

Mineralogical evolutions of carbonate-hosted Zn-Pb-(F-Mo) deposits in Kuhbanan-Bahabad area, Central Iran: metal source approach

Ali Amiri¹

1- Department of Geology, Islamic Azad University, Zarand Branch, Kerman, Iran.

* Corresponding Author: aliamiri@iauzar.ac.ir, aliamiri731@yahoo.com

Received: 24 March 2016 / Accepted: 25 January 2017 / Published online: 26 January 2017

Abstract

Over forty nonsulfide dominated Zn (-Pb) deposits with the same character are situated at the Kuhbanan-Bahabad area (KBA), Central Iran. The host rock of these deposits is the Upper Permian (-Lower Triassic) carbonate rocks. Mineralogical studies showed that three dependent mineralization have been occurred in the area. Firstly, a unique and less common disseminated sulfide (sphalerite, galena and pyrite) have formed during the diagenesis stages in the Upper Permian carbonate rocks as a syndiagenetic mineralization. Secondly, because of the later tectonic squeezing of the sulfide bearing strata of Upper Permian, the economic vein-type sulfide mineralization has formed hydrothermally and is present in a few deposits of the area (Tajkuh and Tarz deposits). Sphalerite, galena and pyrite are the main sulfide minerals and a lesser amounts of chalcopyrite and arsenopyrite is accompanied the ore. Sulfur stable isotope studies on the main sulfide minerals showed that the mineralization is comparable with the MVT deposits and the mixing model is the best model for sulfide precipitation. Finally, the third mineralization evolution is outcropping the vein-type sulfide mineralization and exposing to the oxidation conditions and so, formation of the nonsulfide Zn (-Pb) ore has occurred. Smithsonite, hydrozincite and hemimorphite are the most abundant nonsulfide minerals and some minor to accessory minerals such as cerussite, anglesite, willemite and wulfenite are present in some cases. Carbon and oxygen stable isotope studies showed that combination of meteoric, ground and entrapped connate waters are the fluids responsible for transformation of sulfide to nonsulfide minerals. It seems that the Upper Permian carbonate rocks have played two separate important roles, source and host rock for the mineralization in the KBA.

Keywords: Nonsulfide Zinc Deposits; Mineralogy; MVT; Mixing Model; Supergene; Kuhbanan-Bahabad.

1- Introduction

Nonsulfide zinc deposits (NSZDs) are relatively uncommon ore types that predominantly hosted in carbonate (limestone and dolomite) rocks (Large, 2001; Hitzman *et al.*, 2003). They were the major source for zinc metal, and recently have enjoyed resurgence in interest due to new processing technologies and applying solvent extraction and electrowinning techniques. Scientific research, resulting from the economic interest shown by many mining companies in this style of mineralization, has focused on

several potentially economic “zinc oxide” deposits in Iran (e.g., Irankuh, Ghazban *et al.*, 1994; Anguran, Gilg *et al.*, 2005; Mehdi-Abad, Iran-Kuh, and Kuh-e-Surmeh, Reichert and Borg, 2008). Although attention to NSZDs is refer to 20th century, exploitation of this type of zinc mineralization in Central Iran, including northern Kerman and east and south-east of Yazd provinces was started at thousands years ago and ancient remnants of mining is still exist now, as far as in these area, a word is applied as

“Shaddadi mining”. This word means the ancient mining with unidentified age and frequently can be seen as shallow descending excavation which more or less complies with principles of engineering. Shaddadi mining works can be found abundantly in all of the Central Iranian zinc deposit including the thirteen deposits as targets of this research.

In most cases of NSZDs of the KBA, mining is mainly performed at the nonsulfide ores. Zinc ore was the main products of the area, but in some cases, lead and fluorite were exploited. For example, some parts of the Gavar mine are composed mainly of cerussite. Also, to the north-west of the area, fluorite can be seen as a main to minor mineral in some deposits. For example, at the Kuh-e-Bijahan (15 km NW Ahmadabad), a fluorite vein-type mineralization with the same character as the other NSZDs is explored recently. In this case, a 230 meter vein of fluorite with up to 4 meters thickness is hosted by Permo-Triassic carbonate rocks and barite and celestite together with calcite, dolomite and silica are the main gangue minerals (Kavoshgaran Paradis Co., 2013).

Two major types of NSZDs are indicated consisting of hypogene and supergene types (Heyl and Bozion, 1962), which can be distinguished according to their geological setting and mineralogical aspects (Hitzman *et al.*, 2003). Of these two types, the supergene type is more frequent and based on many researches (e.g. Large, 2001; Hitzman *et al.*, 2003; Mondillo *et al.*, 2014; Paradis *et al.*, 2016), they can originate from Mississippi Valley type (MVT) deposits as protore. In recent years, many researches have been conducted on NSZDs around the world. For example, Large (2001) proposed a mineralogical categorization of NSZDs to calamine (smithsonite/hemimorphite)-dominant, silicate (willemite, franklinite)-dominant and hydrated zinc silicate deposits. Their formation also is primarily controlled by climatic factors

(humidity, temperature and biological activity), the composition of the protore (sulfide diversity) and the composition and structures of the wall rocks (Reichert and Borg, 2008).

In this paper, I focused on supergene type, because this type is predominantly the main type of Central Iranian zinc deposit. In the KBA (Central Iran), more than 40 cases of NSZDs is known and some of these have studied in detail. For example, Amiri (2007) has completed his dissertation on Ravar- Bafgh area. Also, Amiri *et al.* (2009) were studied geochemistry and stable isotope of some of these deposits. But the subject of mineralogy and mineralogical evolutions in this area has not been studied in detail yet. This issue is very important to exploration and consequently to prediction of ore composition since exploitation and ore beneficiation. Furthermore, detailed observation of mineralogy and evolution of mineral phases can be determined genesis of these deposits too.

2- Geological setting

The KBA is located at the intersection of Kerman and Yazd provinces (longitude E055°, 33' to 056°, 50' and latitude N31°, 21' to 31°, 56') and contains an important occurrence of carbonate-hosted Zn-Pb deposits (Fig. 1). In this area, at least forty cases with analogous character of NZDs are exist (Amiri, 2007). Among these cases, only a few are in operation (Tarz, Gujer, Tajkuh and Gicherkuh) and others are inactive for various reasons. Unfortunately, there is no documented information of ore reserve of these deposits.

In this area, geological formations toward the present time are comprised Cambrian (Desu Formation, dolomite and gypsum; Dahu Formation, red sandstone, shale and conglomerate; Kuhbanan or Mila Formation, limestone), unidentified Ordovician- Silurian (limestone, sandstone and green shale), Upper Permian-Carboniferous (Sardar and Jamal Formations?, red sandstone and conglomerate,

limestone and dolomitic limestone), Triassic (Shotori and Nayband Formations, dolomite and limestone), Jurassic (Liassic coal-bearing shale and sandstone), Cretaceous (limestone) and Cenozoic (old and new terraces). Also, doleritic dykes and sills have been intruded various strata from Cambrian to Cretaceous (Fig. 2). A simplified and not to scale stratigraphic column of the area is shown in Figure 3.

The intended Zn-Pb deposits are located mainly in the Upper Permian (and less common in the Lower Triassic) carbonate rocks as strata-bound mineralization. The two major faults, Kuhban and Bahabad faults, with north-west to south-east directions are the main geological structures of the area.

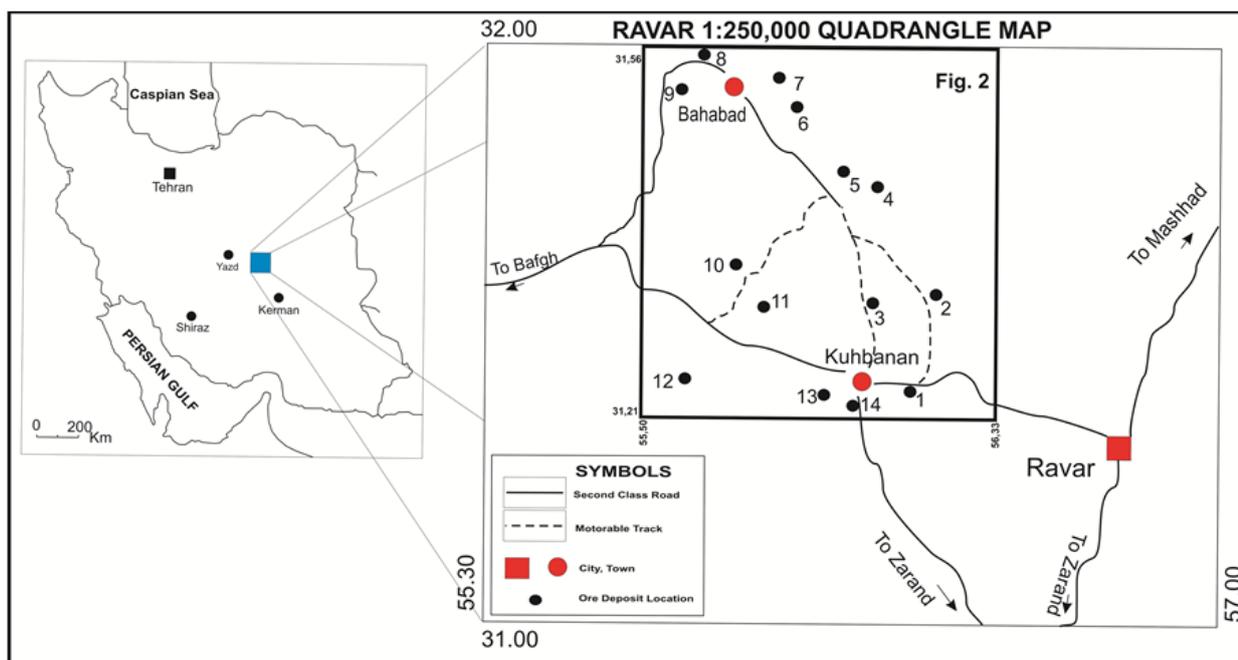


Figure 1) Geographical setting and access road of KBA (Fig.2) and situation of this area in the Ravar 1:250,000 quadrangle map. The numbers 1-14 are introduced in Fig. 2.

3- Material and methods

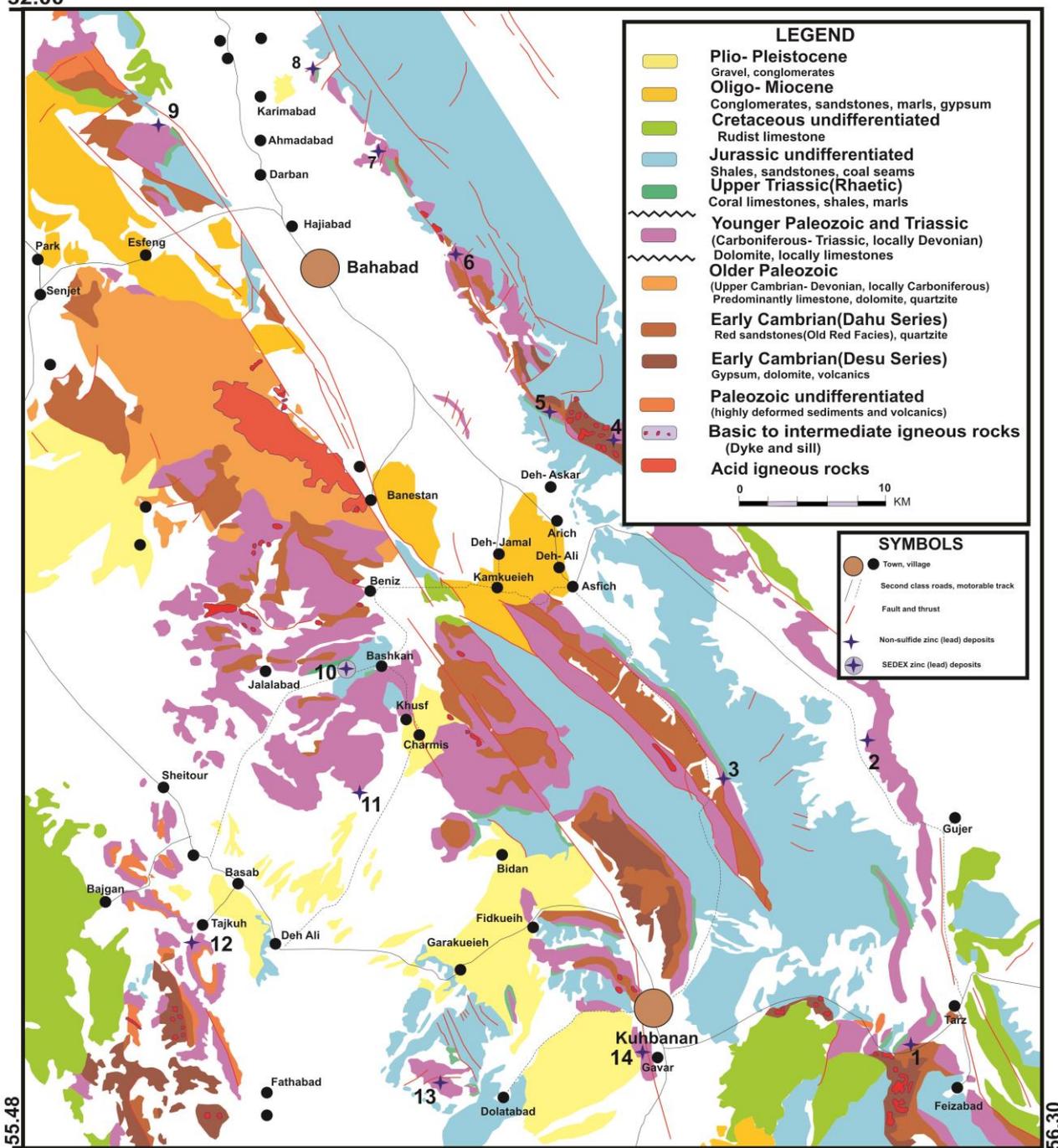
In order to study of petrography and textural analysis of host rocks and other rock units, a ninety-four thin section of various rock types were prepared (twenty samples of lower Paleozoic sandstone, twenty-three samples of igneous rocks, twenty-one samples of Liassic shale and thirty samples of carbonate rocks). After the completion of petrography in transmitted polarizing light, a set of sixty-three samples of ore were taken from different location and deposits of KBA. Ore minerals were examined by reflected polarizing light. Both the petrography and ore microscopy were performed at the Islamic Azad University, Zarand Branch, Iran by Olympus and Kyowa

microscope respectively. After classifying the rock types, and to a more accurate detection of major, minor and trace minerals, a seventy-five ore samples were collected for powder X-ray diffraction (XRD) analysis (Amiri, 2007) and the results were used in appropriate places. XRD analysis was performed at the Kansaran Binaloud Research Company, Tehran. The target used in X-Ray tubes is Cu which emits wavelengths of 1.542 Å (Cu K_α radiation, 4–60° 2θ range and 0.5° 2θ/min speed). In order to drawing lithogeochemical column, existing data (Amiri, 2007) was used. To avoid mining contaminations, the samples were taken far from the mines and indications.

