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Genesis of Chah-Talkh nonsulfide Zn-Pb deposit (south of Iran): Evidence from Geology, Mineralogy, Geochemistry and Stable Isotope (C, O) data

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Genesis of Chah-Talkh nonsulfide Zn-Pb deposit (south of Iran): Evidence from Geology, Mineralogy, Geochemistry and Stable Isotope (C, O) data

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Abstract

Chah-Talkh nonsulfide Zn-Pb deposit with about more than 720000 t at 15% Zn in the form of Zn carbonates and silicates is a target resource in the south of Iran. In this preliminary study, some cases likes geology, mineralogy and geochemistry (major and trace element data and stable Isotope) of this deposit in surface and depth are investigated for determine of genesis. The analyses carried out on samples from 14 drill cores and 15 surface profiles (vertical to veins strike). Mineralization occurs in 3 main veins with thickness about 0.5 to 3 meters in the length about 900 m that in (resent) exploration this length increases. Main ore minerals are hydrozincite, hemimorphite and smithsonite. The mineralogical and geochemical evidences indicate that Chah-Talkh deposit is a typical supergene nonsulfide Zn-Pb deposit in carbonate rocks that primary sulfide ores almost has been affected by deeply weathered. Mineralization in Chah-Talkh is generally associated with fracture zones and dolomitization. It seems that distribution of hemimorphite, smithsonite and hydrozincite is reflection of existing of clay minerals in host rocks. In presence of clay minerals (in marly limestone) main ore mineral is hemimorphite and in absence of clay minerals (micritic limestone) main ore mineral is hydrozincite and smithsonite. The $\delta^{18}O_{vsmow}$ value of hydrozincite ranges from 7.57 to 15.15 per mil that is very lower than this value in other nonsulfide deposits and has extent range. C and O isotopes and fluid inclusion data indicate that Zn oxide minerals were formed at temperatures □ 80° to 100°C by meteoric and metamorphic waters. There are evidences of both direct replacement and wallrock replacement in mineralization. EPMA analyzes and map elements of minerals show that in first stage of weathering fO_2 was very high then gradually fCO_2 increases. It seems that primary source of Zn and Pb could be Permian metamorphic unites (essentially shale and shiest).

Keywords: Chah-Talkh deposit, nonsulfide Zn mineralization, supergene, stable isotope

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Introduction

Nonsulfide Zn deposits have experienced a significant revival over the recent years, as a consequence of new developments in hydrometallurgical acid-leaching, solvent extraction, and electro winning techniques (Large, 2001).

Iran is host to more than 600 deposits and indexes of Zn and Pb (Ehya et al., 2010); many of them are of the nonsulfide type. Some deposits, as Angouran and Mehdiabad have a large tonnage and are renowned in the world. Other deposits are small to medium size, as the nonsulfide bodies of the Kuhbanan-Bahabad area. Some of them have sulfide ore (sphalerite and galena) in depth, but others such as Chah-Talkh do not carry sulfides. The Chah-Talkh deposit is situated in the Kerman Province (southern Iran), about 45 km southwest of Sirjan (which is 980 km south of Tehran). Some old mining activities have been observed at Chah-Talkh, but it is not clear when the mine was really active. The nonsulfide ores at Chah-talkh, which consist mainly of smithsonite, hydrozincite and hemimorphite were exploited from 1958 until 1971. In this period about 200,000 ton of ore, grading 23% Zn and minor lead was exploited, and a concentrated product with 45% Zn was exported to USSR. The deposit resource has been estimated (Sabzehei and Afrooz, 1989) to more than 720000 tons.

