende compose the major phenocrysts of the rock. Malakoutian and Haghnazar (2010) based on their 13 chemical analyses of the andesite-basalt unit have considered a tholeiitic within plate (rifting-related) origin for the andesite-basalt with a continental magma mixing origin.

The petrographic and mineralogical data suggest the (amygdaloidal) andesite-basalt unit of Veshnaveh originated from a gas-rich magma that has erupted under subaerial or even submarine (lacustrine) conditions and has undergone a low-grade metamorphic phase of prehnite - pumpellyite facies and a hydrothermal alteration. Amygdaloidal andesite-basalt units are a rather common feature in the Middle-Upper Eocene volcanic assemblages of Iran, from which some contain similar low-sulfide copper mineralization. Heating of the fluids contained in the underneath rock units and their expulsion upwards through the volcanic pile may account for the metamorphism in the area.

Alteration and metamorphism

The host rock for the copper mineralization at Veshnaveh is characterized by at least two stages of alteration; one burial metamorphism and the other the hydrothermal alteration. The low-grade burial metamorphism belongs to the prehnite-pumpellyite facies (prehnite, laumontite, pumpellyite, chlorite, quartz and calcite) in the andesite-basalt unit, while the hydrothermal alteration has occurred in the form of albitization and propylitic alteration (mostly chloritization) in the host rocks of mineralization (Figure 4e and 4f).

Intergrowths among prehnite, chlorite, and zeolite minerals and sulfide minerals is seen (Figure 6e). This may imply the co-occurrence of part of the mineralization and the burial metamorphism.

The fluids resulted from burial metamorphism, these together with hydrothermal fluids have traveled through permeable horizons (including fractures and fissures) of the andesite-basalt unit and have caused the mineralization. Evidence of a meager supergene stage can also be observed in the mineralization.

The copper mineralization and mineralogy of the ore

The mine comprises three main mining sites of Mazrayeh (1.5km southwest of the village), Lāghe Morād (ca 4.5 km south of village) and Chāle Ghār (4 km southeast of the village) (Stöllner, et al., 2004; Stöllner, Mireskandari and Roustaei, 2011). The mine was reworked in the 1960s.

The copper mineralization at Veshnaveh is confined to the andesite-basalt unit and therefore is strata bound. It mainly occurs as thin lenses and pockets (which have almost totally been exploited by ancient miners), small veins and veinlets, disseminations in the groundmass and amygdales, and impregnations (Figures 6a, b, c, d, and f). East-W and N-S are the main trends of the veins and veinlets which are from several millimeters to several centimeters in width and up to several me-



Figure 6. a) veinlets of mineralization, b) veinlets of mineralization, c) a calcite-quartz-chalcocite cobble, probably the residue of a mineralization pocket or vein, d) copper dissemination and impregnation in the host rock, e) mineralization of chalcocite in an amygdale (length of the image 5.5cm), f) part of a veinlet of chalcocite (length of the image 4cm).

ters in length. Disseminated grains of copper sulfides are scattered in the matrix of the rock as well as in the center of some amygdales (Figures 6e and 7e). The most abundant primary sulfide mineral of the mineralization is chalcocite, which in some cases is intergrown with bornite and digenite (Figures 6 and 7).³ The primary ore mineralization consists of chalcocite, bornite, hematite, digenite, chalcopyrite, native copper, pyrite, in approximate order of abundance (Figure 7). Chalcopyrite, pyrite, and covelline occur to considerably lesser extents compared to chalcocite. Covelline occurs as a secondary mineral from chalcocite. Chalcocite is the dominant sulfide mineral at Veshnaveh, and occurs as vein infill, disseminations in the matrix, and amygdale infill (Figures 6 and 7). Malachite and atacamite are abundant within the secondary mineralization of copper in the deposit. The major gangue minerals are quartz, calcite, chlorite, barite, prehnite and pumpellyite, which are visible as amygdales as well as veinlets and dissemination in the host rock.

Ore Microscopy shows that a symplectitic texture is common between digenite and bornite (Figure 7a). Symplectic intergrowths (symplectites) are vermicular intergrowths of minerals that grow simultaneously in a solid-state metamorphic-hydrothermal reaction. Experiments have shown that the minerals in symplectic inter-



200µm

Figure 7. a) Symplectic texture between bornite and digenite, b) lattice of hematite laths crosscutting / or infilled by iron copper sulphides, in the middle of the picture a grain of native copper is visible, c & d) intergrown of copper sulphides and copper iron sulphides primarily consisting of chalcocite, bornite, and digenite, e) intergrown of chalcocite, chlorite, and prehnite in an amygdale, f) massive hematite crosscut / or being replaced by chalcocite.

growths grow simultaneously (Vernon 2004); therefore digenite and bornite have probably occurred coevally.

Massive hematite seems to be the first mineral to be occurred, while chalcocite, bornite, digenite and native copper have occurred as primary minerals after hematite, and chalcopyrite which is rather rare has occurred later. Covelline is the product of supergene alteration the other copper minerals. Some hematite laths crosscut the main sulfide minerals, these laths could well be occurred after the sulfide mineralization.

The ore minerals are clearly mostly intergrown with minerals like calcite, prehnite, chlorite, pumpellyite, and quartz which have themselves filled the amygdales and fractures of the rock. Barite is also a rather frequent mineral together with the copper mineralization and occurs as disseminations and the filling of open spaces. The mineralization in the three ore bodies of Mazrayeh, Lāghe Morād, and Chāle Ghār is identical and does not show much diversity.

Geochemistry of the ore

In order to better understand the trace element pattern of the ore and related host rocks, 22 samples were analyzed for 44 elements using a Single Collector ICP-MS. Different types of the ore were analyzed for this purpose including the disseminated ore, impregnation and veinlets. Two concentrated ore samples were analyzed also in order to simulate the selected and concentrated ore of the ancient miners. The ICP-MS results are presented in Table 2.