Preparation of all samples comprises of sorting, drying, crushing, splitting and pulverizing and then digestion by standard 4 acid (hydrofluoric, perchloric, nitric and hydrochloric acid)

technique. Major, minor and trace elements were analyzed by IC3E and IC3M analyzing methods at Amdel Laboratory, Australia.

32.00



31.17

Figure 2) Simplified geological map of KBA (modified after Hukeride et al., 1962 and Amiri, 2007) and location of major carbonate hosted NSZDs: 1-Tarz, 2- Gujer, 3- Karvangah, 4- Tappeh Sorkh, 5- Seniedu (Deh Askar), 6- Gicherkuh, 7- Abheydar, 8- Kuh-e-Bijahan, 9- Ahmadabad (Boneh Anar), 10- Chahmir, a Cambrian SEDEX type (Rajabi et al., 2015), 11- Kuh Ghal'eh, 12- Tajkuh (Tashku), 13- Magasou, and 14- Gavar (Javar).

In order to control the precision of the data, about ten percent of samples have been duplicated and checked by conventional

methods and data precision was verified as well. Also, eleven samples of purified sulfide and nonsulfide minerals were analyzed by Amiri

(2007) for sulfur, oxygen and carbon stable isotopes by ICP-MS at Central Science Laboratory Research, University of Tasmania, Australia. In present study, the mentioned data was used.

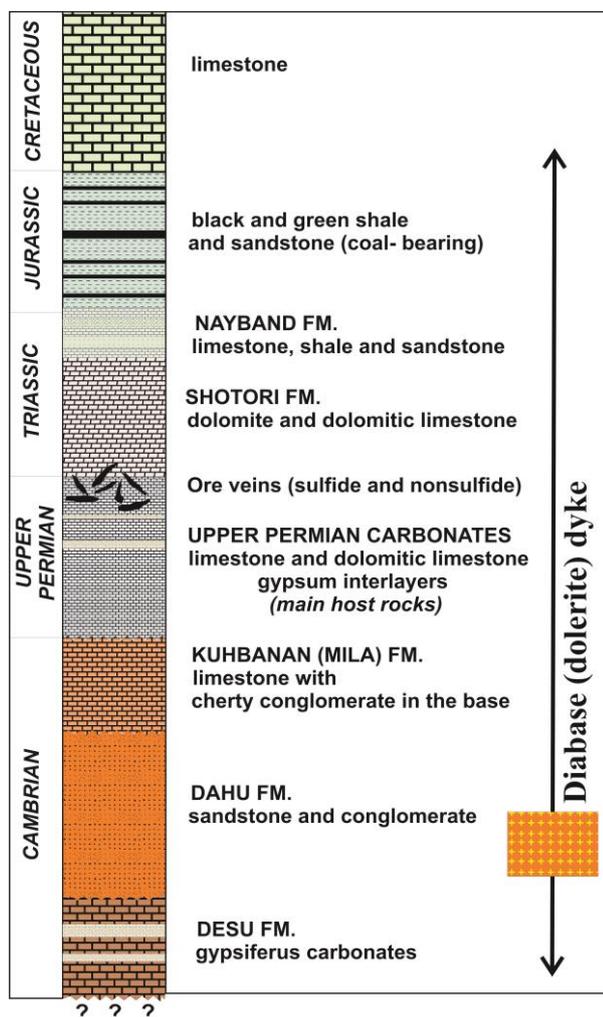


Figure 3) Very simplified and not to scale stratigraphy column of the KBA.

4- Discussion

4.1- Ore classification

Carbonate-hosted NSZDs consist of diverse mineral phases. These minerals can be classified in carbonates (smithsonite and hydrozincite), silicates (hemimorphite, willemite and franklinite), oxides (zincite and gahnite) and zinc bearing clays (sauconite and fraipontite). Boni and Large (2003) summarized zinc minerals and have pointed some comments for them (Table 1).

Mineralogy of NSZDs at the KBA is relatively complicated and comprises of disseminated ore mineral in carbonate host rocks, vein-type sulfide ore, mixed nonsulfide and sulfide minerals, nonsulfide ore and finally iron hat or gossan. Due to wide extent of the area, it's not possible to introduce and study of minerals at all mine and indications separately and in detail. Therefore, the ore minerals of these deposits are summarized in Table 2 and will be described in details below.

4.1.1- Disseminated primary sulfides

Upper Permian (-Lower Triassic) thick sequence of carbonate host rocks (dolomitic limestone) in some locations (Tarz, Tajkuh and Kuh Ghal'eh) contains a unique primary sulfide mineralization and this type of mineralization may be found at other deposits and it is needed to more investigations. Among the cases studied, Tajkuh deposit shows disseminated sulfide minerals better than the others (Fig. 4). In this case, main sulfide ore vein is hosted by steeply dipping medium layers of dolomitic limestone and adjacent dark gray layers (with a thickness of about 70 to 110 meters) contain euhedral crystals of brown Fe-bearing sphalerite and galena (first generation) with a lesser amounts of pyrite and chalcopyrite (Fig. 5). Such a situation can be seen up to about fifty meters around the ore vein and in some cases, remnant of organic matter (bitumen) can be found in these layers. These sulfide minerals commonly have no relation to (micro-) cracks and joints and hence, it seems that formed during the stages of diagenesis (Amiri, 2007). The size of disseminated sulfide minerals frequently are less than 0.1 millimeter and in rare cases, the size of these minerals reach to over 5 millimeters in voids of carbonate country rocks. Also, accumulations of sphalerite and galena are present in the porosity voids and across the micro cracks of rock, and it is considered as later diagenesis stages for formation of these minerals (second generation).

So, it can be classified disseminated sulfide minerals to two subtypes; a) first generation that composed mainly of separate submicroscopic (less than 0.1 millimeter) idiomorphic tetrahedral cubic brown sphalerite and with a lesser amount of galena (Fig.6 A-F) and b) second generation that comprised of anhedral void- filling coarse-grained galena and minor sphalerite (Fig.6 G-H). Relative high contents of

galena compared to sphalerite in this subtype can be represent that the sphalerite was more soluble than the galena and so, during the later stages of diagenesis, sphalerite mainly leached out and removed from the primary environment and therefore, concentration of lead was increased relative to zinc in this subtype.

Table 1. Common minerals of NSZDs and their comments (Boni and Large, 2003).

Mineral	Formula	comments
Smithsonite	ZnCO ₃	Common component of “calamine”; concretionary Cd-rich variety known as “turkey fat”
Hydrozincite	Zn ₅ (OH) ₆ (CO ₃) ₂	Known as zinc “bloom”
Franklinite	ZnFe ₂ O ₄ or (Fe,Zn,Mn)(Fe,Mn ₂)O ₄	Zn spinel (in metamorphosed deposits)
Gahnite	ZnAl ₂ O ₄	Zn spinel (in metamorphosed deposits)
Hemimorphite	Zn ₄ Si ₂ O ₇ (OH) ₂ · 2H ₂ O	Common component of “calamine”
Sauconite	Na _{0.3} (Zn,Mg) ₃ (Si,Al) ₄ ·OH ₂ ·nH ₂ O	Zn saponite (small micaceous plates); several formulas reported by various authors
Fraipontite	(Zn,Al) ₃ (Si,Al) ₂ O ₅ (OH) ₄	Zn clay similar to kaolinite
Willemite	Zn ₂ SiO ₄	Common in hydrothermal deposits
Zincite	ZnO	Present in gossans

Table 2. General distribution of various ore matter in the NSZDs at KBA (modified from Amiri, 2007).

	Name of deposit	Disseminated primary sulfide ore	Sulfide vein ore	Mixed sulfide and nonsulfide ore	Nonsulfide ore	Gossan
1	Tarz	+	+	+	+	+
2	Gujer	-	-(?)	±(?)	+	+
3	Karvangah	-	-	-(?)	+	+
4	Tappeh Sorkh	±(?)	-	-	+	-
5	Seniedu	-	-	-	+	+
6	Gicherkuh	-	-	-	+	+
7	Abheydar	-	-	-	+	±(?)
8	Ahmadabad	-	-	±(?)	+	+
9	Kuh Ghal'eh	+	+(?)	-	+	+
10	Tajkuh	+	+	+	+	+
11	Magasou	-	-	-	+	±
12	Gavar	-	-	±(?)	+	±
13	Kuh-e-Bijahan	±(?)	+(?)	-	-	-

Distribution and habit of sulfide minerals of first subtype (a) shows that these minerals have no evidence of entering to the country rock as a later mineral phase. Against this, it can be observed that due to breakdown of these minerals, Fe oxyhydroxides and nonsulfide zinc minerals (especially smithsonite) were developed across the intersecting micro joints

(Fig.6 E-F). Some evidence such as anhedral habit, void-filling and control by interlayer micro structures of second subtype (b) show that, in comparison to the first subtype, this mineralization is related to the later stages of diagenesis and remobilization of ore metals. By enclosing of both subtypes in distinct carbonate layers in addition to other evidences show

syngenetic genesis for disseminated sulfide mineralization at the KBA. Also, disseminate and in some cases colloform textures of sulfide minerals can be considered as low temperature

formation of this type of mineralization and hence can be coincidence with diagenesis processes (Amiri, 2007).

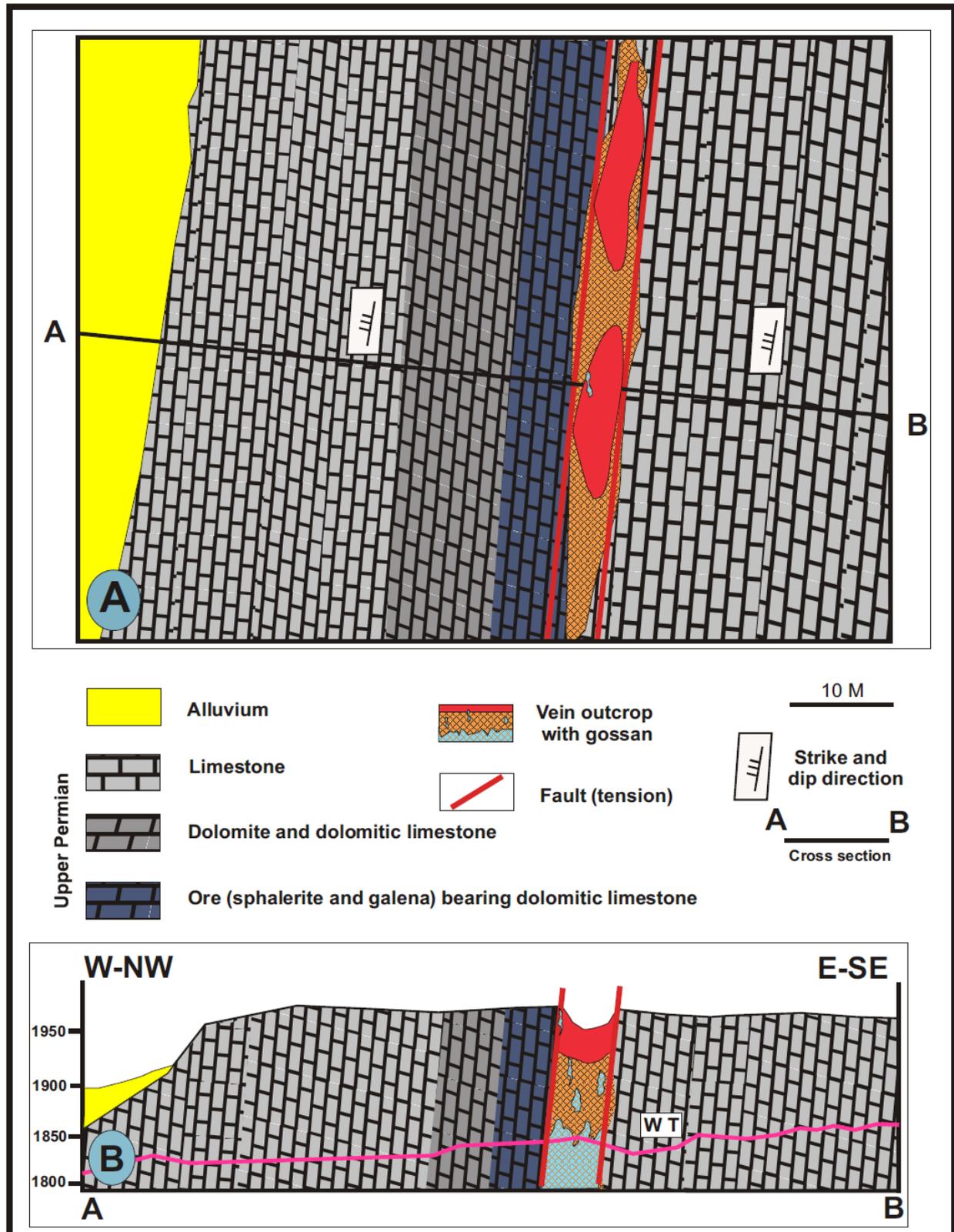


Figure 4) Schematic geological map (A) and cross section (B) of the main ore vein at the Tajkuh sulfide-nonsulfide Zn-Pb deposit.

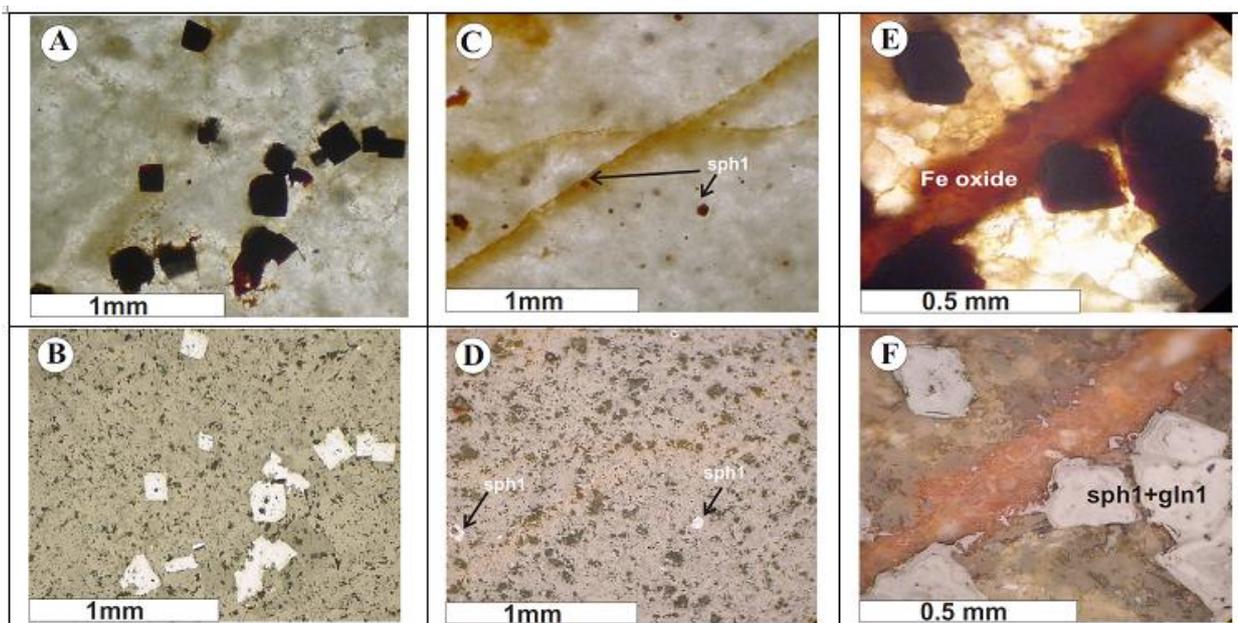


Figure 5) Photomicrograph of disseminated sulfide minerals in the dolomitic limestone layers as host rocks of the vein-type sulfide mineralization in the Tajkuh deposit. A and B shows disseminated euhedral pyrite crystals, C and D represents sphalerite idiomorphic crystals and finally E and F indicates interaction between first generation of sphalerite and galena with (micro-) joints and forming Fe-oxides secondary minerals. A, C and E in transmitted plan polarized light (ppl), B, D and F same view in reflected ppl, sph1 and gln1 represents first generation of sphalerite and galena respectively.