Regional geology

The Chah-talkh deposit is located in the southern Sanandaj-Sirjan Zone of the Zagros orogenic belt, close to the Urumieh-Dokhtar Magmatic Arc (Fig. 1). The Zagros Belt formed as a consequence of Tertiary continental collision between the Afro-Arabian plate and smaller Gondwana-derived microplates, after subduction of the Neotethys ocean during the Cretaceous (Boni et al., 2007). This north west - south east trending zone (Sanandaj-Sirjan) is divided into a northern and southern section (Aghanabati, 2004): the Chah-Talkh deposit is situated in the southern section. The geology of Sanandaj-Sirjan Zone in the Chah-talkh area is dominated by upper Paleozoic rocks consist of slate, phyllite, black schist, quartzite, mica schist, amphibolite, gneiss, metarhyolite and green schist, covered by Cretaceous limestone. The nonsulfide mineralization in the Chah-talkh deposit is hosted by a late Cretaceous limestone sequence that overlies a calcareous sandstone unit.

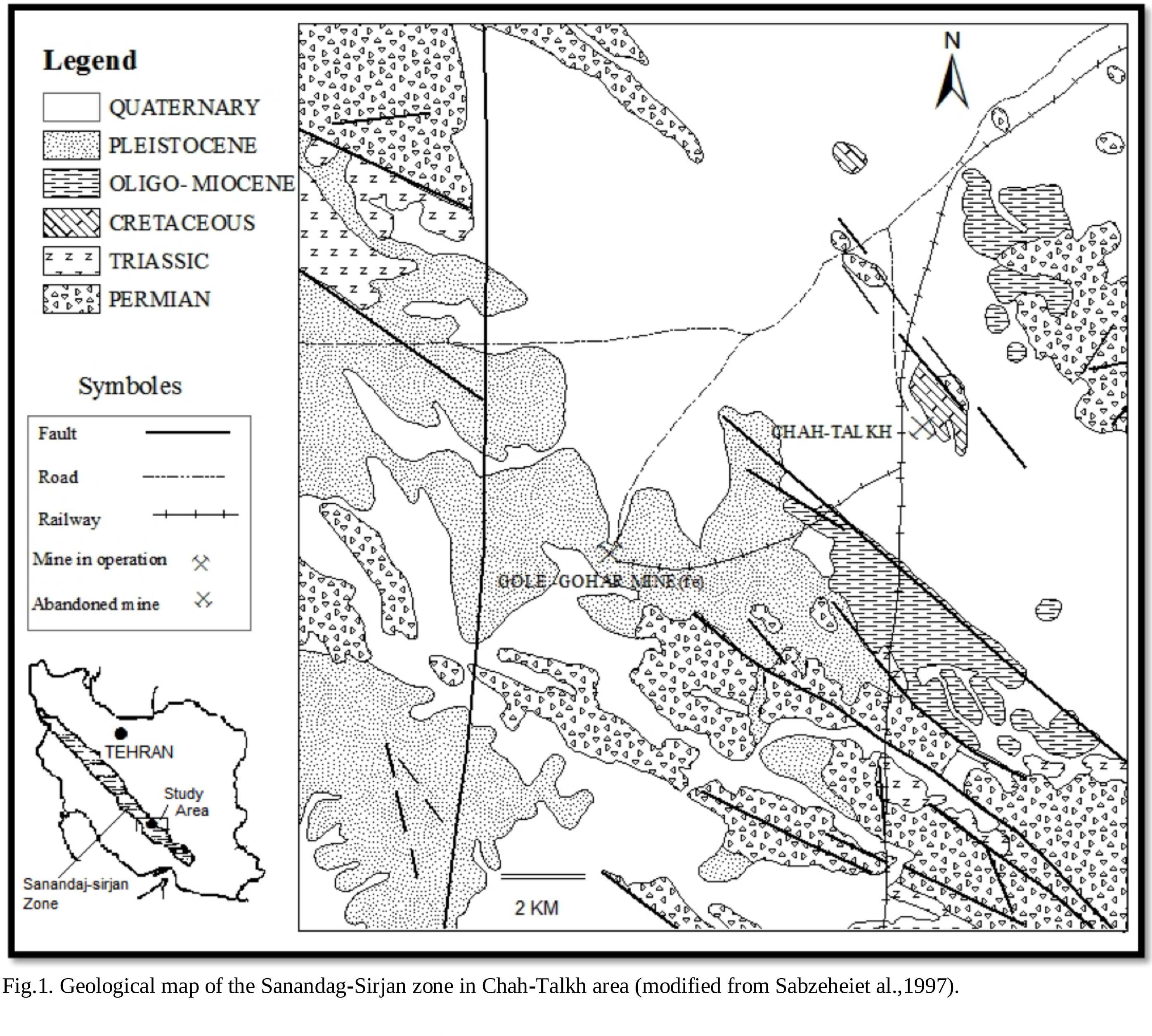


Fig.1. Geological map of the Sanandag-Sirjan zone in Chah-Talkh area (modified from Sabzeheiet al.,1997).

The Cretaceous limestone is a variable sequence of thin to medium bedded, gray biomicrites or oomicrites, and limestones with marly interbeds. Both rock units (limestone and marly limestone) are dolomitized. These units have been deposited in a shallow marine environment.

Deposit Geology

The Chah-Talkh orebody lies in a NW-striking structural belt in the Upper Cretaceous dolomitic limestone. The host rock appears as a syncline whose axis strikes NW-SE and plunges southward at 15-20°. North - south oriented faults cut the syncline at several points. The western limb of the syncline dips about 65° to the east and