According to the geochemical results, copper is the only extractable metal for ancient metallurgical purposes. Gold, arsenic, tin, antimony, zinc, lead, nickel, and cobalt show only low (to very low) contents. Silver, with up to 370 ppm (0.037 %) in the concentrated copper ore (with 34.5 % copper), is anomalous, although rarely of interest for the ancient metallurgist in such amount. Silver shows a clear correlation with copper. Barium, manganese, and phosphorous are found in significant amounts in the ore (Table 2).

The ore is sulfide-poor with a maximum of 7.31% sulfur. Iron oxide is an important component and reaches up to 17.5 %. The highest content of copper is 34.5 % for the concentrated ore from a veinlet.

The copper content of the amygdaloidal andesite, which is the major host rock ranges from 10 to 75 ppm, although in one case where it hosts a dissemination of the ore the copper content reaches 1400 ppm. Among the amygdaloidal andesite samples, the ones that are red in color and seem to be more leached show the lowest amounts of copper. The copper content of a dyke that crosscuts the mineralization in the Mazrayeh location is 480 ppm. Copper, iron, and sulfur show a positive correlation, especially in the copper-rich ore.

SEM results of the ore show locally high contents of silver (up to 22%) in chalcocite and the other copper sulfide minerals. Arsenic and other elements are very low in these minerals.

Lead isotope investigation

The study of lead isotope ratios has nowadays consolidated its status in geosciences including mineral exploration as well as scientific archaeology and greatly contributed to the present picture of the Earth's development, ore forming processes and provenance studies (Bielicki and Tischendorf, 1991; Pernicka, et al., 1984).

The lead isotopic variation within the ore minerals of a single ore deposit is usually limited. Therefore the lead isotope signatures of the ore of a single ore deposit can be used as a fingerprint for finding the artifacts produced from its ore (see below). This can only be utilized, if we assume that the isotope ratios of the ore have remained unaffected by anthropogenic processes and there was no mixing of ore from different sources (Muhly, 1985; Gale and Stos-Gale, 1985; Gulson, 1986; Pernicka, et al., 1997; Weeks, 2004).

The lead content of the Veshnaveh samples is rather low (from 7 to 160 ppm, see Table 2), but high enough to be measured for lead isotope signatures. The present study on lead isotopes of Veshnaveh follows two major aims:

- Investigation of the source of mineralizing fluids, tectonic setting of the mineralization environment and relationship between the ore and the host rocks.
- (2) Comparison of the lead isotope ratios of the ore of Veshnaveh with the ancient copper-based artifacts from Arisman, Tappeh Sialk and a number of recently excavated ancient sites near Qom including Tappeh Sarm and Qolī Darvish (Jamkarān).

A total of 13 ore and 11 host rock samples were analyzed for their lead isotope signatures at Goethe-University Frankfurt (Table 3), two additional samples had been analyzed already at Freiberg University. It is noteworthy that the host rock lead isotope signatures are not only useful for geological investigations, but also could be of interest for archaeological purposes. Even after the hand-picking, or cobbing, of the ore, considerable amount of host rock may have been stuck to it and put into the smelting process, hence the lead isotope signature of host rock could also play a role in the final isotope ratios of finished artifact. Therefore an isotopically different host rock could produce a totally different isotopic signature in the final product compared to the pure ore, although as it will be seen, the isotopic signatures of the ore and the host rock at Veshnaveh are very similar.

In addition to the samples that were measured in Frankfurt, 12 copper-base samples unearthed from the archaeological excavations at Tappeh Sarm and Jamkarān ancient sites were also analyzed for their lead isotope ratios at Curt-Engelhorn Zentrum Archäometrie-Mannheim (see Table 1). Tappeh Sarm of Kahak and Jamkarān ancient sites are located in the vicinity of the Veshnaveh deposit (see above). These results were also compared with the results already published (Schreiner, 2002, Schreiner, Heimann and Pernicka, 2003; Nezafati and