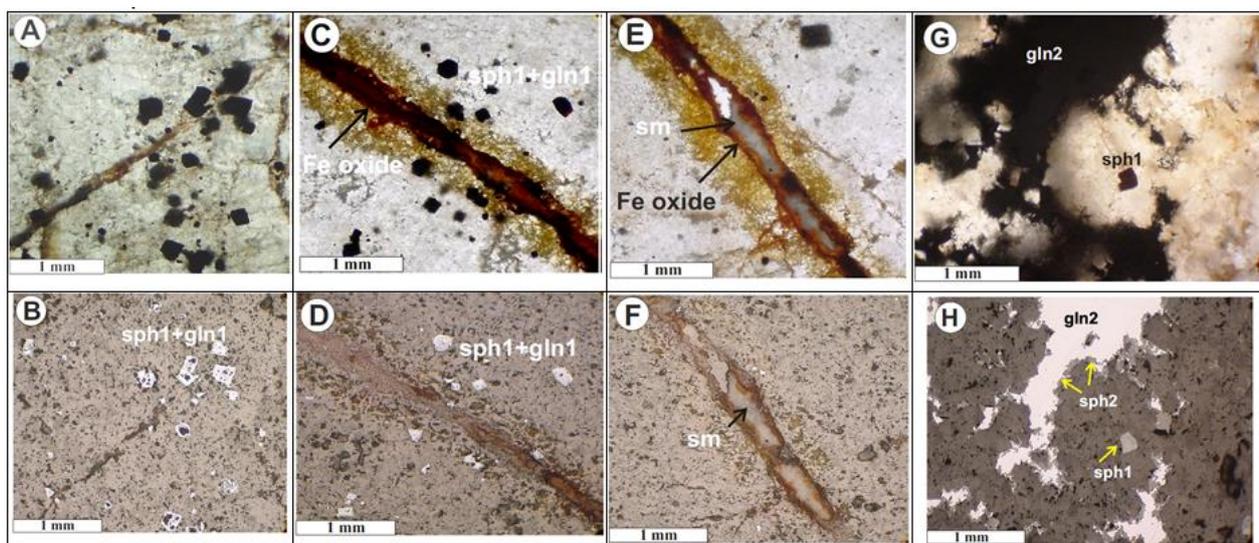


Figure 6) A to F, Photomicrograph of the first generation sphalerite (sph1) and galena (gln1). In E and F smithsonite has formed in the open space of the micro-crack. There is no relation between sulfide minerals and micro cracks, all samples from Tarz deposit. G-H, Photomicrograph of second generation sphalerite (sph2) and galena (gln2), Tajkuh deposit. A, C, E and Galena in transmitted ppl, B, D, F and H same field in reflected ppl.

As previously mentioned, in addition to sphalerite and galena, lesser amounts of chalcopyrite and pyrite are found in disseminated sulfide mineralization. The chalcopyrite is distinguished by its golden yellow color and lower polishing hardness. This

mineral is found associated with the first generation sphalerite and galena and sometimes as very small inclusions in the sphalerite. Also, chalcopyrite was observed with second generation of sphalerite and galena in a trace amounts.

helps to circulation of fluids through the sphalerite and galena bearing (first generation) carbonate rocks and have been caused alteration of sulfide minerals at low temperature. As a result, at the open spaces of microscopic cracks, large crystals of dolomite as second generation (dol2) have been formed. This generation of dolomite in comparison to the first generation is more transparent and coarser. During the alteration of the first generation galena and sphalerite, zinc and lead had been dissolved partially and circulated through the joint and pores of carbonate rocks. In the following, most parts of lead have been fixed as second generation galena at the pore and fractures. Also, some parts of dissolved zinc has been replaced the first generation galena. Another part of dissolved zinc ions has been formed zinc carbonate (smithsonite) across the joints which the frequency of this mineral is not important. Most parts of zinc ions have been migrated and which will be discussed in more detail later. Figure 7 shows paragenetic sequence of disseminated sulfide mineralization in KBA.

After deposition of Upper Permian carbonate sediments and during the diagenesis stages, primary sulfide minerals were fixed the ore metals (Zn+Pb±Cu) and nonmetals (F+Ba±Sr) and sometimes, concentration of the ore metals reaches to over one percent. In these cases, some parts of Upper Permian (-Lower Triassic) thick sequence carbonate rocks can be considered as a future ore reserves with large volume and low grade ore same as the porphyry deposits.

Here we are dealing with a basic problem; how these disseminated minerals were formed? Indeed, it must be identified that what is the source of ore metals (Zn+Pb±Cu) and non-metals (F+Ba±Sr)? Based on field data, petrography-mineralogy and geochemical studies, Amiri (2007) has been proposed a submarine exhalation process for supplying

these elements. Enclosing the disseminated sulfide minerals in a distinct horizon of Upper Permian carbonate rocks (Fig. 8A), lack or scarcity of fossils in the horizon (existence of only a few microfossils comprising of the *Agathamina* sp., *Hemigordius* sp., *Fronicularia* sp., *Glomospira* sp., *Archaesphaera* sp. have been observed in this horizon), and distinct increasing of ore elements in lithochemical columns of the KBA (Fig. 24) are the most important evidence convinced us that during the formation of these carbonate rocks, a considerable amounts of ore elements have been entered to the sedimentary basin. Also, in the detailed studies of petrography of disseminated sulfide bearing carbonate horizon at Kuh Ghal'eh, remnants of silicic volcanic patches (Fig. 8B) was observed.

4.1.2- Vein-type sulfide ore

Although there are several hundred known sulfide minerals, only a half dozen of them are sufficiently abundant as to be regarded as “rock-forming minerals” (pyrite, pyrrhotite, galena, sphalerite, chalcopyrite and chalcocite) (Vaughan, 2006). It seems that the first stage of economic ore formation has been started by the vein-type sulfide mineralization in the studied area. Indeed, this type of mineralization at the KBA is the main precursor for nonsulfide ore and can be seen obviously and frequently at Tajkuh and Tarz mines. Recently, this type of ore has been explored and extracted by mining operations in the Gavar and Gujer deposits. Vein-type sulfide ore commonly have been cut the Upper Permian (-Lower Triassic) carbonate host rocks, but sometimes they are concordant with the host rocks (Fig. 3). However, in the Tarz and Tajkuh deposits, sulfide ores are widely extracted at the past and present periods and in other deposits of the KBA, existence of the sulfide mineralization in deeper parts of nonsulfide ore veins, especially beneath the water table is probable.

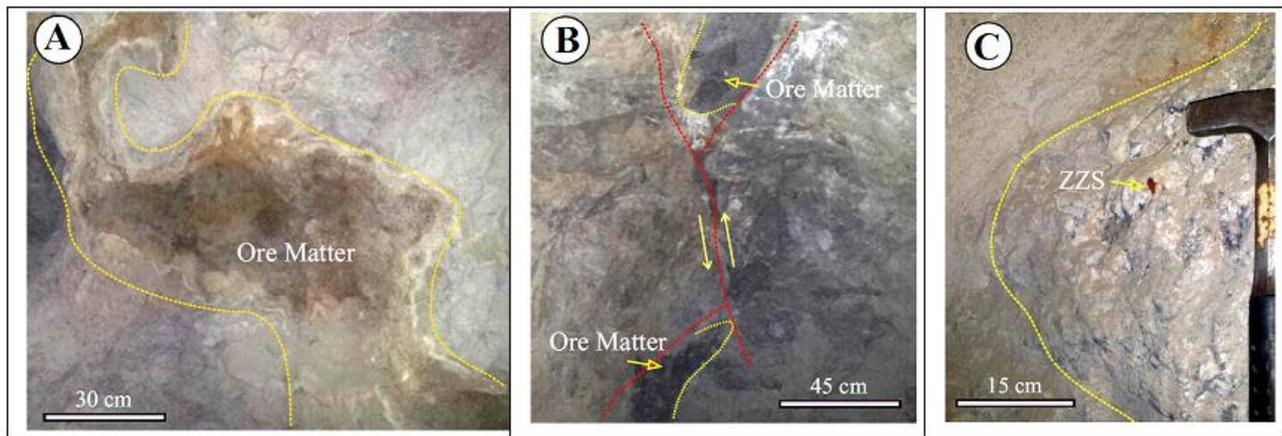


Figure 9) The important textures of sulfide vein-type mineralization at the KBA. A. Karstic replacement of dolomitic limestone with zinc ore, Tarz mine (sphalerite is replacing with smithsonite and hydrozincite), B. Sinistral faulting and filling of fault gouge by sphalerite, galena and pyrite (Tajkuh mine) and C. Fault breccia cementation by sulfide (galena and sphalerite) minerals, Tarz mine; replacing of the sphalerite by smithsonite and hydrozincite is distinct (ZZS, zinc zap staining effect).

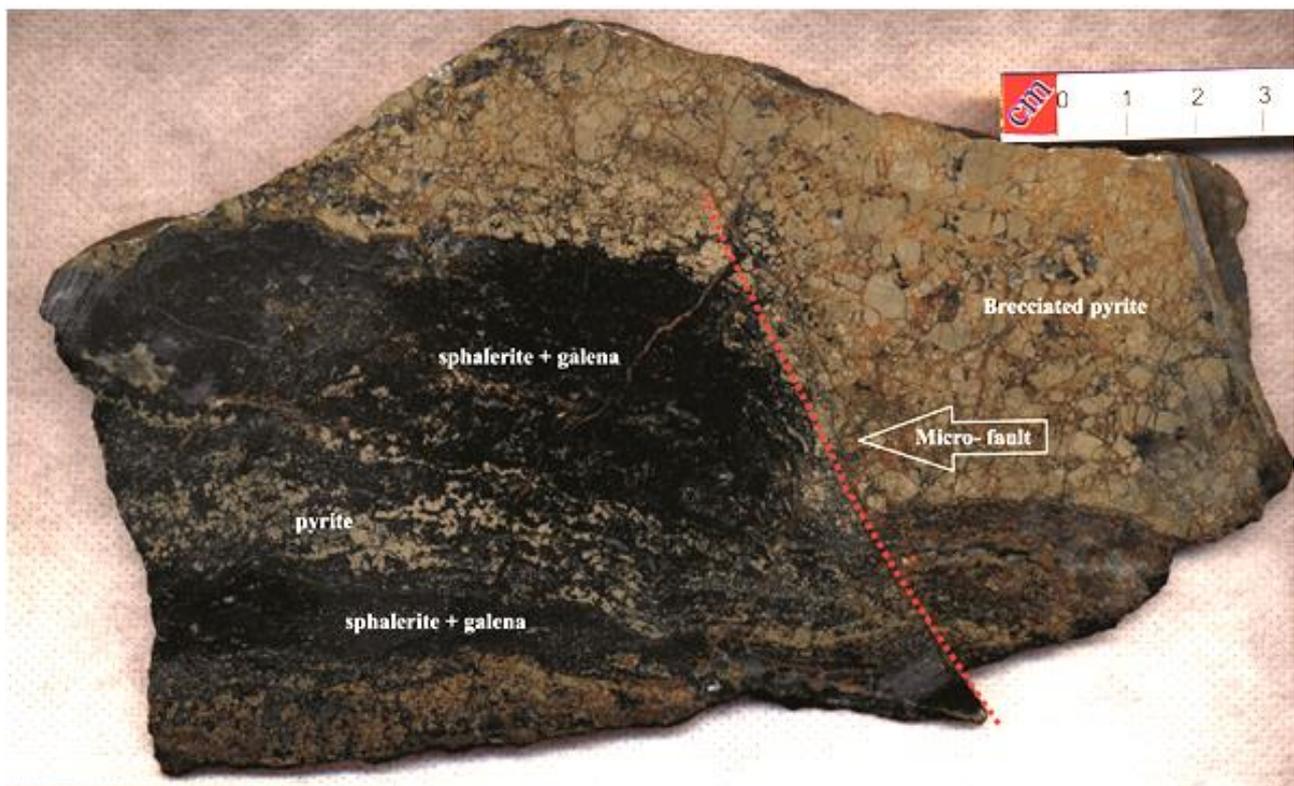


Figure 10) Hand specimen polished slab of the massive and brecciated textures, Tajkuh sulfide ore vein.

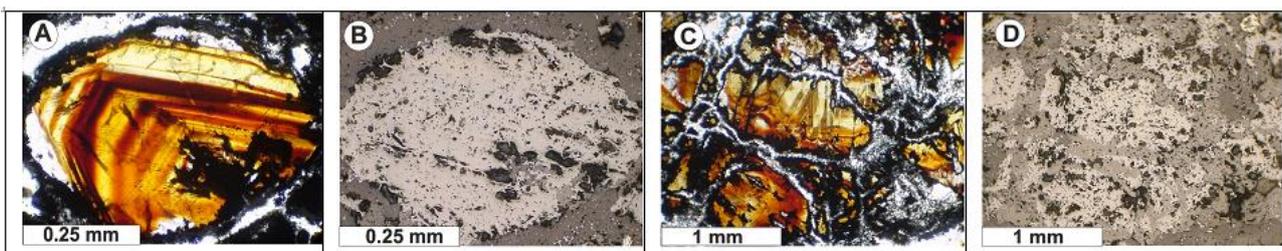


Figure 11) Photomicrograph of the third generation sphalerite (A and C) Zoning of the sphalerite, the Tarz and Tajkuh mines respectively, transmitted ppl, (B and D) The same fields view in reflected ppl.

To prove this hypothesis, it's needed to operate especial exploration projects such as IP-RS geophysical surveys and diamond drilling with coring at the suitable locations. In such circumstances, sulfide ore veins, because of lack of oxidation conditions, has not been oxidized and weathered and can be seen as a fresh sulfide ore. Sphalerite, galena and pyrite are the most abundant sulfide minerals with open space filling, breccia cement and replacement and karstic textures in the sulfide vein-type mineralization (Fig. 9). In hand specimens, massive and brecciated sulfides are the main ore textures (Fig. 10). Carbonate minerals (calcite and dolomite) and silica are the principal gangue minerals associated sulfide ore veins. Other sulfide minerals, such as chalcopyrite and arsenopyrite are present in lesser amounts. Based on microscopic investigations, it seems that these accessory sulfide minerals have been formed prior to the sphalerite and replacing them by sphalerite is obvious. The size of ore minerals is ranging from less than 0.1 to over 5 millimeters and sometimes, large grain of sulfides has grown on the open spaces. In the following, the main sulfide minerals will be described.