eastern limb dips 60° to the west. Three main faults are located in this deposit. The Said Abad fault in the east, and the Chah-Talkh fault in the center and in the west. The Chah-Talkh fault in the west of the syncline is parallel to sub- parallel to the axis of syncline. Mineralization occurs along a minor fault, which lies between the middle dolomitic limestone (k^{ld}_2) and the lower marly limestone (k^{lm}_1) in the west of syncline, near of west Chah-Talkh fault. This is a permeable zone, which is believed to have acted as conduit for the hydrothermal fluids. The age of host rock in the Chah-Talkh ore deposit is different from the other Zn-Pb deposits in Sanandag-Sirjan zone such as Irankouh (hosted in Lower Cretaceous) and Angouran (hosted in the Cambrian). The host rock limestone of the Chah-Talkh deposit (Upper Cretaceous) lie unconformably on a sandy conglomerate unit, and is considered to have been sedimented in shallow shelf to marginal marine environment. Limestone shows high-energy (oolitic unit) to moderate energy (bioclastic unit) and low energy conditions (micritic wackestone with sparse bioclasts). The host rock limestone has been subdivided into five units, which from the low to top are: lower dolomitic limestone (k^{ld}_1), lower marly limestone (k^{lm}_1), middle dolomitic limestone (k^{ld}_2), upper marly limestone (k^{lm}_2) and upper dolomitic limestone (k^{ld}_3) (Fig. 2). The main part of the mineralization is located in a fault zone between the k^{lm}_1 and k^{ld}_2 units. For simplicity in the geological map of Fig. XX, k^{ld}_2, k^{lm}_2 and k^{ld}_3 are represented as the kldm unit.

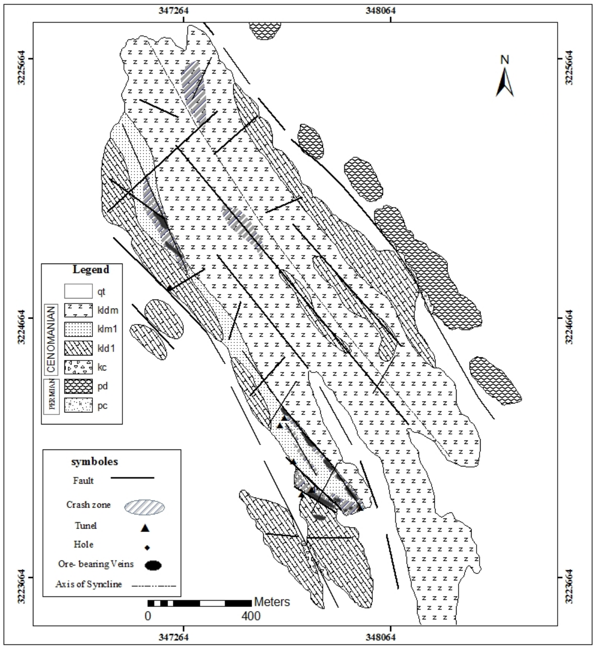


Fig 2: Simplified geological map of Chah-Talkh (modified from IMIDRO, 2010).