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with(i)is(i)(i	Se	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.												
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SumpleQiAgAgSiFeQAiSiFeQAiSiFeQAiSiFeQAiSiFeQAiSiFeQAiSiFeQAiSi <td>ï</td> <td>25</td> <td>55</td> <td>9</td> <td>60</td> <td>65</td> <td>35</td> <td>30</td> <td>2</td> <td>35</td> <td>5</td> <td>30</td> <td>40</td> <td>35</td> <td>50</td> <td>8</td> <td>5</td> <td>б</td> <td>20</td> <td>25</td> <td>15</td> <td>6</td> <td>60</td>	ï	25	55	9	60	65	35	30	2	35	5	30	40	35	50	8	5	б	20	25	15	6	60
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Sumple(Na)As(S) <th< td=""><td>Λ</td><td>140</td><td>170</td><td>170</td><td>130</td><td>200</td><td>180</td><td>170</td><td>40</td><td>200</td><td>130</td><td>180</td><td>140</td><td>150</td><td>190</td><td>230</td><td>170</td><td>180</td><td>150</td><td>210</td><td>120</td><td>150</td><td>220</td></th<>	Λ	140	170	170	130	200	180	170	40	200	130	180	140	150	190	230	170	180	150	210	120	150	220
SumpleCu (s)Val (s)Val (s)Fe (s)Val (s)Fe (s)Val (s)Fe (s)Val (s)Fe (s)Val (s)Fe (s)Val (s)FeVal (s)Fe (s)Fe (s)Fe <td>Р</td> <td>780</td> <td>1600</td> <td>430</td> <td>1600</td> <td>2100</td> <td>2500</td> <td>1900</td> <td>370</td> <td>2100</td> <td>1400</td> <td>1500</td> <td>1400</td> <td>1900</td> <td>2600</td> <td>2000</td> <td>3500</td> <td>1800</td> <td>1100</td> <td>3300</td> <td>1300</td> <td>690</td> <td>3100</td>	Р	780	1600	430	1600	2100	2500	1900	370	2100	1400	1500	1400	1900	2600	2000	3500	1800	1100	3300	1300	690	3100
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SumpleCall (%)Ag(%)	Bi	0.6	0.2	n.d.	n.d.	n.d.	n.d.	0.1	0.2	n.d.	n.d.	n.d.	0.2	n.d.	0.2	0.1	n.d.	0.6	0.7	n.d.	0.5	0.8	0.05
Sumple C_{14}^{0} A_{2} S_{2}^{0} A_{2} S_{2}^{0} A_{2} S_{2}^{0} A_{2} S_{2}^{0} A_{2} S_{2}^{0} A_{2} S_{2}^{0} A_{2} A_{2}^{0}	Pb	40	40	15	10	15	20	25	~	25	20	160	95	10	25	20	8	20	40	30	10	160	20
Sample C_{01} Ag S_{0} F_{0} Au Sn Sn Table Ta	M	n.d.	n.d.	2	n.d.	1	1	0.1	n.d.	n.d.	n.d.	0.5	n.d.	n.d.	0.4	0.2	0.2	n.d.	n.d.	n.d.	n.d.	0.7	n.d.
Sample C_{ab} As S_{ab} F_{ab} <	Ba	25	130	450	2500	5700	1700	2300	180	n.d.	n.d.	n.d.	160	35	400	290	1200	340	150	1400	n.d.	50	730
Sample Q_{u} As A_{s} S_{s} AsAnSnSh (w_{0}) <td>Te</td> <td>1</td> <td>0.6</td> <td>~</td> <td>0.5</td> <td>4</td> <td>б</td> <td>0.4</td> <td>0.3</td> <td>0.7</td> <td>n.d.</td> <td>0.3</td> <td>n.d.</td> <td>0.2</td> <td>n.d.</td> <td>n.d.</td> <td>1</td> <td>n.d.</td> <td>0.2</td> <td>n.d.</td> <td>n.d.</td> <td>n.d.</td> <td>n.d.</td>	Te	1	0.6	~	0.5	4	б	0.4	0.3	0.7	n.d.	0.3	n.d.	0.2	n.d.	n.d.	1	n.d.	0.2	n.d.	n.d.	n.d.	n.d.
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SampleCu (6)AsAsSSA (96) (96) (96) (96) (96) (96) (96) (96) $4686-14$ $(0.02$ 100 8 1.54 7.46 $n.d.$ $4687-14$ 5.00 75 8 0.49 10.2 $n.d.$ $4687-14$ 5.00 75 8 0.49 10.2 $n.d.$ $4687-14$ 0.0055 0.4 $n.d.$ 0.008 8.99 $n.d.$ $4690-14$ 0.0045 2.2 4.4 0.008 9.19 $n.d.$ $4692-14$ 0.0015 0.8 1.6 0.003 9.19 $n.d.$ $4692-14$ 0.0015 0.8 1.6 0.014 9.19 $n.d.$ $4692-14$ 0.0055 0.5 0.6 0.033 0.014 0.14 $4692-14$ 0.0055 0.5 0.011 7.68 $n.d.$ $4692-14$ 0.014 3.17 0.029 0.13 0.14 $4692-14$ 0.014 3.17 0.13 0.14 $4692-14$ 0.014 3.17 0.13 0.14 $4692-14$ 0.014 3.17 0.13 0.14 $4692-14$ 0.014 3.17 0.13 0.14 $4692-14$ 0.014 3.17 0.13 0.14 $4692-14$ 0.014 3.17 0.13 0.14 $4702-14$ 0.14 0.012 0.12 0.14 $4702-14$ 0.14 0.010 0	Sn	Ч	0.7	0.6	0.8	1	1	1	0.6	0.6	б	0.8	0.5	1	0.8	0.7	1	0.5	0.6	1	0.8	15	0.8
SampleCu (%)AgAs S_{ϕ} S_{ϕ} $(88c)$ LH (90) (90) (90) (90) $(88c)$ LH (002) 100 8 1.54 7.46 $(488c)$ LH 5.00 75 8 0.49 10.2 $(488c)$ LH 5.00 75 8 0.49 10.2 $(469c)$ LH 0.0055 0.4 1.00 8.39 $(469c)$ LH 0.0045 0.2 4 0.0035 $(469c)$ LH 0.0045 0.2 1.26 9.19 $(469c)$ LH 0.0045 0.2 0.011 9.19 $(469c)$ LH 0.0045 0.2 0.012 0.035 $(469c)$ LH 0.0045 0.2 0.014 9.19 $(469c)$ LH 0.0045 0.2 0.011 9.136 $(469c)$ LH 0.0045 0.2 0.011 0.136 $(469c)$ LH 0.0045 0.2 0.011 0.136 $(499c)$ LH 0.0045 0.012 0.012 0.012 (4702) LH 0.0055 0.5 0.23 0.011 (4702) LH 0.0045 0.020 0.37 (4702) LH 0.0015 0.020 0.37 (4702) LH 0.0015 0.020 0.37 (4702) LH 0.0016 0.020 0.37 $(4$	Чu	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.												
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Sample $Cu(\%)AgAs4686_1146.0210084686_1145.007584689_1140.00550.4n.d.4690_1140.00550.4n.d.4690_1140.00752244691_1140.00752244692_1140.00150.8154692_1140.00150.8154692_1140.00550.8154692_1140.00550.684692_1140.00550.684699_1140.00550.684699_1140.00550.684699_1140.00550.684701_1140.00550.6154702_1140.00350.6164702_1140.0011184702_1140.001115104708_1140.001115104708_1140.0045111004709_1140.0045111004700_1140.0492711204700_1140.492711204700_1140.492111004700_1140.492111004700_1140.492111004700_1140.492111004700_1140.49211$	S (%)	1.54	0.49	0.008	0.035	0.0085	0.011	0.008	0.29	0.014	0.009	0.03	1.27	0.011	0.37	0.020	0.009	0.24	6.50	0.006	2.13	7.31	0.038
Sample Cu (%) Ag 4686_14 6.02 100 4687_14 5.00 75 4689_14 5.00 75 4689_14 5.00 75 4689_14 0.0055 0.4 4690_14 0.0075 2 4691_14 0.0015 0.8 4691_14 0.0015 0.8 4693_14 0.0015 0.8 4693_14 0.0015 0.8 4699_14 0.0055 0.6 4699_14 0.0055 0.6 4699_14 0.0055 0.6 4699_14 0.0055 0.6 4701_14 0.0055 0.6 4701_14 0.0035 0.6 4703_14 2.21 20 4701_14 0.0015 1 4701_14 0.0016 1 4701_14 0.0016 1 4701_14 0.0016 1 4701_14 0.0016 1 4701	As	8	8	n.d.	9	4	15	15	n.d.	30	8	30	10	15	25	15	8	10	15	10	9	15	20
SampleCu $(\%)$ 4686_14 6.02 4686_14 6.02 4687_14 5.00 4689_14 0.0055 4690_14 0.0075 4691_14 0.0075 4692_14 0.0015 4692_14 0.0015 4692_14 0.0045 4692_14 0.0055 4692_14 0.0055 4692_14 0.0055 4692_14 0.0055 4699_14 0.0055 4701_14 0.0055 4701_14 0.0035 4702_14 0.0035 4702_14 0.0016 4705_14 0.0016 4708_14 0.0016 4708_14 0.0045 4708_14 0.0045 4708_14 0.0045 4701_14 0.0045 4701_14 0.0045 4701_14 0.0045 4701_14 0.0045 4701_14 0.0045 4711_14 0.49	Ag	100	75	0.4	1.0	2	0.8	0.7	20	0.5	0.6	3	50	0.6	20	15	1	35	270	1	120	370	2
Sample 4686_14 4687_14 4689_14 4689_14 4690_14 4691_14 4693_14 4693_14 4698_14 4698_14 4698_14 4698_14 4701_14 4701_14 4703_14 4703_14 4703_14 4703_14 4703_14 4703_14 4703_14 4703_14 4709_14 4709_14	Cu (%)	6.02	5.00	0.0055	0.048	0.0075	0.0015	0.004	1.90	0.0055	0.055	0.14	4.45	0.0035	2.21	2.71	0.001	6.43	25.0	0.0045	9.21	34.5	0.49
	Sample	4686_14	4687_14	4689_14	4690_14	4691_14	4692_14	4693_14	4694_14	4695_14	4696_14	4698_14	4699_14	$4701_{-}14$	4702_14	4703_14	4704_14	4705_14	4707_14	4708_14	4709_14	4710_14	4711_14