Sphalerite: Sphalerite is the most frequent and important mineral in the vein-type sulfide mineralization at the KBA (third generation, sph3). This mineral is transparent to semitransparent in the transmitted light and in this respect, among the sulfide minerals is an exception. Having a honey-yellow color, relatively high relief and at least three sets of cleavage are the main microscopic features of the sphalerite. Also, zoning and intriguing concentric structure of sphalerite is very characteristics, especially in the sulfide ore of the Tarz mine (Fig. 11A). In the Tajkuh mine, the same features have been recognized more and less (Fig. 11B) and the size of this mineral is more than 1 millimeter. Also, the shape of sphalerite is ranging from idiomorphic to open space-filling anhedral grains. Calcite (-aragonite) and quartz are the main gangue minerals associated with the sphalerite, both gangue minerals have mosaic texture and are fine-grained related to sphalerite. Sometimes and scarcely, dolomite is present in association with the sulfide minerals.

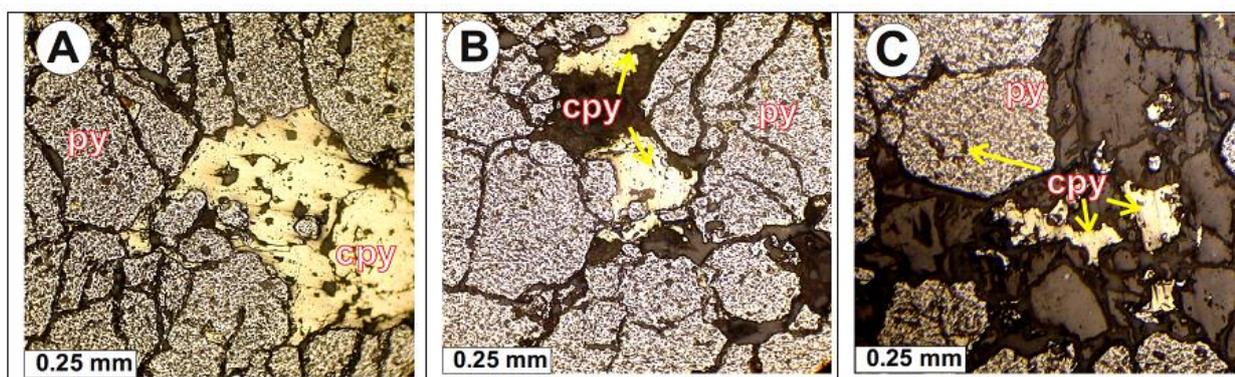


Figure 12) (A-B) Photomicrograph of replacement the chalcopyrite (cpy) by the porous pyrite (py), Tarz mine. (C) The porous pyrite with the chalcopyrite inclusions in a carbonate gangue, Tajkuh mine. All images in reflected ppl.

Sphalerite in this type of ore is introduced as third generation sphalerite and based on microscopic studies, it can be accepted that the relatively weak replacement of this generation of sphalerite by galena is the most mineralogical

evolution. The sph3 has numerous small to medium sized fluid inclusions and from this point of view, in comparison to the other minerals (ore and gangue) has exceptional situation. Petrography of these fluid inclusions

revealed that they are of two phase type (liquid-vapor) and the volume of gas bubbles have been estimated about 12 to 15 percent. Finally, it is noteworthy that in the third generation sphalerite, inclusions of chalcopyrite and sometimes euhedral pyrite are present.

Pyrite: After the sphalerite, pyrite is the most abundant sulfide mineral in the sulfide veins of the KBA. In many cases, the pyrite is even more frequent than the sphalerite, so that, it can be the main sulfide mineral, and other sulfide minerals are as accessory minerals. For example, in the Tarz mine, some parts of sulfide veins are composed completely of the pyrite and only trace amounts of chalcopyrite and arsenopyrite can be seen with it. The size of the pyrite is larger than the other sulfide minerals and occasionally, its reach to over four millimeters. The euhedral and square shapes of the pyrite in thin-polished sections are common both in the carbonate and silicic gangue and fragmentation of pyrite along the fractures causes its decomposition. As mentioned above, remnants of pyrite is present in the third generation sphalerite and it's not clear precisely which earlier formed.

The most important mineralogical evolution of pyrite is replacement of this mineral instead of chalcopyrite that is obvious in the microscopic polished sections (Fig. 12). Furthermore, there are numerous inclusions of arsenopyrite in the pyrite (especially in Tarz mine) that indicates the arsenopyrite has been formed before the pyrite. Chalcopyrite and arsenopyrite characteristics will be discussed below.

Galena: In the vein-type sulfide ore, there is a relatively low frequency of the galena. This mineral is formed as a very thin rim, in a few hundredths of a millimeter around the third generation sphalerite (Fig. 13) and in the microscopic investigations, replacement of the third generation sphalerite by the galena are clearly visible. This mineral is introduced as third generation galena (gln3). In the Tarz mine, third generation galena has euhedral shape around the sph3 (Fig. 14), whilst in Tajkuh, anhedral shape of gln3 is predominant (Fig. 14D).

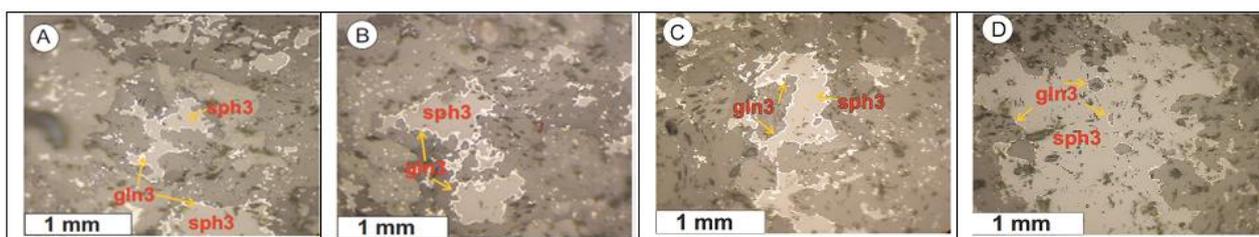


Figure 13) Replacement of third generation sphalerite (sph3) by a very thin rim galena (gln3). A-D from Tajkuh mine, all in reflected ppl.

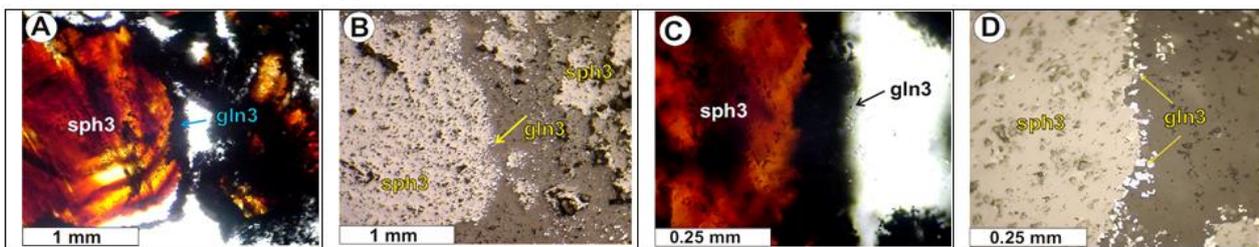


Figure 14) Replacement of third generation sphalerite (sph3) by a very thin rim idiomorph shape galena (gln3), A and C in transmitted ppl, B and D in reflected ppl. Idiomorphic crystals of galena are obvious in D.

Chalcopyrite and arsenopyrite: In the vein type sulfide mineralization of the KBA, both

chalcopyrite and arsenopyrite are present in a trace amounts and of these two minerals, the

4.1.3- Mixed sulfide and nonsulfide ore

Exposed sulfide minerals are not stable at the oxidizing and slightly acidic surface conditions. In this status, they easily transformed to oxide, hydroxide, carbonate and silicate mineral phases. Pyrite is one of the most frequent sulfide mineral associated with most ore deposits. Chemical weathering of pyrite produces sufficient amount of sulfuric acid and helps to increase chemical weathering and decomposition of other sulfides and so, the ore metals (Zn, Cu, Pb and Ag) would be released and enters to the descending solutions. These acidic descending solutions can transport most of the ore metals and during the chemical reaction with the wall rocks (especially carbonate rocks), it is possible to fix some of these metals as nonsulfide minerals. Presence of carbonate minerals in the reaction environment will increase the pH of the solutions and so, precipitation of new nonsulfide minerals take places.

In most zinc (-lead) deposits of the KBA, the sphalerite is more abundant than the galena. Pyrite is also present as a main sulfide gangue and sometimes reaches over twenty percent. Other sulfide minerals such as chalcopyrite and arsenopyrite are present in lesser amounts. During the chemical weathering of the exposed sulfide ore of the KBA, sphalerite is completely decomposed and in most cases, this mineral is absent at the surface. Toward deep parts of the sulfide veins, stability of the sphalerite increases and beneath the water table, this mineral together with other sulfide minerals have no considerable decomposition. Between the surface and water table, mixed sulfide and nonsulfide ore is developed and toward surface and water table, it is transformed to gossan and sulfide ore respectively. Despite the sphalerite, galena is more stable at this condition and because of armouring with cerussite (and sometimes anglesite), presence of the galena near surface and even in the gossan is relatively frequent.

Mixed sulfide-nonsulfide ore is only present in the deposits that they have a sulfide mineralization as an earlier and exposed mineralization. In particular, this type of ore is found and extracted in Tarz and Tajkuh deposits (Fig. 9). In the Tajkuh deposit, for a depth of about 70 meters from the main shaft entrance (access and transport shaft), it can be seen traces of oxidizing sulfides beside nonsulfide minerals. After this depth and toward deeper parts of the veins, increasing the sulfide contents is obvious gradually and at a depth beneath 90 meters (approximate water table), sulfide minerals is formed major parts of ore. In other words, at depths of 70 to 90 meters, mixed sulfide-nonsulfide ore with various ratios can be seen. Indeed, at depths less than 70 meters and over 90 meters, the ore has been composed of nonsulfide and sulfide respectively. In this mine, galena is the only exposed sulfide at the surface and it may be due to higher chemical stability of the galena respect to the other sulfide minerals. Also, because of armouring the galena by cerussite, persistence of this mineral on the surface is more than the other existing sulfide minerals. Beneath the depths of over 90 meters, nonsulfide minerals are present in a trace amounts only and two more common nonsulfide minerals are smithsonite and hemimorphite. Considering the discussion of the sulfide and nonsulfide mineralization separately, it is clear that the mixed ore has characteristics of two types and there is no need for a separate description.

4.1.4- Nonsulfide ore

Nonsulfide zinc (-lead) deposits are as attractive exploration targets because of many reasons (Hitzman *et al.*, 2003) and recently, many exploration companies are looking for these type of deposits around the world including Central Iran. Low lead contents and other contaminant elements (e.g. arsenic) in the ore and low-cost processing methods, such as solvent extraction (SX) and electro-winning

(EW) are the most important advantage of this type of mineralization.

This type of ore is present in all carbonate hosted zinc (-lead) deposits of the KBA and hence, these deposits are known more as nonsulfide deposits. Therefore, in all mines and

indications of the KBA, nonsulfide ore has been the main products of these mining area both in the past (Shaddadi mining) and present extraction periods. Shaddadi mining and ancient works has been almost completely been done in order to extract this ore type.

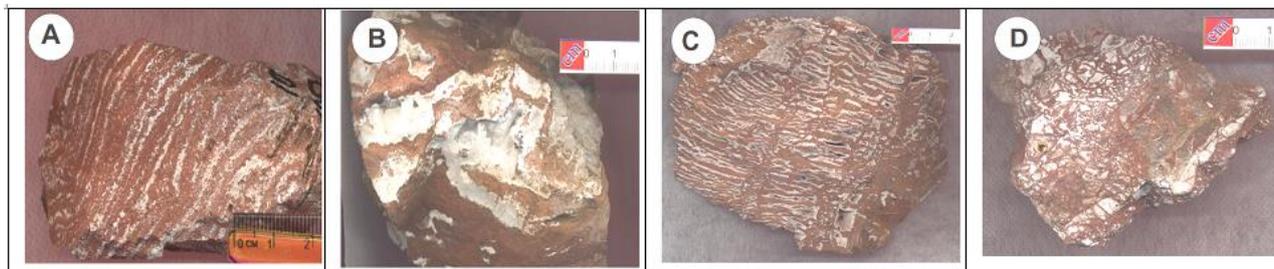


Figure 17) Hand specimens of nonsulfide ore in the KBA. A. Laminar hydrozincite in Gujer mine, B. Open-space filling hemimorphite and smithsonite in the Tajkuh mine, C. Zebra texture of hemimorphite in Gavar mine and D. direct replacement of primary sulfide minerals by nonsulfide (mostly smithsonite) as brecciated ore, Gujer mine.

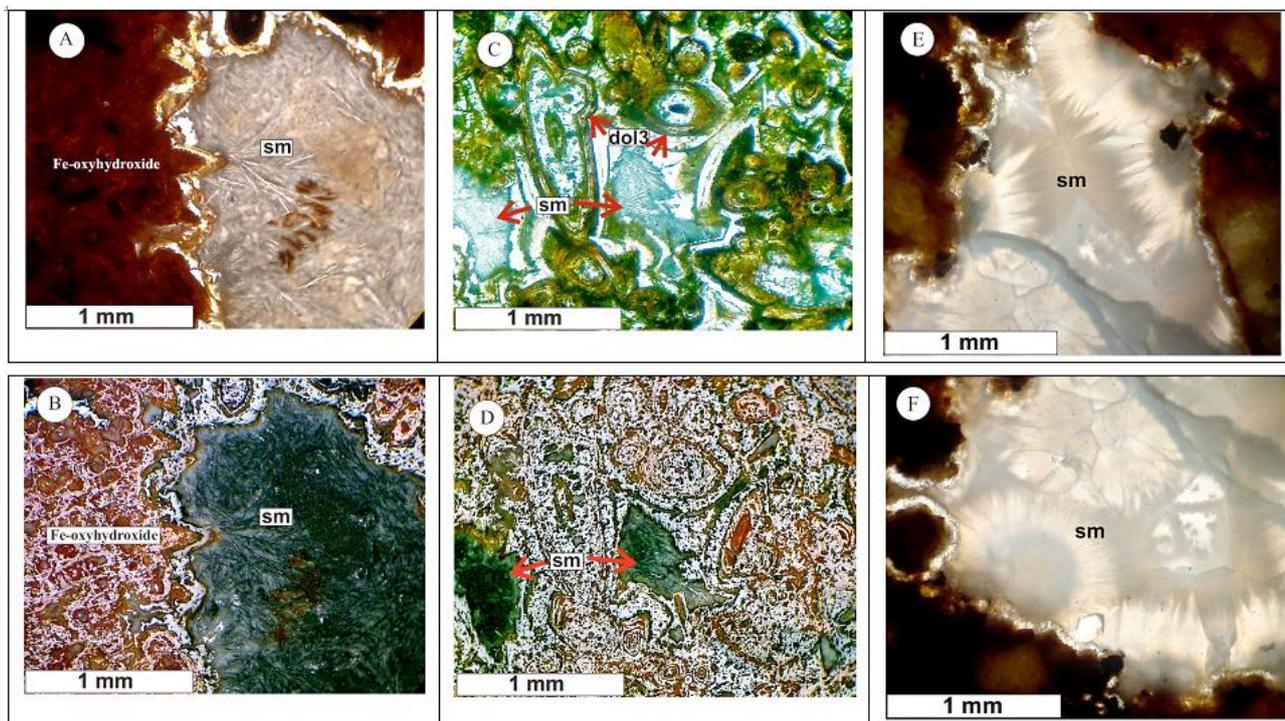


Figure 18) Photomicrograph images of smithsonite (sm) from the KBA. A-B. Acicular aggregate of the smithsonite beside Fe-oxyhydroxides, Tarz mine, C-D. The acicular smithsonite as intergranular cement, primary sedimentary texture (dolomitized allochems- dol3) is visible, Tajkuh mine, E-F. The acicular and colloform smithsonite as open-space filling texture, Tappeh Sorkh deposit. A, C, E and F in transmitted ppl, B and D in reflected ppl.