The Chah-Talkh orebody is located in the hanging wall of an NW-SE trending fault; morphology of the ore body is stratabound, but subdivided in multiple veins. Maximum throw of this fault is about 500 m. The mineralization lies in the fracture zone and is considered to be epigenetic. The strike of the veins is parallel to the bedding of the host limestone (k^{lm}_1 and k^{ld}_2).

The hypogene ore comprises galena, sphalerite and pyrite that are present as remnants in the supergene ore. The epigenetic mineralization was accompanied by dolomitization (main alteration), which occurred with the precipitation of calcite and dolomite in veins and cavities. The main association of nonsulfide minerals at Chah-talkh consists of smithsonite, hemimorphite and hydrozincite. Sabzehei and Afrooz (1989) estimated the ore resource of Chah-Talkh at about 720,000 tons at 15% Zn and 8% Pb, but the results of recent exploration have raised the amount of the resources considerably.

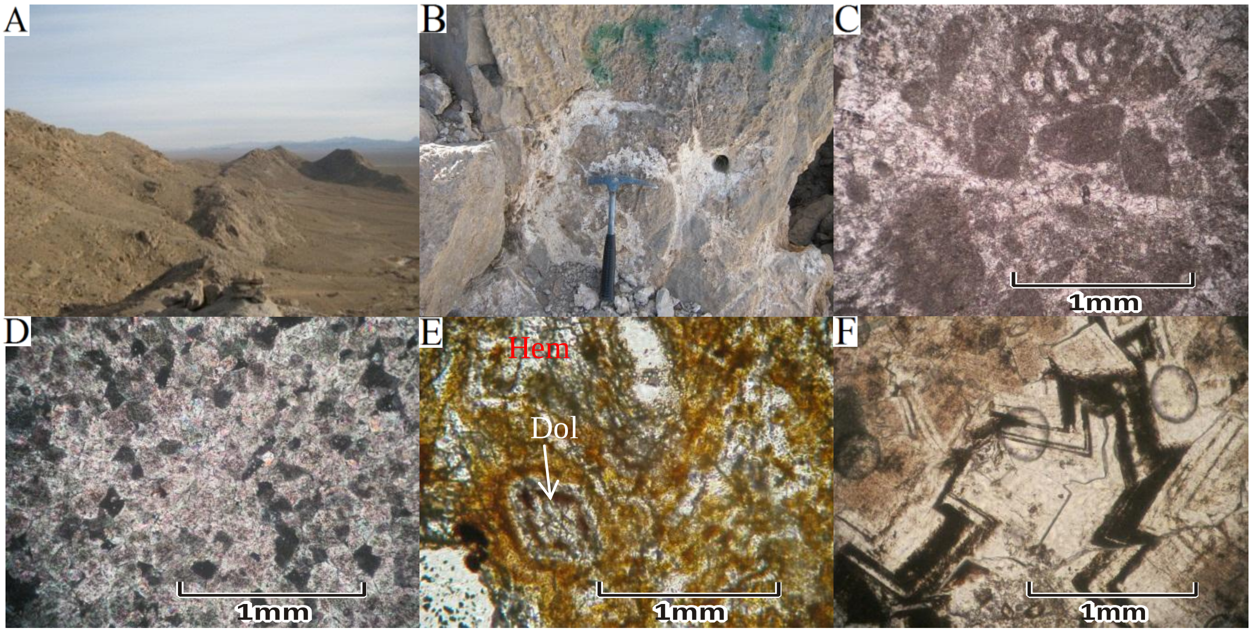


Fig. 3: A: West limb of the Chah-Talkh syncline and location of nonsulfide mineralization; B: fracture filled by nonsulfide Zn ores (hydrozincite and smithsonite) in the lower dolomitic limestone (k^{ld}_1); C: k^{ld}_1 (host rock) in thin section (rounded spaces of micrite in the sparite matrix) (PPL). D: first stage dolomitization that has no relation to mineralization (PPL); E: second stage dolomitization, which is in relation to the nonsulfide mineralization and fracture zones (PPL); F: third stage dolomitization that occurred together with mineralization (PPL).