Table 3. Trace element analysis results of the Veshnaveh geological samples by SC-ICP-MS at the DBM. All values are in ppm, unless otherwise stated. The "n.d." means below the detection limit:

Pernicka, 2005; 2012; Pernicka, et al., 2011). These comparisons lead to the following conclusions:

- The lead isotope ratios from 11 Veshnaveh ore samples are very similar and plot within a narrow range between 18.581 and 18.631 for 206 Pb/ 204 Pb (avg. 18.614), 15.620 to 15.632 for 207 Pb/ 204 Pb (avg. 15.627) and 38.622 to 38.691 for 208 Pb/ 204 Pb (avg. 38.667). All 2σ (95% confidence level) errors are less than 0.05% for the 207 Pb/ 206 Pb and 208 Pb/ 206 Pb ratios. The 11 whole-rock samples of host rocks yielded lead isotope values in the range of the ore lead signatures. This is an indication of close genetic kinship of the ore and its host rock.
- One sample from the so-called feeder dykes that intersects the Mazrayeh mineralization indicates a rather different lead isotope signature from the ore

and the main host rock, therefore this dyke probably has not played a role in the mineralization.

- The lead isotope ratios of four artifacts from the site of Kahak indicate a possible match to the ore of Veshnaveh (Table 1, No. 1, 2, 5 and 8) although this match is much less in the case of the objects of Jamkarān/Qolī Darvish site. Only one sample, a slag sample, from Jamkarān site (Table 1, No. 18) shows a rather good match with the ore of Veshnaveh and provides evidence for the smelting of copper at a workshop at Qolī Darvish.
- The lead isotope signature of the Veshnaveh ore does not correspond well with the archaeometallurgical remains of Arismān and Sialk, and this might suggest that the Veshnaveh ancient mine has probably not been the supplier of raw materials for those an-

Table 4. Lead isotope analysis results of the Veshnaveh ore and host-rock samples. Samples prepared at the DBM and measured at the Goethe-Universität Frankfurt am Main by MC-ICP-MS.