Nonsulfide zinc (-lead) ore of the KBA deposits is a combination of nonsulfide minerals (mainly zinc minerals) with a variable amounts of Fe oxyhydroxide and nonsulfide lead minerals. Amiri (2007) has reported that the Fe

oxyhydroxide contents of this ore type are ranging from less than five to over ten percent. The category of ore with low iron contents (<5%) is important in a few deposits, (e.g. Tappeh Sorkh deposit). While, the iron-rich nonsulfide ore (>10%) is present in many

deposits of the area. For example, existence of this type ore in Gujer, Gicherkuh, Karvanganh, Tarz, Senjedu, Gavar, Magasu and Tajkuh deposits is dominant. This categorization is somewhat same as classification of nonsulfide zinc ore to red and white by Reichert and Borg (2008). Based on their classification, “economically, red zinc ore is less attractive than white zinc ore due to its higher concentrations of Pb, As, and other heavy metals. Economically and ecologically more attractive is the so called ‘white zinc ore’ with its low concentrations of Fe (typically <7%), consisting mainly of zinc carbonates and only subordinate amounts of hydrous zinc silicates and lead carbonates”.

The iron contents of the nonsulfide zinc ores is related primarily to the amounts of pyrite in the primary precursor sulfide ore. So that, the large amounts of pyrite in primary sulfide ore and oxidation of this mineral creates sufficient acid and provide leaching conditions for releasing ore metals (especially Zn). On the other hand, chemical weathering of pyrite generates

adequate iron oxyhydroxides and in addition to creating red color in the oxidizing environment, produces insoluble oxides as iron cap or gossan at the surface. Moreover to the pyrite, the sphalerite also have a small amount of iron in its composition and during the oxidation and chemical weathering, it can be produces a few iron oxides and such a situation was described above. Sometimes, accompanied iron oxide with nonsulfide ore is due to this process.

In general, in the nonsulfide zinc (-lead) deposits of the KBA, the most important nonsulfide zinc minerals are smithsonite, hydrozincite and hemimorphite. Moreover to these minerals, nonsulfide lead minerals also exist in a lesser amounts and cerussite is the most frequent nonsulfide lead mineral. In hand specimens, the most important textures are laminar, open-space filling, dissolution fabric, breccia cement and replacement of breccia fragments (Fig. 17). Besides the main minerals, the accessory and trace minerals are anglesite, willemite and wulfenite and all of these minerals are not present at the all deposits.

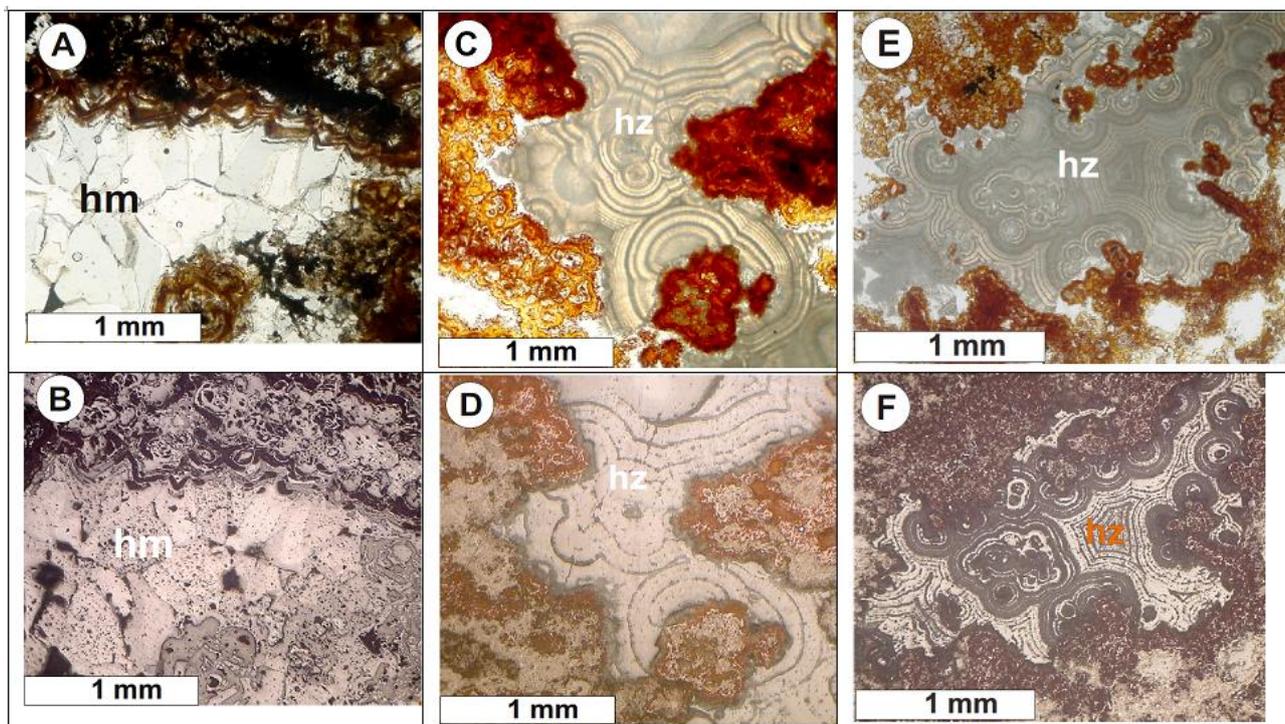


Figure 19) Photomicrograph of hemimorphite (hm) and hydrozincite (hz) from the KBA. A-B. The mosaic texture of hemimorphite, Tajkuh mine, C to F. The colloform texture of hydrozincite, Tappeh Sorkh deposit. A, C and E in transmitted ppl, B, D and E in reflected ppl.

Smithsonite: Smithsonite ($ZnCO_3$) almost is present in all deposits of the KBA as a main to minor mineral. This mineral shows acicular and radial habits and already has been filled the open spaces of the carbonate host rocks (Fig. 18). Because of its small size, it is difficult to identify smithsonite in hand specimen and detection of this mineral is possible by microscopic techniques and X-ray diffraction (XRD) and the both methods were used during this research. In Tajkuh, Tarz, Gicherkuh and Gujer mines, the smithsonite mineral has been detected by XRD technique.

As can be seen in Fig. 18, smithsonite has formed later than the adjoining minerals. Also, in Fig.18C, the acicular and radial crystals of smithsonite has been filled the dolomitized pores of carbonate rock in Tajkuh mine. In addition to the open-space filing and intercrystalline textures, colloform texture of smithsonite is found in some locations of the KBA. For example, colloform smithsonite is observed in the white ore of Tappeh Sorkh abandoned mine (Fig. 18 E-F). Replacement of smithsonite instead of the primary sulfide minerals and carbonate fragments in brecciated and fractured rocks is a common feature in some deposits such as the Gujer.

Hemimorphite: Hemimorphite [$Zn_4Si_2O_7(OH)_2 \cdot H_2O$] is a common nonsulfide zinc mineral in the KBA. The mineral also like the smithsonite,

exists with variable abundance as a major to trace mineral in the nonsulfide ore of all zinc deposits of the KBA. Idiomorphic transparent vitreous crystals of hemimorphite is recognizable easily in hand specimen (Fig. 17B) and as a result of zinc zap effect, in comparison to the smithsonite and hydrozincite, it becomes slowly to red color. Based on the microscopic investigations, hemimorphite has elongate shape, relatively high relief and distinct longitudinal cleavage (at least one set) and so, it's distinguishes rapidly. Their texture is blocky and mosaic and the size of crystals reach to over 5 millimeters (Figs. 17B and 19A, B). Commonly, the hemimorphite has grown perpendicular to the underlying surface of fractures and open spaces. The most beautiful examples of this mineral can be found in Gicherkuh, Tajkuh and Tarz mines. Moreover to the microscopic studies, hemimorphite has also been detected by XRD technique in most deposits of the KBA.

In the cases that hemimorphite is abundant, the carbonate host rocks have considerable silica impurities and so, it seems that the formation of this mineral is related to silica impurity primarily. Furthermore, high silica contents of primary sulfide ore are also effective to formation of the hemimorphite. Both alternatives are able to supply sufficient quantities of silica to form the hemimorphite in the KBA.

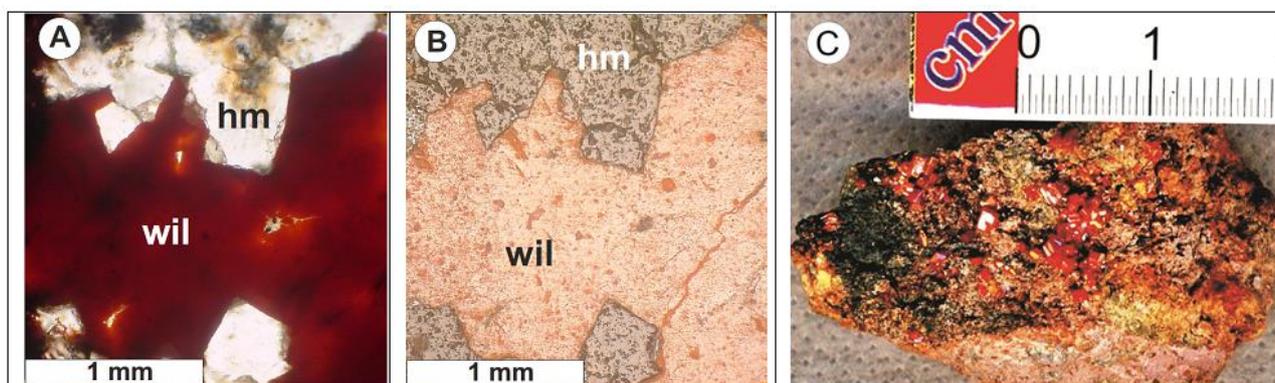


Figure 20) A-B. Photomicrograph of the willemite (wil) beside the hemimorphite (hm) in transmitted and reflected ppl respectively, Tarz mine, C. The hand specimen of wulfenite on cerussite ore, Gavar mine.

Hydrozincite: Hydrozincite [$Zn_5(CO_3)_2(OH)_6$] is also one of the most common nonsulfide zinc minerals of the KBA. In the Gujer, Tappeh Sorkh, Tarz, Tajkuh, Senjedu, Abheydar, Ahmadabad, Magasu and Gicherkuh, the hydrozincite is found abundantly as main zinc mineral. Because of similarity to the smithsonite, field identification of hydrozincite is not so easy and it's needed to use of microscopic and XRD techniques. Under the microscope, hydrozincite has colloform, concentric and globular textures (Fig. 19) and the size of globules are averagely about one millimeter and sometimes reaches to over six millimeters (in Tappeh Sorkh). In some cases, the globules are cracked radially which shows changes after it is formed. Microscopic investigations also indicate that the iron oxyhydroxides, especially goethite have been grown on and onto the hydrozincite and so, obviously formed after it (Figs. 19C-F).

Cerussite: The most abundant nonsulfide lead mineral in the KBA is the cerussite ($PbCO_3$). In some cases such as the Gavar deposit, cerussite has a considerable frequency in some parts and so that, in these parts, extracted ore has a higher concentration of lead. In this mine and at depths of 30 meters from the main transport shaft entrance, ore vein composed chiefly of the cerussite. This case is an exception compared to the other locations, and in other deposits of the KBA, cerussite with this abundance is not common.

It is obvious that the cerussite has been formed from chemical weathering of the galena. According to the microscopic observations of polished thin sections from different mines in the area, it can be seen the remnants of galena within the cerussite abundantly. Considering that the nonsulfide ore is developed in the KBA associated with the sulfide vein, it can be concluded that cerussite mainly formed from weathering of the third generation galena (gln3).

Cerussite mainly filled open spaces and intergranular pores of carbonate gangue (dolomite) as anhedral to subidiomorphic crystals. Based on textural relations, it's conducted that the cerussite is formed at the same time or before the hemimorphite.

Other minerals: In addition to the smithsonite, hydrozincite, hemimorphite and cerussite, as the most abundant nonsulfide Zn-Pb minerals in the zinc (-lead) deposits of the KBA, some minor to trace minerals are also present. Among the most important accessory minerals, it can be cited to the willemite, wulfenite and anglesite.

Willemite (Zn_2SiO_4) is usually formed as an alteration product of previously existing sphalerite ore bodies, and is usually associated with limestone. Also, it forms during hydrothermal processes as a primary mineral (Brugger *et al.*, 2003). In the KBA, willemite is found in Tarz and Gavar mines and in other deposits, presence of this mineral is probable and it's needed to more investigations. In the Tarz mine, the willemite has a red color and has been formed as an accessory mineral in nonsulfide ore only. Also, by X-ray diffraction (XRD) examinations, willemite is detected as a major mineral phase in this deposit. Furthermore, this mineral is distinguished in microscopic studies with the distinct red color (Fig.20 A-B). It seems that the willemite is a product of weathering and oxidation of sphalerite. Such a situation was reported at a low temperature and arid climate by Takahashi (1960) and Brugger *et al.* (2003).

Wulfenite is a lead molybdate mineral with the formula $PbMoO_4$. It can be most often found as thin tabular crystals with a bright orange-red to yellow-orange color in many deposits of the KBA, especially in deposits with high lead concentration. In this respect, the Ahmadabad (Boneh Anar), Gavar, Tarz, Tajkuh and Senjedu (Deh Askar) deposits have the highest amounts of the wulfenite, so that, in the Ahmadabad deposit, the concentration of molybdenum

The hemimorphite crystals together with the dolomite have been filled the open spaces and sometimes, it is formed after the dolomite. Also, it can be seen that the hemimorphite has been formed before the two important nonsulfide zinc minerals, smithsonite and hydrozincite. Between the two minerals smithsonite and hydrozincite, usually smithsonite has been formed prior to hydrozincite. Also, it seems that the hydrozincite is the latest nonsulfide zinc mineral that formed in open spaces and between the other minerals. The most important gangue minerals are quartz, calcite and goethite (with other iron oxyhydroxides) and these minerals usually is accompanied various type ore matter of supergene origin. With increasing depths, iron oxides decreases and conversely quartz amounts shows increasing. Finally, it can be stated that the wulfenite as a trace mineral phase, is formed with cerussite or even later than the mineral.

4.1.5- Gossan

The most nonsulfide zinc deposits of the KBA have a distinct iron hat or gossan on its uppermost parts. In some cases (e.g. Tajkuh and Karvangah), the thickness of gossan is considerable, while in others is negligible. It is evident that the formation of gossan is primarily related to sulfide minerals, particularly to the pyrite contents of the veins-type sulfide ore. Fe oxyhydroxide is a common product of pyrite (and iron bearing sphalerite). Non-oxidized pyrite-rich sulfide ore matters are, in some cases, such as the Tarz and Tajkuh deposits confirmed the above relationship. Pyrite is found abundantly in the Tarz and Tajkuh deposits so that, for example, in many cases of these two deposits, the main components of the ore is composed of the pyrite and sometimes, the amounts of this mineral reaches to over 20 percent. Also, in other deposits of the KBA, abundance of pyrite is possible at greater depths. As a result of oxidation of pyrite, insoluble iron oxides have been formed and thus, presence of these minerals in combination

with other supergene products (especially high silica contents), is a good exploration key in the area. Based on XRD analyses on the Tajkuh gossan samples, a mixture of secondary minerals and hematite, goethite, calcite, quartz and dolomite have been detected. Moreover to these minerals, in some samples, hemimorphite, hydrozincite and wulfenite have been identified as minor to trace mineral phases. Also, in the Gujer, Gavar and Tarz deposits, malachite, azurite and aurichalcite have been found and can be considered as a product of the copper sulfide minerals (e.g. chalcopyrite).

According to the field observations, deep red color and relatively high hardness are the main features of the gossan. Red color and highly hardness is related to iron oxides and silica contents respectively. Boxworks of pyrite dissolution also can be seen in the field (Fig. 22E). Microscopic studies and textural relations show that in the gossan, dolomite crystals have been replaced by goethite. Also, replacement of hemimorphite by goethite is frequently seen in the gossan (Figs. 22C-D). As can be seen in Figure 22A-B, during the growth of dolomite crystals, hemimorphite has been formed intermittently and in some cases, the two minerals are replaced by goethite. Therefore, it can be concluded that the dolomite and hemimorphite have been formed at a same time and before the goethite.

4.2- Chemical reactions involved in the formation of nonsulfide ore

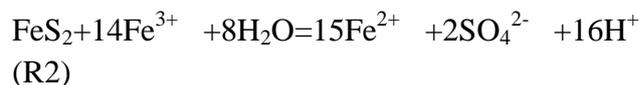
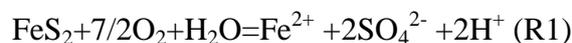
Description of the nonsulfide mineral assemblages requires knowledge of chemical reactions between the mineral phases. Generally, reactions between the minerals and evolution of them are related to some factors. According to Reichert and Borg (2008), the formation of carbonate-hosted nonsulfide zinc deposits is primarily controlled by three factors: climate, protore composition, and geology (lithology and structure) of the wall rocks. They have been stated that the climate controls the

oxidation and metal transport, predominantly through the amount of meteoric water and the availability of oxygen, which indirectly is controlled through the thickness of the soil cover and biogenic oxygen consumption. Favorable conditions for oxidation are an arid climate with minimal biogenic activity within the soil. Consequently, oxygen can reach the sulfide minerals easily, resulting in higher metal concentrations of the supergene aqueous solutions. Dry climates are associated with a low water table, preventing descending Zn-bearing fluids from contact with the aquifer and thus from dilution, dispersion and removal of metals. Such a situation is prevailing in the KBA. Low annual precipitations (≈ 130 millimeters), low water table depths (≈ 70 -90 meters) and poor vegetation cover are the predominant conditions in the Central Iran area (including the KBA).

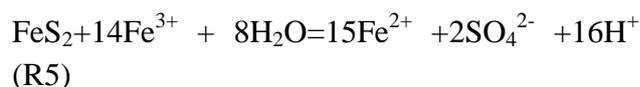
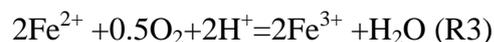
In the oxidation zone, the most important process affecting the protore is the direct oxidation of solid sulfides by molecular oxygen. Another important process of sulfide (and especially pyrite-) oxidation is the reaction of sulfides with Fe^{3+} -ions and/or-complexes. Here, Fe^{3+} acts as an electron acceptor instead of oxygen. Fe^{3+} is generated through the oxidation of Fe^{2+} by oxygen or by microbially-driven oxidation of Fe^{2+} to Fe^{3+} . Other oxidants, such as nitrate or manganese (IV), may also be present in the sulfide-bearing rocks (Herbert, 1999), but are generally negligible due to the low concentrations of these less common oxidants (Reichert and Borg, 2008). However, in the KBA, the frequency of manganese is considerable in some cases such as the Kuh Ghal'eh deposit and it should not be ignored the role of this element in oxidation processes .

The oxidation rate of pyrite under different conditions is well-documented (Williamson and Rimstidt, 1994; Domènech *et al.*, 2002). Pyrite oxidation and the subsequent hydrolysis of ferric iron play an important role in the genesis

of nonsulfide ore deposits due to their acid production. The resulting sulfuric acid is the most important cause of a low pH within the active oxidation zone of a sulfide orebody. The following reactions describe the oxidation of pyrite by oxygen (R₁) and by ferric iron (R₂) (Herbert, 1999):



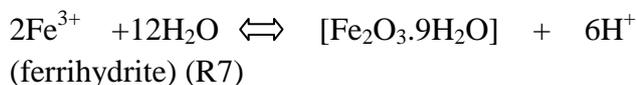
Moreover to the R₁ and R₂ reactions, Lawson (1982) has been introduced several oxidation reactions of pyrite and pyrrhotite that produces sufficient H^+ and reduces pH. Also, he has been studied the fate of the intermediate oxidation products. The other reactions are presented here:



Considering the above reactions, equation (R₁) represents the overall stoichiometry of pyrite oxidation to ferrous ion and sulfate. Ferric iron is also a strong oxidant of pyrite. Therefore, the existence of Fe^{3+} in the reaction environment of low pH (<4.5) same as equation (R₂), could intensify oxidation of pyrite rather than the oxygen (Herbert, 1999). Such a situation is common in the deeper and oxygen-undersaturated depths of a sulfide vein (Reichert and Borg, 2008). Equation (R₃) is also catalyzed by bacteria, particularly *Thiobacillus ferrooxidans* (Lawson, 1982). Equation (R₅) is abiotic, but it is believed to be one of the most important acids forming reaction under anoxic conditions. Generally, it is obvious that oxidation of pyrite as an important sulfide mineral of vein-type protore in the KBA, for exposed veins and beneath the surface, produces sufficient acid solutions and promote leaching of other sulfide minerals. Surficial and near surface oxidation products of pyrite (and somehow sphalerite and chalcopyrite) is iron

oxyhydroxide minerals and these phases are frequent in the top of many nonsulfide veins (e.g. in the Tajkuh, Kuh Ghal'eh, Ahmadabad and Abheydar). For a rough comparison, in the case of sphalerite, Fe is able to substitute Zn within the sphalerite up to 15 mol percent. Based on the microscopic investigations of the sphalerite in the Tarz and Tajkuh deposits, it is obvious that the honey-yellow color of the mineral indicates the high concentration of iron. Therefore, the Fe-bearing sphalerite can generate additional acid due to hydrolysis reactions.

This acid-generating step of the oxidation is followed by a neutralization reaction, in which the released H^+ (protons) react with the carbonate minerals, capable to neutralize acidic solutions. The elimination of most of the protons shifts the hydrolysis equation R6 and R7 to the right side and will thus stabilize the precipitated Fe-oxyhydroxides.

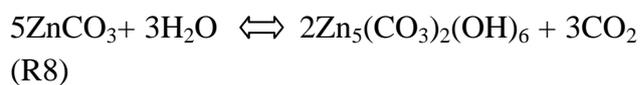


After acid production reactions, it is apparent that the acid cannot remain unchanged for a long time because of its reaction with existing minerals such as carbonate and silicate minerals. It is obvious that the most important neutralizing minerals are calcite and dolomite. In many carbonate-hosted deposits, such as deposits of the KBA, both carbonate minerals occur closely intergrown with the sulfide ore minerals. Without neutralization, the acid from the oxidation of pyrite and other sulfides, would result in a pH between 4 and 1, and even lower (Seal *et al.*, 2002), although it is not possible in the nature. In case of high concentration of sulfate ions, a film of gypsum is formed as an armoring agent around the carbonate minerals and will act as a preservation factor against acid solutions and neutralization will be delayed. Existence of gypsum as a common

accessory mineral in deposits of the KBA, such as the Tarz, Gujer, Ahmadabad and many of other deposits can be considered as an evidence of this processes.

Carbonate minerals and H^+ ions are consumed during the neutralization, releasing dissolved cations (Ca^{2+} and Mg^{2+}) and bicarbonate HCO_3^- into the solution. The carbonate and bicarbonate may react and bond with metal ions such as Cd^{2+} , Mn^{2+} , Zn^{2+} , Pb^{2+} and precipitate these elements in secondary minerals. However, the precipitation of secondary carbonates depends strongly on the pH of the aqueous solution and requires high pH values. Additionally, the precipitates are able to buffer the aqueous solutions within different ranges of pH (Blowes and Ptacek, 1994).

During the reaction of acid solution of pyrite oxidation, a significant amount of CO_2 will be generated. As a result, increase of $CO_{2(g)}$ partial pressure leads to a greater stability of Zn-Pb carbonates within the relevant pH interval in carbonate host rocks (Fig. 23). The precipitation of smithsonite is restricted to relatively high $CO_{2(g)}$ pressure values ($\log CO_{2(g)} = 0.4$ kPa at 298.2 K) (Brugger *et al.*, 2003). Atmospheric pressure of CO_2 (actual $\log PCO_{2(g)}$) is -1.5 kPa (Drever, 1997) and it is not possible to precipitate smithsonite from an aqueous solution, which is in equilibrium with the atmosphere. A minimum $\log PCO_{2(g)} = 0.4$ kPa is necessary for the formation of smithsonite according to equation R8 (after Takahashi, 1960):



In case of $\log PCO_{2(g)} < 0.4$ kPa, the reaction would be driven to the right hand and hydrozincite would precipitate. These conditions are common for aqueous solutions, which are in equilibrium with the atmosphere, such as surface or near-surface solutions in unsaturated zones. In contrast to these equilibrium conditions, aqueous solutions at

deeper levels or water-saturated zones are in disequilibrium with the atmospheric $\text{CO}_{2(g)}$ and reach values, which are favorable for the precipitation of smithsonite. For this reason, smithsonite has been formed at deeper parts of veins and even beneath the water table in the KBA.

The quantitative precipitation of hemimorphite and other zinc silicates depends primarily on the availability of silica. Thus it is necessary to consider the geochemical behavior of such fluids with respect to SiO_2 as well. The solubility of silica phases increases drastically from crystalline quartz to amorphous silica (Dove and Rimstidt, 1994). Thus, opal (amorphous silica) releases the highest concentrations of SiO_2 into aqueous solutions. $\text{H}_4\text{SiO}_{4(aq)}$ is a weak acid and dissociates appreciably about two pH units above neutrality (Dove and Rimstidt, 1994). The availability of dissolved silica is limited by the solubility of SiO_2 in water and the slow dissolution rate of SiO_2 (polymorphs). Thus, the amount of $\text{H}_4\text{SiO}_{4(aq)}$ within natural waters is generally not sufficient for an effective and quantitative binding of high zinc concentrations. The low concentrations of dissolved silica lead to the precipitation of small amounts of Zn-silicates only and consequently, zinc precipitates at the supergene oxidation stage predominantly as zinc carbonates. As mentioned before, silica (chert) is present in the carbonate host rocks and as a gangue mineral in the vein type sulfide mineralization of the KBA. Relatively low abundance of silica compared to the carbonate minerals explains the low frequency of hemimorphite in the KBA deposits. So that, hemimorphite is present in minor amounts in many of studied deposits and willemite as other trace zinc silicate is only found in Ahmadabad, Gavar, Tajkuh, Senjedu (Deh Askar) and Tarz deposits.

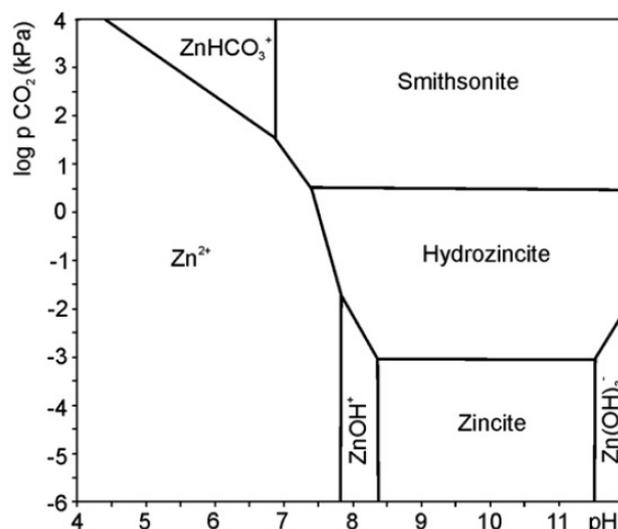


Figure 23) Stability of zinc carbonates in the chemical system Zn–O–H–C in relation to $\text{PCO}_{2(g)}$ and pH. The activity of zinc is $a(\text{Zn})=10^{-5} \text{ mol/l}$ (after McPhail et al., 2003).

Equation R9 shows the dependence of the formation of anglesite and cerussite on the activities of pH, $\text{H}_2\text{CO}_{3(aq)}$ and SO_4^{2-} (Reichert and Borg, 2008):



It is obvious that the conditions of oxidation stage, because of high concentration of SO_4^{2-} and H^+ ions, is suitable for anglesite precipitation. The solubility of anglesite in pure water is relatively high (Reichert and Borg, 2008) and formation of anglesite needs additional source of SO_4^{2-} . Presence of gypsum and other sulphate-bearing minerals show a high concentration of SO_4^{2-} ion and so that precipitation of anglesite becomes possible. Gypsum is present in some deposits of the KBA such as Tarz, Tajkuh, Tappeh Sorkh and in these deposits, formation of anglesite is imaginable. But, as mentioned above, relative to cerussite, stability of anglesite is low and during the later evolutions, consuming H^+ and increasing the pH value to neutral or alkaline, it will be transformed to cerussite and such a situation is found frequently in the KBA. So, it is obvious that the anglesite must be found less than the cerussite and equation (R9) is shifted to the right hand. Replacement of anglesite by

cerussit has been noted previously by Sangameshwar and Barnes (1983).

4.3- Probable sources of ore components

In a general view, the sulfide and nonsulfide zinc (-lead) deposits of the KBA are restricted to the Upper Permian (-Lower Triassic) carbonate rocks as a unique ore-bearing horizon. Indeed, these deposits show strata-bound mineralization characteristics. The carbonate host rock is enclosed between two separate carbonate formations; the Kuhbanan (Mila equivalent in Alborz Mountains, northern Iran) and the Shotori and Nayband formations at the base and top respectively (Fig. 3) and here, with emphasize on component source materials (metals and non-metals), the stratigraphic sequence is summarized as Fig. 24.