Sample No.	Location	Sample type	²⁰⁸ Pb / ²⁰⁶ Pb	²⁰⁷ Pb / ²⁰⁶ Pb	²⁰⁶ Pb / ²⁰⁴ Pb
4686-14	Mazrayeh	Ore (+ Host rock)	2.0772	0.83921	18.623
4687-14	Mazrayeh	Ore	2.0775	0.83937	18.623
4689-14	Mazrayeh	Andesite porphyry	2.0774	0.83997	18.600
4690-14	Mazrayeh	Andesite-Basalt	2.0792	0.84167	18.563
4691-14	Mazrayeh	Amygdaloidal andesite	2.0778	0.83981	18.611
4692-14	Mazrayeh	Red amygdaloidal andesite	2.0769	0.83938	18.613
4693-14	Mazrayeh	Host rock + Fe-Oxide	2.0768	0.83916	18.623
4694-14	Mazrayeh	Ore+Host rock	2.0787	0.84084	18.581
4695-14	Chāle Ghār	Host rock	2.0771	0.83942	18.613
4696-14	Chāle Ghār	Host rock (+ore)	2.0767	0.83932	18.614
4698-14	Chāle Ghār	Host rock	2.0773	0.83934	18.618
4699-14	Chāle Ghār	Ore (+ Host rock)	2.0773	0.83929	18.622
4701-14	Lāghe Morād	Host rock	2.0775	0.83959	18.609
4702-14	Lāghe Morād	Ore	2.0776	0.83998	18.607
4703-14	Lāghe Morād	Ore+Qz+Cc	2.0771	0.83983	18.608
4704-14	Lāghe Morād	Host rock	2.0753	0.83850	18.634
4705-14	Lāghe Morād	Ore+Qz+Cc	2.0758	0.83884	18.632
4707-14	Veshnaveh, Unspecified	Ore	2.0775	0.83937	18.621
4708-14	Lāghe Morād	Amigdaloidal Andesite-Basalt	2.0770	0.83926	18.621
4709-14	Lāghe Morād, mine 1	Ore	2.0774	0.83955	18.613
4710-14	Lāghe Morād, mine 1	Ore	2.0775	0.83934	18.625
4711-14	Lāghe Morād, mine 6	Ore	2.0772	0.83973	18.603
Table 1/26	Chāle Ghār, mine 3	Ore	2.0779	0.83919	18.630
Table 1/27	Mazrayeh	Ore	2.0775	0.83891	18.640
Table 1/28	Lāghe Morād, mine 1	Ore	2.0782	0.83916	18.637

Table 5. Lead isotope analysis results of metals and slags from Tappeh Sarm and Qolī Darvish (Jamkarān) (LIA at the CEZ in Mannheim, MC-ICP-MS).

Sample No.	Location	Sample type	²⁰⁸ Pb / ²⁰⁶ Pb	²⁰⁷ Pb / ²⁰⁶ Pb	²⁰⁶ Pb / ²⁰⁴ Pb
Table 1/1	Tappeh Sarm	metal	2.0763	0.83900	18.663
Table 1/2	Tappeh Sarm	metal	2.0780	0.83845	18.747
Table 1/3	Tappeh Sarm	metal	2.0732	0.83670	18.715
Table 1/5	Tappeh Sarm	metal	2.0837	0.84325	18.561
Table 1/6	Tappeh Sarm	metal	2.0727	0.83556	18.753
Table 1/8	Tappeh Sarm	metal	2.0762	0.83777	18.650
Table 1/15	Jamkaran, Qolī Darvish	metal fragment	2.0499	0.83454	18.721
Table 1/16	Jamkaran, Qolī Darvish	slagged furnace lining	2.0706	0.83427	18.785
Table 1/18	Jamkaran, Qolī Darvish	smelting slag	2.0773	0.83932	18.628
Table 1/19	Jamkaran, Qolī Darvish	copper-rich slag	2.0839	0.84262	18.561

Table 6. Chemical composition of metals and metal fragments from Qolī Darvish (Jamkarān) and Tappeh Sarm (Kahak) XRF-analyses at the CEZ Mannheim. The "n.d." means below the detection limit: Co, Ni, As, Au, Pb and Bi (<0.01 %), Zn (<0.2 %) and Se, Sn and Te (<0.005 %).

	Cu %	Fe %	Co %	Ni %	Zn %	As %	Se %	Ag %	Sn %	Sb %	Te %	Au %	Pb %	Bi %
Table 1/1	92	0.38	n.d.	n.d.	n.d.	0.089	n.d.	0.092	7.3	0.026	0.008	n.d.	0.232	n.d.
Table 1/2	88	0.173	n.d.	0.021	n.d.	0.148	n.d.	0.231	11.4	0.021	n.d.	n.d.	0.189	n.d.
Table 1/3	91	0.234	n.d.	0.011	n.d.	0.35	n.d.	0.093	8.2	0.076	n.d.	n.d.	0.204	n.d.
Table 1/5	93	0.31	n.d.	0.025	n.d.	0.172	n.d.	0.067	5.6	0.091	n.d.	n.d.	0.185	n.d.
Table 1/6	99	0.02	n.d.	n.d.	n.d.	0.47	n.d.	0.264	0.046	0.043	n.d.	n.d.	0.052	0.021
Table 1/7	91	0.038	n.d.	0.015	n.d.	n.d.	n.d.	0.053	9.0	0.005	n.d.	0.014	0.058	n.d.
Table 1/8	99	0.257	n.d.	0.024	n.d.	0.208	n.d.	0.109	0.44	0.014	n.d.	n.d.	0.048	n.d.
Table 1/9	95	0.49	n.d.	0.018	n.d.	n.d.	0.006	0.128	3.9	0.048	n.d.	0.011	0.025	n.d.
Table 1/10	98	0.02	n.d.	n.d.	n.d.	0.011	n.d.	1.14	n.d.	0.69	n.d.	n.d.	n.d.	n.d.
Table 1/11	98	0.118	n.d.	0.020	n.d.	1.38	n.d.	0.008	0.006	0.012	n.d.	n.d.	0.69	n.d.
Table 1/12	99	0.255	n.d.	0.019	n.d.	0.67	n.d.	0.109	0.008	0.012	n.d.	n.d.	0.055	n.d.
Table 1/14	93	0.133	n.d.	n.d.	n.d.	n.d.	n.d.	0.090	3.2	0.063	0.001	n.d.	3.8	0.003
Table 1/15	70	16.0	n.d.	n.d.	5.4	2.49	0.097	0.145	0.178	2.23	n.d.	1.96	1.07	n.d.
Table 1/21	89	0.278	n.d.	n.d.	n.d.	0.64	0.010	0.128	9.5	0.029	n.d.	n.d.	0.219	n.d.
Table 1/22	92	0.35	n.d.	n.d.	n.d.	0.113	n.d.	0.047	6.8	0.013	n.d.	n.d.	0.225	n.d.
Table 1/23	93	0.156	n.d.	n.d.	n.d.	n.d.	n.d.	0.089	2.78	0.050	n.d.	n.d.	3.9	n.d.
Table 1/24	93	0.126	n.d.	n.d.	n.d.	n.d.	n.d.	0.095	3.0	0.063	n.d.	n.d.	3.8	n.d.