According to Figure 24, the two formations are considered as potential metal source; the Dahu formation at the base and the Liassic shale at the top. In some researches (e.g. Everett *et al.*, 2003), the sandstone has been played a role in supplying lead for mineralization. Also, in many other researches (e.g. Coveney and Glascock, 1989), shale has been introduced as metal source for carbonate hosted Pb-Zn deposits. These rocks have played the same role for supplying Pb, Zn and Ba in brine of oil fields (Carpenter *et al.*, 1974). Also, Ghazban and Hajikazemi (1994) have been studied the Irankuh base metal deposits (Isfahan Province, west Central Iran) and have proposed the Upper Jurassic shale as metal source for mineralization in the area. They have noted that during the diagenetic decomposition of potassium feldspar, mica and clay minerals of shale, the elements Pb, Zn, Ba and Sr have released and entered into the ore-bearing fluids. Furthermore, clay minerals transformation and dehydration of shale can provide the adequate amounts of magnesium for dolomitization associated with the base metal mineralization.

Based on previous research (Amiri, 2007), two hypothesis were considered for metal supplying:

The sandstone of Dahu formation (especially for lead supply) and the Liassic shale formation (particularly for zinc supply). In the first alternative, the ascending hydrothermal fluids while passing through the sandstone have been enriched of ore metals and in the second ones, descending fluids during the circulation in the Liassic shale have been gained adequate amounts of ore needed elements. To investigate these assumptions, geochemical tools were used and several samples were taken from the various formations (two samples of the Lower Paleozoic sandstone, seven samples of the Kuhbanan formation, four samples from the Upper Permian carbonate rocks as ore horizon, four samples of the Shotori and Nayband formations and three samples of the Liassic shale). To avoid of samples contamination, sampling was done far from the mining activities. Then relative mean values variations of the elements were plotted along the lithological column (Fig. 24). These investigations, in opposite to the conventional imaginations, show that the two assumed formations (Lower Paleozoic sandstone and Liassic shale) because of low concentration of ore elements, have no important role in the supplying metals for mineralization. In contrast, as can be seen in the Fig. 24, carbonate host rocks (ore bearing horizon) have a distinct enrichment of major and trace elements involved in the mineralization.

Also, igneous intrusive bodies as an alternative to supplying ore metals were studied and three samples of diabase dykes that intruded the Lower Paleozoic sandstone and to a lesser extent in younger formations, including the carbonate host rocks, were analyzed and show no significant enrichment of ore elements.

As a result of these geochemical investigations, three alternative hypotheses for metal sources (Lower Paleozoic sandstone, Liassic shale and intrusive bodies) were rejected. If ascending metal-bearing fluids considered as agent of mineralization, there is no reason for lack of

mineralization in the underlying carbonate rocks (Kuhbanan formation). Also, descending ore bearing fluids must be mineralized the Nayband formation that it is not occurred. So, a new and less common hypothesis was proposed; carbonate host rocks as source rocks. Indeed, the Upper Permian carbonate rocks have two important roles in the KBA, the source and the host of mineralization. In addition to

geochemical investigations, the mineralogy and mineralogy of this rock unit have been confirmed the new hypothesis. Existence of disseminated sulfide minerals in the Upper Permian carbonate rocks and lack or scarcity of fossils in the rock (toxicity of the sedimentary environment) is a new finding that verified the source role of the host rocks.

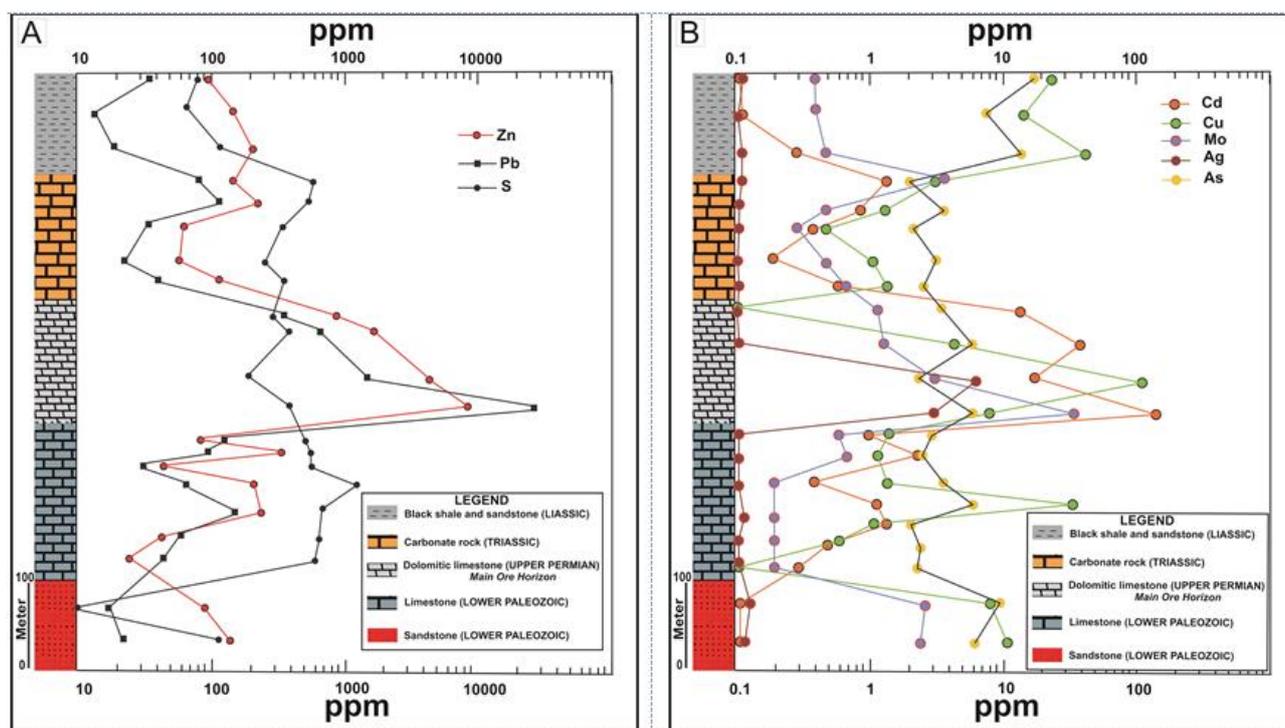


Figure 24) Simplified stratigraphic column of The KBA and variation of ore elements along the column. A. The main ore elements (Zn, Pb, S) and B. Trace elements (Cd, Cu, Mo, Ag, As). Enrichment of all elements can be seen on the Upper Permian carbonate host rocks.

5- Ore genesis model

In order to explain a genetic model for nonsulfide zinc (-lead) deposits of the KBA, it must be reviewed and combined the existing data. So that, several features of the deposits are used and the genetic model subdivided to three stages.

a) In the first stage, a unique and less common mineralization has been occurred in the Upper Permian carbonate sediments. Several features were confirmed the mineralization of the mentioned carbonate rocks in the KBA. Existence of primary (and not-related to micro cracks) sulfide minerals and high concentration

of ore metals relative to other carbonate formations of the area are the most important features that outstanding the carbonate host rocks. The concentrations of Zn, Pb, Cd, Mo and Ag in the ore horizon are abnormally high. In these rocks, the arithmetic mean value of Zn is 3723 ppm (186 times more than Clark value of carbonate rocks). Other elements have enrichments from tens to hundreds of times related to ordinary carbonate rocks (Pb: 397 times, Cd: 618 times, Ag: 26 times and Mo: 26 times). High amounts of metals in the sea water causes toxicity of the environment and therefore, the living conditions in the sedimentary basin have been omitted. Lack or

scarcity of fossils in the ore horizon is confirmed the toxicity of sea water.

It seems that the Upper Permian sedimentary basin has been accompanied with a submarine exhalative process (Amiri, 2007) and has been gained adequate ore metals to form disseminated sulfide minerals during the diagenesis stages. Traces of these submarine activities have been observed in the Kuh Ghal'eh deposit (Fig. 8B). Carbonate source for metals can be admitted with substitution of metals in the lattice of metastable minerals like the aragonite or magnesian calcite. During the diagenesis stages, these metals can re-enters to the pore water and because of its relative high temperature, can be play a role as ore-bearing fluids. So, it can be stated that the metals have been entered primarily by submarine exhalation to the sedimentary basin and fixed firstly by carbonate metastable minerals and then, re-entered to the pore water and fixed with the reduced sulfur and forms primary sulfide minerals. Reduced sulfur may supply by bacteria activities. Thus, it can be said that the Upper Permian carbonate rocks have been fixed the ore metals and played the main role as primary protore of other later mineralization (sulfide and nonsulfide) in the KBA.

b) In the second stage, the ore-bearing horizon of the Upper Permian (-Lower Triassic) carbonate rocks have been undergone tectonic squeezing and so, folding, faulting and brecciation of the strata have been occurred. These events have been started at the post Permian orogeny phases (Cimmerian, Laramide or even younger events) and provided needed conditions for circulation of basinal fluids and during these processes, ore metals have been leached out from the mentioned carbonate horizon by the fluids. Fault gouges have been the best conduits for focusing the migrated metal-bearing fluids. After these evolutions, the basis for the vein-type sulfide mineralization has been provided. On the other hand, based on stable isotope geochemistry, Amiri *et al.* (2009)

have been concluded that the reduced sulfur for fixing metals as sulfide minerals have been provided from two sources; the Lower Paleozoic gypsum-bearing Desu formation (main source) and the thin gypsiferous interlayers of Upper Permian carbonate host rocks. According to their research, sulfide minerals of the KBA have narrow $\Delta^{34}\text{S}_{\text{CDT}}$ range between 11.03 (Tajkuh sphalerite) and 18.55 per mil (Tarz sphalerite). Other sulfide minerals have a value of $\Delta^{34}\text{S}_{\text{CDT}}$ between the two above values (mean values of pyrite: 14.83 and galena: 12.11 per mil). These values is resemble to the some Mississippi Valley-type deposits, especially to the southeast Missouri and Upper Mississippi Valley, USA and Pine Point, Canada (Heyl *et al.*, 1974), but it has no similarity with Alpine-type base metal deposits (Brigo *et al.*, 1977). So, it can be stated that the ascending hydrothermal fluids during passing through the gypsum-bearing strata of Desu formation, have been dissolved enough sulfate ions and transferred to the fault gouges of the Upper Permian carbonate rocks. In the site of mineralization, the sulfate ions have been reduced thermochemically by the bitumen components of the host rocks and produced HS^- for fixing dissolved metals (derived from host rocks) as sulfide minerals. Also, based on equilibrated sulfide pairs (pyrite-sphalerite), Amiri *et al.* (2009) have been evaluated temperature of the sulfide mineralization between 55 to 114 °C and compatible with the thermochemical sulfate reduction (TSR) (Orr, 1974, 1977; Krouse *et al.*, 1988). Therefore, the mixing model is the best model for sulfide precipitation in the KBA (Fig. 25A). Mixing model has been proposed previously in many cases for Mississippi Valley type mineralization (e.g. Beales and Jackson, 1966; Anderson, 1983; Sverjensky, 1989; Corbella *et al.*, 2004; Leach *et al.*, 2010).

c) As explained above, sulfide mineralization has occurred at depths corresponding to a temperature of about 55 to 114 °C. After the

formation of vein-type sulfide mineralization, because of tectonic compression and exposure of sulfide veins to the surface or near surface, an important stage of evolution has happened. Oxidation of the sulfide minerals is the most important events that have affected this type of ore. In other words, sulfide ores as a result of exposing to the surface, have subjected to the weathering and then, nonsulfide ores have formed. High amount of pyrite in the sulfide ores causes the extent chemical weathering and leaching of metals downwards. Reactions between this metal-bearing fluids and carbonate rocks have formed the nonsulfide minerals.

Textural studies showed that the smithsonite as the most abundant nonsulfide zinc mineral is formed before the other nonsulfide zinc minerals and then transformed to smithsonite and hemimorphite. Studies conducted on the carbon and oxygen isotopes of the smithsonite mineral (Amiri and Rassa, 2007) showed that the $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{SMOW \& PDB}}$ of this mineral is very similar to the sea water and consequently it can be concluded that the fluids responsible for the formation of this mineral mainly was the basinal fluids entrapped in the carbonate rocks.

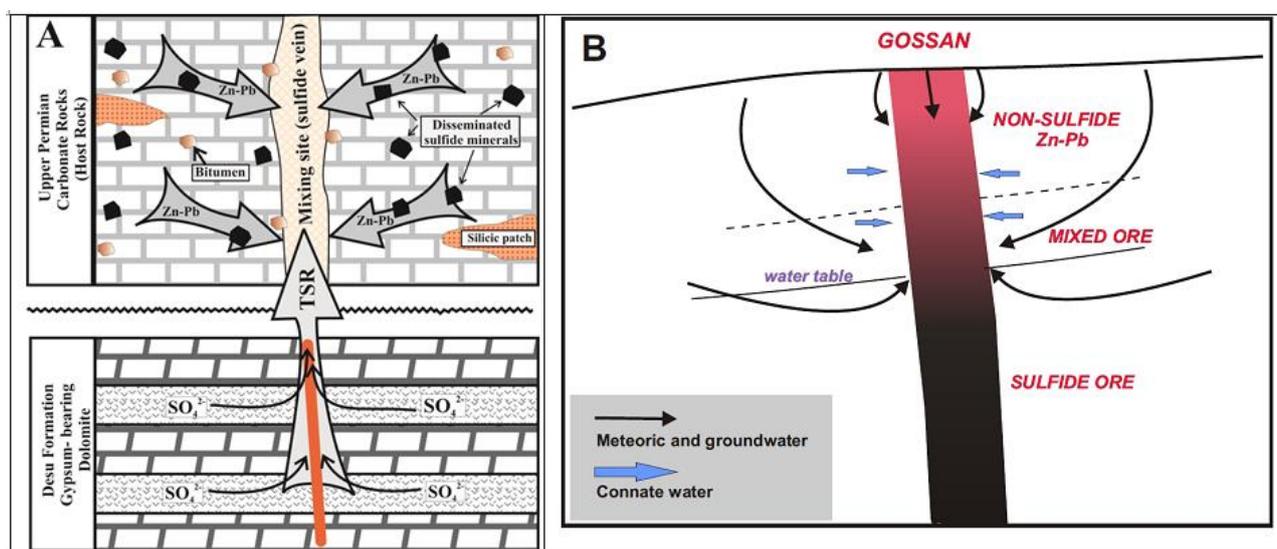


Figure 25) A. Mixing model for precipitation and formation of vein-type sulfide mineralization and B. Fluids involved in the formation of the nonsulfide zinc (-lead) ore in the KBA.

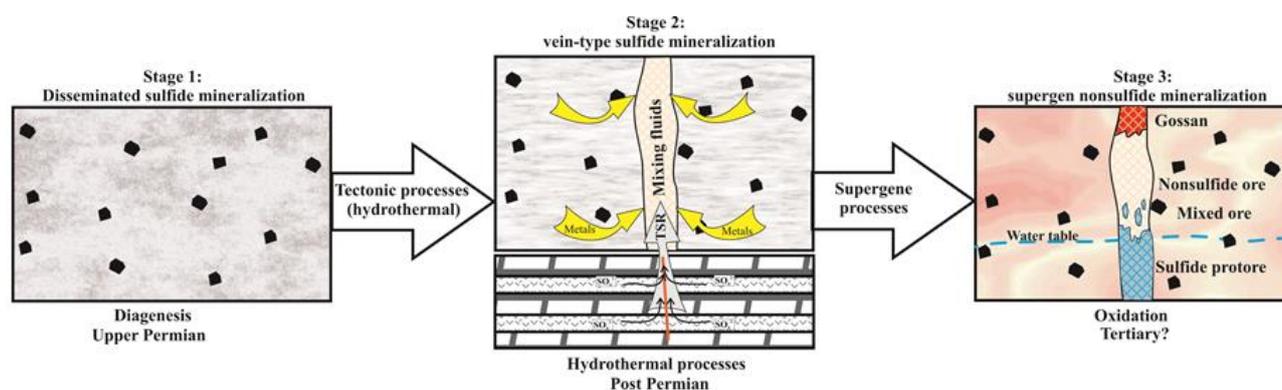


Figure 26) Simplified stages of Zn (-Pb) mineralization in the KBA. See text for explanations.

Against to this result, $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{SMOW \& PDB}}$ values of hemimorphite and other nonsulfide ores indicated that the meteoric waters and ground waters are responsible for the formation of these minerals (Fig.25B). Thus, it

can be concluded that the combinations of basinal fluids, ground waters and meteoric waters have the main role in the formation of nonsulfide ores. Mineralogical and textural evidence showed that the nonsulfide ores of the KBA can be categorized into direct replacement

and wall-rock replacement variety (Hitzman *et al.*, 2003).

6- Conclusions

Three dependent sulfide and nonsulfide zinc (-lead) mineralization have been formed in the KBA; disseminated sulfide minerals, vein-type sulfide and nonsulfide ore. The ore matters have been occurred in a stratigraphic horizon of the Upper Permian (-Lower Triassic) as a strata-bound mineralization. Field and laboratory investigations show that the disseminated sulfide minerals at least is present in the Tarz, Tajkuh, Kuh Ghal;eh, Tappeh Sorkh and Kuh-e-Bijahan deposits. The nonsulfide ore can be seen in all deposits of the KBA and the sulfide mineralization is only present in a few deposits (Tarz and Tajkuh deposits). Based on extensive mineralogical and geochemical studies on the sulfide and nonsulfide zinc (-lead) deposits of the KBA, these deposits have formed during three stages (Fig. 26) and the following results were obtained.

1. In the Upper Permian sedimentary basin, a unique and less common disseminated sulfide mineralization has formed (Fig. 26, stage 1). Submarine activity contemporary with the carbonate sediments has been responsible for the supplying the ore metals. During the diagenesis stages, as a result of bacteria activity, reduced sulfur has been provided and sulfide minerals have formed. Sphalerite and galena with lesser amounts of pyrite and chalcopyrite are the sulfide minerals that composed the disseminated sulfide mineralization. These minerals have no relation to (micro-) cracks and joints and hence, syndiagenetic genesis is proposed for this mineralization. High amounts of ore elements in this stratigraphic horizon (sometimes over one percent sum ore metals) is a new finding that can be considered as a future low grade and large volume ore reserve same as porphyry deposits. It seems that this

mineralization is the main precursor for the other mineralization of the KBA.

- 2- After the formation of disseminated sulfide mineralization, the ore-bearing carbonate strata have undergone tectonic stress and squeezing. Therefore, folding, faulting and brecciation of the strata have been occurred and prepared the suitable conditions for a new sulfide mineralization (Fig. 26, stage 2). As a result of fluids circulation through the mentioned strata, the ore metals have been leached out and focused to the fault gouges. In the site of vein-type sulfide mineralization, ascending sulfate bearing fluids derived from gypsum bearing Desu formation have mixed with the metal bearing fluids derived from the Upper Permian carbonate rocks and so, because of the thermochemical sulfate reduction (TSR) and provide adequate reduced sulfur (HS⁻), ore metals have been fixed as new sulfide minerals. Sphalerite, pyrite and galena are the most abundant sulfide minerals that composed vein-type sulfide mineralization and a lesser amount of chalcopyrite and arsenopyrite accompanied the sulfide ore.

- 3- Tectonic movements have caused outcrops the vein-type sulfide mineralization and exposing to the oxidation and supergene processes (Fig. 26, stage 3). Therefore, the sulfide minerals, especially the pyrite have been oxidized and produced adequate acid solutions to leaching of other sulfide minerals, particularly the sphalerite. During the oxidation processes, the iron is fixed as oxyhydroxides and has formed gossan as an important field exploration key. Pregnant and chiefly zinc-bearing descending solutions have been passed from surface to the deeper parts and react with the carbonate wall rocks and then, have formed newly nonsulfide zinc minerals. Smithsonite is the most important nonsulfide zinc mineral and has formed prior to the other zinc minerals. It seems that the reaction of acid solutions with the carbonate minerals have formed high partial pressure of CO₂ and caused suitable conditions

for formation of the smithsonite. Later reactions of the smithsonite with the low CO₂ bearing solutions caused formation of the hydrozincite. Furthermore, because of the low concentration of silica both in the carbonate host rocks and in the sulfide ore, the hemimorphite is a minor mineral and the willemite is a trace mineral in the nonsulfide ore deposits of the KBA. Oxygen and carbon stable isotope investigations show that the meteoric and ground water along with entrapped connate water are the main fluids responsible for the formation of nonsulfide ore. Based on the classification of nonsulfide zinc deposits (Hitzman *et al.*, 2003), the KBA nonsulfide zinc (-lead) deposits are categorized as direct replacement and wall rock replacement.

References

- Anderson, G. M. 1983. Some geochemical aspects of sulfide precipitation in carbonate rocks. In: Kisvarsanyi, G., Grant, S. K., Pratt, W. P., Koenig, J. W. (Eds.), International conference on Mississippi Valley-Type lead-zinc deposits; Proceedings Volume: Rolla, University of Missouri, pp. 61–76.
- Amiri, A. 2007. The Geological and geochemical characteristics and genesis of the carbonate-hosted zinc-lead deposits in the Ravar-Bafgh area. Unpublished Ph.D dissertation, Islamic Azad University, Science and Research Branch, Tehran, 315p, (in Farsi).
- Amiri, A. Rassa, I. 2007. The nonsulfide ore formation conditions of Ravar-Bafgha rea, findings of carbon and oxygen stable isotopes. Journal of Applied Geology, Islamic Azad University, Zahedan Branch: 3, 95–103 (in Farsi).
- Amiri, A., Rassa, I., Khakzad, A., Adabi, M. H. 2009. Thermometry and formation model of carbonate-hosted Zn-Pb sulfide deposits in the Ravar-Bafgh area based on sulfur stable isotopes. Scientific Quarterly Journal, Geosciences: 18, 3–10 (in Farsi).
- Beales, F. W., Jackson, S. A. 1966. Precipitation of lead-zinc ores in carbonate reservoirs as illustrated by Pine Point ore field, Canada. Institution of Mining and Metallurgy Transactions, Section B: 75, 278–285.
- Blowes, D. W., Ptacek, C. J. 1994. Acid-neutralization mechanisms in inactive mine tailings. In: Jambor, J.L., Blowes, D.W. (Eds.), Environmental Geochemistry of Sulfide Mine Waste. Short Course Handbook, Mineralogical Association of Canada: 22, 271–291.
- Boni, M., Large, D. 2003. Non-sulphide zinc mineralisation in Europe: an overview. Economic Geology: 98, 715–729.
- Brigo, L., Kostelka, L., Omenetto, P., Schneider, H. J., Schulz, O., Štucl, I. 1977. Comparative reflections on four Alpine Pb-Zn deposits. In: Klemm, D.D., Schneider, H-J. (Eds.), Time and strata-bound ore deposits. Springer-Verlag, New York, 273–293.
- Brugger, J., McPhail, D. C., Wallace, M., Waters, J. 2003. Formation of willemite in hydrothermal environments. Economic Geology: 98, 819–835.
- Carpenter, A. B., Trout, M. L., Pickett, E. E. 1974. Preliminary report on the origin and chemical evolution of lead and zinc-rich oil field brines in Central Mississippi. Economic Geology: 69, 1191–1206.
- Corbella, M., Ayora, C., Cardellach, E. 2004. Hydrothermal mixing, carbonate dissolution and sulfide precipitation in Mississippi Valley-Type deposits. Mineralium Deposita: 39, 344–357.
- Coveney, R. M., Glascock, M. D. 1989. A review of the origins of the metal-rich Pennsylvanian black shales, Central U. S. A., with an inferred role for basinal brines. Applied Geochemistry: 4, 374–367.

- Domènech, C., De Pablo, J., Ayora, C. 2002. Oxidative dissolution of pyritic sludge from the Aznalcóllar mine (SW Spain). *Chemical Geology*: 190, 339–353.
- Dove, P. M., Rimstidt, J. D. 1994. Silica–water interactions. In: Heaney PJ Prewitt CT Gibbs GV (Eds) *Silica, physical behavior, geochemistry and materials applications*. *Reviews in Mineralogy*: 29, 259–308.
- Drever, J. I. 1997. *The geochemistry of natural waters: surface and groundwater environments*, 3rd edition. Prentice-Hall International, New Jersey, 436 pp.
- Everett, C. E., Rye, D. M., Ellam, R. M. 2003. Source or sink? An assessment of the role of the Old Red Sandstone in the genesis of the Irish Zn-Pb deposits. *Economic Geology*: 98, 31–50.
- Heyl, A. V., Bozion, C. N. 1962. Oxidized zinc deposits of the United States. Part 1. *General Geology*. U.S. Geological Survey Bulletin: 1135-A, 52p.
- Heyl, A. V., Landis, G. P., Zartman, R. E. 1974. Isotopic evidence for the origin of Mississippi Valley-type mineral deposits: a review *Economic Geology*: 69, 992–1006.
- Hitzman, M. W. Reynolds, N. A., Sangster, D.F., Allen, C.R., Carman, C.E. 2003. Classification, genesis and exploration guides for nonsulfide zinc deposits. *Economic Geology*: 98, 685–714.
- Huckriede, R., Kürsten, M., Venzlaff, H. 1962. Zur geologie des gebiets zwischen Kerman und Saghand (Iran). *Beihefte zum Geologischen Jahrbuch*: 51, 197 p.
- Ghazban, F., Hajikazemi, E. 1994. Genesis of the sediment-hosted Zn-Pb-Ba deposits in Irankuh district, west Central Iran (Abs.). *Geological survey of America Annual Meeting, Abstract and Programs*: 26, A-222.
- Ghazban, F., McNutt, R. H., Schwarcz, H. P. 1994. Genesis of sediment hosted Zn–Pb–Ba deposits in the Irankuh district, Esfahan area, West-Central Iran. *Economic Geology*: 89, 1262–1278.
- Gilg, H. A., Boni, M., Balassone, G., Allen, C. R., Banks, D., Moore, F. 2005. Marble-hosted sulfide ores in the Angouran Zn-(Pb–Ag) deposit, NW Iran: interaction of sedimentary brines with a metamorphic core complex. *Mineralium Deposita*: 41, 1–16.
- Herbert, R. B. 1999. Sulphide oxidation in mine waste deposits, a review with emphasis on dysoxic weathering. Mitigation of the environmental impact from mining waste (MiMi). MiMi Print, Luleå, Sweden.
- Kavoshgaran Paradis Co. 2013. Final report of fluorite exploration at Kuh-e- Bijahan, north-west Bahabad, Yazd Province, central Iran. 119p (in Farsi).
- Krouse, R. H. Viau, C. A., Eluik, L. S., Ueda, A., Halas, S. 1988. Chemical and isotopic evidence of thermochemical sulfate reduction by light hydrocarbon gases in deep carbonate reservoirs. *Nature*: 333, 415–419.
- Large, D. 2001. The geology of nonsulphide zinc deposits, an overview. *Erzmetall*: 54, 264–276.
- Leach, D. L., Taylor, R. D., Fey, D. L. Diehl, S. F., Saltus, R. W. 2010. A deposit model for Mississippi Valley-Type lead-zinc ores, chap. A of *Mineral deposit models for resource assessment*: U.S. Geological Survey Scientific Investigations Report: 5070–A, 52p.
- Lowson, R. T. 1982. Aqueous Oxidation of Pyrite by Molecular Oxygen. *Chemical Reviews*: 82, 461–497.
- McPhail, D. C. Summerhayes, E., Welch, S., Brugger, J. 2003. The Geochemistry of Zinc in the Regolith. In: Roach, I. C. (Ed.), *Advances in Regolith*. CRC for Landscape Environments and Mineral Exploration, 287–291.

- Mondillo, N., Boni, M., Balassone, G., Villa, I. M. 2014. The Yanque Prospect (Peru): from polymetallic Zn-Pb mineralization to a nonsulfide deposit. *Economic Geology*: 109, 1735–1762.
- Orr, W. L. 1974. Changes in sulfur content and isotopic ratios of sulfur during petroleum maturation- study of Big Horn Basin Paleozoic oils. *American Association of Petroleum Geologist Bulletin*: 58, 2295–2318.
- Orr, W. L. 1977. Geologic and geochemical controls on the distribution of hydrogen sulfide in natural gas. In: Campos, R., Goni, J. (Eds.). *Advances in Organic Geochemistry*, Madrid, Enadisma, 572–597.
- Paradis, S., Simandl, G. J., Keevil, H., Raudsepp, M. 2016. Carbonate-hosted nonsulfide Pb-Zn deposits of the Quesnel Lake District, British Columbia, Canada. *Economic Geology*: 111, 179–198.
- Rajabi, A., Rastad, E., Canet, C., Alfonso, P. 2015. The early Cambrian Chahmir shale-hosted Zn–Pb deposit, Central Iran: an example of vent-proximal SEDEX mineralization. *Mineralium Deposita*: 50, 571–590.
- Reichert, J., Borg, G. 2008. Numerical simulation and geochemical model of supergene carbonate-hosted non-sulphide zinc deposits. *Ore Geology Reviews*: 33, 134–151.
- Sangameshwar, S. R., Barnes, H. L. 1983. Supergene processes in zinc-lead-silver sulfide ores in carbonates. *Economic Geology*: 78, 1379–1397.
- Seal II, R. R., Foley, N. K., Wanty, R. B. 2002. Introduction to geoenvironmental models of mineral deposits. In: Seal II, R.R., Foley, N.K. (Eds.), *Progress on geoenvironmental models for selected mineral deposit types*. USGS Open File Report 02-195, 1–7.
- Sverjensky, D. A. 1989. The diverse origins of Mississippi Valley-Type Zn-Pb-Ba-F deposits. *Chronique de la recherche minière*: 495, 5–13.
- Takahashi, T. 1960. Supergene alteration of zinc and lead deposits in limestone. *Economic Geology*: 55, 1083–1115.
- Williamson, M. A., Rimstidt, J. D. 1994. The kinetics and electrochemical rate-determining step of aqueous pyrite oxidation. *Geochimica et Cosmochimica Acta*: 58, 5443–5454.
- Vaughan, D. J. 2006. Sulfide mineralogy and geochemistry: introduction and overview. *Reviews in Mineralogy and Geochemistry*: 61, 1–5.