Table 7. Comparison of the major geological and mineralogical characteristics of the Veshnaveh copper deposit and "Manto type" copper deposits. After Ruiz, et al., 1971, Sato, 1984, Espinoza, et al., 1996, Cupo, 2000.

	Manto type (Type I)	Manto type (Type II)	Veshnāveh
Host rock	Subaerial andesitic flows + Minor pyroclastics, ignimbrite, Volcanoclastic sandstone, siltstone, and limestone	Andesite to quartz dacite	Subaerial andesitic flows
Alteration	Little to no wall rock alteration (occurs in prehnite-pumpellyite metamorphic facies)	Extensive chloritization, albitization, silicification- hematitization	prehnite-pumpellyite metamorphic facies
Morphology of the ore body	Manto shaped peneconformable orebodies	irregular pseudostratiform orebodies obliquely cutting host rock strata	Manto shaped peneconformable orebodies
Sulphide assemblage	Chalcocite, bornite (chalcopyrite)	bornite, digenite, chalcopyrite + minor pyrite and galena	Chalcocite, bornite
Secondary mineralization	atacamite, chrysocolla	Minor chalcocite, covelline, pyrite, galena	atacamite, malachite
Formation age	Variable (often Mid-Late Jurassic to Early Cretaceous)	Late Triassic-Early Jurassic	Middle-Upper Eocene
Type of mineralization	Veins, veinlets, dissemination, amygdale infilling	Dissemination	Veins, veinlets, dissemination, amygdale infilling
Ore genesis	Two stages; metamorphic and hydrothermal	Metamorphic-seawater circulation with a magmatic heat source	Two stages; metamorphic and hydrothermal
Timing of Mineralization	Epigenetic	Epigenetic	Epigenetic-Syngenetic?
Fluid types	metamorphic to hydrothermal	saline hydrothermal fluids	metamorphic to hydrothermal
Example	Buena Speranza and Centenario	Mantos Blancos and El Soldado	

cient sites. It should be noted that despite the proximity of Sialk and Veshnaveh (approx. 50 km), there is no isotopic correspondence between the ore from Veshnaveh and the slag or metal objects from Sialk (Schreiner, Heimann and Pernicka. 2003), although it is assumed that the ancient mine of Veshnaveh was active in the early 3rd millennium BC, which is contemporary with the Sialk IV period (Stöllner, Mireskandari and Roustaei, 2011).

Doe and Zartman (1979) and Zartman and Doe (1981) introduced the plumbotectonics model to account for variations in average lead isotopic composition among different tectonic settings. Based on the lead isotope data of Veshnaveh plotted with the Plumbotectonics model, it seems that the host rock of Veshnaveh mineralization has a lower crustal origin that has contributed to orogeny (Figure 9).

Trace element investigations

The lead isotope data clearly show a possible connection between the Veshnaveh ore-field and the sites of Tappeh Sarm and Qolī Darvish north of the Qom Mountains. Further arguments are needed to identify the provenance of metals, smelted metal debris and slag from both the sites. As their archaeological dating fit best to the majority of archaeological dates from the Veshnaveh mines, this would be a probable assumption.

The trace-element contents of the metal objects from Tappeh Sarm and Qolī Darvish that have been investigated in Bochum by SC-ICP-MS and in Mannheim by XRF were compared with the Veshnaveh ore. This has resulted in different detection limits which made the correlation and comparison of some chalcophile elements (including Co, Zn, and Au) difficult (see Table 3 to Table 6).



Figure 8. a) Isotope plot of lead in the ore and host rock samples from Veshnaveh, b) comparison of the lead signatures of the samples from Kahak (Tappeh Sarm) and Jamkarān (Qolī Darvish) and the slag pieces from Veshnaveh, c) comparison of the lead ratios of Veshnāveh ore with metallurgical remains from Arismān and Sialk, d) comparison of the lead signatures of the samples from Kahak and Jamkarān and the ore of Veshnaveh. All 2-a (95% confidence level) errors are less than 0.05% for the ²⁰⁷Pb / ²⁰⁶Pb and ²⁰⁸Pb / ²⁰⁶Pb ratios.

Five chalcophile trace-elements delivered comparable results in all ore and metal datasets (Sb, Ni, As, Ag, Pb) (see Figure 10): Comparing these five trace elements, Ni shows a rather good concurrence while other elements are divergent on a larger degree. The ore of Veshnaveh shows very low amounts of As, Pb, Sb, and Ni and the pattern of trace elements found in metals would indicate an enrichment of, in some cases, more than 200 times, if the metal had been smelted exclusively from Veshnaveh ore.

This is especially the case for most of the artifacts in respect of their As, Pb and Ag. Some As, Pb and Ag exceed trace elementary status (over 1 %) representing thus rather an alloying effect. This inhibits a general and simple provenance argument: For some artifacts one could consider the fact that chalcophile elements became enriched in the copper during the various smelting and melting processes. An enrichment up to 10 times is not implausible, especially if the metal is remelted several times (Hauptmann 2007). Antimony is the only element that is enriched to an even higher concentration. Four artifacts from the Tappeh Sarm graveyard (Sample No. 1, 2, 5, 8) are in moderate to good lead isotope agreement with the Veshnaveh ore but there is a rather striking enrichment in some of the elements mentioned above.

This even is nearly true for their antimony levels although the number of even higher enriched samples is larger as with Ag, Pb and As. If we consider them as artefacts made of Veshnaveh copper this has to be explained. It is conspicuous that in three cases (No. 1, 2 and 5) tin was added. As it is rather likely that tin-alloying was made with tin smelted from cassiterite, poor in impurities, one can assume that this alloying would not have significantly altered the trace-element pattern. But



Figure 9. Location of the lead isotope compositions from the occurrences of Veshnaveh in the "Plumbotectonics Model" of Doe and Zartman (1981).

let us have a closer look to the artifacts in general: The tanged spearheads No. 22 and 23 obviously have been alloyed with some lead perhaps enabling a better cast; but their other trace elements do not differ from other artifacts. The same is true for the dagger No. 21which is conspicuous for its rather high As content. The arsenic content probably does not derive from alloying while the tin-content is indicative for a deliberate tin-bronze. As we have no measurements of their lead isotope ratios, there can be no further provenance indication of the copper used for the artifacts No. 21 to 23.

Another example is the copper arrowhead No. 10 whose trace elements levels are incompatible, especially with regard to Sb and As, thus possibly providing an argument for a different origin of the copper ore. Looking in detail on artifacts and their chemical composition, it becomes clear that most of the metals in the vicinity of Veshnaveh were made possibly using a mixed-ore basis. Different types of ore were seemingly blended and smelted together. For such an assumption, it is helpful to look at the metal scrap and metal smelting debris from the workshops at Qolī Darvish: objects No. 11-14 are indicative of such mixed metal scrap. The tin-bearing metal

casting droplet No. 14 certainly derived from a process involving alloying or co-smelting with tin ore, while No. 11 and 12 may derive from a copper smelting process by which As and Pb are enriched in the metal. All this indicates that the workshop processes were important in determining the metal composition. But was Veshnaveh ore used at the Qolī Darvish workshop? The lead isotope ratios of the slag (Table 5, No. 1/18) strongly indicates the possible smelting of Veshnaveh ore at the Qolī Darvish workshops. As the metal scrap demonstrates, different metals and ore concentrates were assembled there. This undoubtedly complicates the argument for a single provenance. According to the current state of knowledge, it is thus likely that chalcocite and bornite concentrates from Veshnaveh were brought to settlements and their workshops (such as Qolī Darvish) and were smelted there (there is not a single piece of evidence for contemporaneous smelting activities around Veshnaveh).

Discussion and conclusions

a. Economic geologic aspects

Veshnaveh is a copper deposit, hosted by a Middle-Upper Eocene basalt andesite volcanic sequence in central Iran. It shares several similarities with a broad range of volcanic-hosted copper deposits, including the so called "Manto-type" deposits (Sato 1984, Kojima, et al., 2003; Kojima, Trista-Aguilera and Hayashi, 2009) or "Basalt-andesite copper deposits" (Guilbert and Park, 2007), and or "volcanic red-bed deposits" (Kirkham 1995; Cabral and Beaudoin 2007) respectively reported from Chile (Cretaceous Chilean Manto Type Cu deposits), north Michigan and the west coast of North America (Keweenawan Michigan copper deposits and Canada), and China. Nevertheless, the host rock of the Veshnaveh mineralization is the youngest among the above mentioned deposits. The North American and Chinese types of deposits are less sulphidic with native copper being a major ore mineral, while the Chilean types together with Veshnaveh show a more copper sulphides as major ore. The main characteristic features of the Manto-type copper deposits which distinguish them from other types of copper deposits are as follows (Sato 1984; Espinoza et al. 1996, Kirkham 1996, Kojima, et al., 2003; Kojima, Trista-Aguilera and Hayashi, 2009):4

(1) Occurrence in subaerial amygdaloidal andesite to basaltic-andesite, with no direct association with large intrusive bodies, (2) a main ore assemblage of chalcocite, digenite, bornite, \pm silver (in some cases chalcopyrite),⁵ (3) general absence of abundant pyrite, sphalerite











Figure 10. Comparison of trace-elements As, Ag, Pb, Ni and Sb of Veshnaveh ores (purple, Table 3) and of Tappeh Sarm and Jamkarān metals (red, Table 6) together with the distribution of four metal objects from Tappeh Sarm whose Pb-isotope ratio indicate a modest to rather good match with the Veshnaveh ores.

and galena, (4) rather high concentration of silver in the ore, (5) occurrence of mineralization as disseminations, veins, veinlets, amygdale fillings and fracture coatings within Manto-shaped peneconformable orebodies, (6) a weak to moderate wall rock alteration consisting of an assemblage of quartz, epidote, albite, chlorite, and calcite, (7) presence of low grade prehnite-pumpellyite facies metamorphism associated with mineralization.

This type of mineralization has occurred at different time periods worldwide from Late Precambrian in North America, to Permian in China, Cretaceous in Chile, to Middle-Upper Eocene in Iran. The Chilean Manto type deposits are often subdivided based on morphology and/ or variations in host rock age and lithology. Using morphology as a mean of classification, Sato (1984) recognized two broad types of Chilean Manto deposits:

- Type I: Stacked, tabular deposits. Sulfides occur in permeable units such as amygdaloidal flow tops or in calcareous sedimentary rocks alternating with shales. examples: Buena Esperanza, Los Maquis, Susana de Michilla, Centenario
- Type II: Pseudostratiform deposits. These orebodies crosscut host rock stratigraphy. Sulfides occur as fine-grained disseminations and in veinlets. Many of these deposits display well developed alteration assemblages, examples being: Mantos Blancos, EI Salado, Jardin, Amolanas, Lo Aguirre, El Soldado.

Veshnaveh appears to be a chalcocite-rich end member of the Type I style of Manto-type copper deposits (Table 7).

According to the geological, mineralogical, and geochemical characteristics of the Veshnaveh copper deposit and comparison of these with already known Manto type deposits (Sato 1984; Espinoza et al. 1996, Kirkham 1996, Kojima, et al., 2003; Kojima, Trista-Aguilera and Hayashi, 2009) a possible model for the genesis of the mineralization can be summarized as following stages:

- The extrusion of a gas-rich basaltic magma with a lower crustal origin under a submarine condition.
- Formation of open spaces and fractures in andesite/ basalt due to the fast cooling of the magma; tectonic movements (orogeny?) simultaneously caused a weak metamorphism in the rock.⁶
- Liberation (leaching) of copper from silicate minerals (from andesite-basalt and possibly the surrounding rocks) during metamorphism by the action of chloride-containing hydrothermal fluids, heated by metamorphism.
- Release of fluids from that circulated up through the deposit taking advantage of zones of increased permeability and precipitation of copper in the rock in response to changing pH.
- Egression of the volcanic body out of the water and oxidation of the mineralization.

Implications for exploration

Recent exploration for metallic mineral resources in Iran has shown that a horizon of the Middle-Upper andesite-basalt rocks could host the Manto type of copper mineralization. This horizon which extends from the Azarbaijan Province of Iran to the central (Veshnaveh and Darhand deposits) and east Iran (Abbas Abad and Qaen regions) is characterized by a prehnite-pumpellyite facies metamorphism and a stratabound low-sulfide (and/or native copper) mineralization which in some cases has been exploited by ancient miners.

The Veshnaveh copper deposit has a Cr-(Zn-V)-spinel (possibly hercynite); this could be another indication for productive volcanic rocks for copper mineralization of this type and therefore be an exploration criterion.

b. Archaeometric aspects

Geological, geochemical, and mineralogical work, including the low content of elements like arsenic, antimony, and lead as well as different lead isotope signatures, show that the Veshnaveh ore does not match the ore that

could be of use in the ancient sites of Arisman and Sialk, neither isotopically, nor from the trace elemental pattern point of view (Pernicka, et al., 2011; Nezafati and Pernicka 2012), and this despite the proximity of Veshnaveh to these sites, especially to the site of Sialk. Nevertheless, the Veshnaveh copper mine could have well been an ore supplier, but rather for the second millennium BC ancient sites of Kahak and Jamkarān, a suggestion especially based on lead isotope analyses. This can be ascertained for at least for some of the artifacts found in Tappeh Sarm. The discussion of various trace-elements especially made clear the difficulties to determine copper provenances if different ore and metals were blended and mixed. The analysis of some of the workshop debris from Qolī Darvish underlines the difficulties in understanding the ore-supply if ore-components of different locations are coevally worked in smelting and melting centers. The blending of metal ore or different metal products has been also observed at the older metallurgical foci such as Arisman and Sialk which underlines an even older practice of metal procurement tradition on the Western Iranian central plateau.

A meaningful provenance study needs to be based at least on a series of matches in the geochemical data (trace elements and lead isotopes of the metal in comparison with slag and ore) and of economic and archaeological context, or accordance, such as the temporal correlations between the production and consumption pattern. But none the less the general probability of an economic relation is important to consider. In our case we can argue archaeologically as the pottery found in those mines are most closely related to grey ware and painted ware pottery found in Jamkarān (Qolī Darvish) and Tappeh Sarm (see Piller 2004; Stöllner, Mireskandari and Roustaei, 2011, 601; Sarlak 2004; 2011). This would indicate that regional communities practiced the mining most likely in relation to extensive pastoral strategies. Such a postulation is supported by the spectrum of domestic animals discovered and determined from Bronze Age layers of Veshnaveh: goats and sheep are dominant, but even some cattle and donkeys are evidenced thus allowing for the assumption of mixed herds that accompanied the mining communities (M. Doll in Stöllner, Mireskandari and Roustaei, 2011, p.603). So it would be likely that communities from the valleys and plains north of Veshnaveh were roaming with their herds through the pastoral mountains especially during summer times when water and grazing pastures became scarce in the arid plains. This even may have forced them to stay seasonally in the mountains, something that would have likely induced further economic activity in respect of mining the ore yield of the region.

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Notes

- 1 The samples were provided 2008 by Dr. S. Sarlak, (at that time: National Museum of Iran in Tehran).
- 2 The LIA and XRF investigations were performed by courtesy of Prof. Dr. E. Pernicka at the Curt-Engelhorn-Zentrum at Mannheim; for the specific analytical protocols and machines used there see http://www.cez-archaeometrie.de/?page_id=194. The XRF-analysis was performed by help of an ARL Quant'X EDXRF spectrometer, while the lead isotopes were investigated by a Neptune Plus HR-MC-ICP-MS with inductively coupled argon plasma.
- 3 The contents of Cu and S examined the samples with SEM are closer to chalcocite and/or digenite. The XRD analyses detected chalcocite and digenite while minerals like anilite were not detected. In order to confirm the presence of minor amounts of other copper sulfide minerals microprobe analysis would be required, which was out of the scope of this investigation.
- 4 Although the term of "Manto" was initially used to describe the geometric shape of some ore deposits, at least from 1984 it is also used for a specific type of copper deposits with special genetic characteristics which are called "Manto-Type Copper Deposits". For more information refer to Kojima, Trista-Aguilera and Hayashi, 2009.
- 5 Interestingly, the Michigan-type copper deposits and the Manto-type copper deposits show very similar characteristics and except for the age of their host rocks they seem to be of the same type. A discussion has been initiated on Researchgate in this regard: https://www.researchgate. net/post/Can_we_consider_the_manto-type_copper_deposits_and_basalt-andesite_copper_deposits_including_ Michigan_type_copper_the_same_type_of_mineralization
- 6 Generally, traces of a weak metamorphism have been observed with these types of copper deposits. Some publications (cited in the text above) have proposed simultaneous tectonic movements as the cause of this weak metamorphism.

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Authors

Nima Nezafati (Corrosponding Author) Islamic Azad University, Science and Research Branch, Department of Geology and Geophysics, Pounak 1477893855, Tehran, Iran Nima.nezafati@gmail.com

Thomas Stöllner Ruhr University Bochum/Deutsches Bergbau-Museum Bochum Institute of Archaeological Studies/Research Division Am Bergbaumuseum 31 44791 Bochum thomas.stoellner@rub.de/ thomas.stoellner@bergbaumuseum.de