Dolomitization

The host rock of the Chah- Talkh nonsulfide Zn-Pb deposit is dolomitized (Rezaeian et al., 2010). At least three dolomitization stages can be distinguished in the Chah-Talkh mine (Fig. 3). Early nonferroan dolomite in the micritic limestone, which is widespread in the whole Chah-Talkh syncline. This dolomitization stage is not related to mineralization. The dolomite precipitated in a second stage is weakly ferroan, and is in relation with both mineralization and brecciation. This dolomite is coarse grained, very altered and later replaced by hemimorphite. This dolomitization stage occurred at the same time as primary sulfide mineralization. Last-stage ferroan coarse grained dolomite occurs along fractures and fills cavities and breccia zones. This dolomitization stage occurs togeter with nonsulfide mineralization, and is considered related to it (third stage dolomitization).

Sampling and analytical methods:

To investigate the distribution of secondary Zn- and Pb- bearing minerals, Iranian Mines & Mining Industries Development & Renovation Organization (IMIDRO) carried out fourteen drillings in the southern part of the Chah-Talkh deposit along the main veins. The mineralization is covered locally by recent alluvial sediments. The drill cores have maximum depth of 134 m (N.2 hole), and clear evidence of the presence of supergene minerals can be traced down to maximum 82 m hole N.8). From the fourteen diamond drill cores 536 samples were prepared for this study. All samples are from the nonsulfide section: in the drill cores the sulfide zone is not represented. 127 samples were collected from selected outcrops and from the carbonate host rocks on surface at Chah-Thalkh, 3 samples from the slags, and 8 samples from the veins. Ore minerals are detected by petrographic study and XRD (table 1) and EPMA analysis.

Optical microscopy (OM) and powder X-ray diffraction (XRD) were used to examine the samples. Selected thin sections of smithsonite, hemimorphite, hydrozincite and cerussite-bearing assemblages were analyzed by electron microprobe operating at the Iran Mineral Processing Research Center (IMPRC). Selected major, minor and trace elements of the Chah-Talkh ore have been measured at ALS Chemex laboratories in Vancouver, Canada with ME-ICP61a.

O and C isotopes have been measured on hydrozincites at the Cornell Isotope Laboratory (COIL, USA).

Mineralization

The main Chah-Talkh orebody contains supergene zinc minerals with some remnants of sulfides disseminated in the supergene ore. Mineralization occurs in a main vein and in two minor veins. Major vein is at least 900 m in length on the surface. This vein is situated in the upper part of k^{lm}_1 unit in the adjacent of k^{ld}_2 unit. Other veins are smaller than the major vein and have a maximum length of 65 m. Nonsulfide zinc minerals are dominated by smithsonite ($ZnCO_3$), hemimorphite [$Zn_4Si_2O_7(OH)_2{\cdot}H_2O$)] and hydrozincite [$Zn_5(CO_3)_2(OH)_6$]. Zincite [(Zn,Mn)O] , willemite and rare sweetite [$Zn(OH)_2$] also occur. Almost in all samples these minerals can occur together. Smithsonite and hydrozincite are more common in the lower dolomitic limestone (k^{ld}_1) but hemimorphite is more common in lower marly limestone (k^{lm}_1). Nonsulfide zinc minerals occur in many textures such as earthy masses, breccia cement, replacement and open space filling in fractures and karstic cavities. Hydrozincite shows a colloform texture and seems to be last phase of mineralization. Willemite is only found by XRD in one sample (64-D) from the tunnel no.6 (in k^{lm}_1 unit). Sweetite occurs as traces in sample CT-55 (in the main vein at klm1 unit). Lead occurs as cerussite ($PbCO_3$) and rare massicot (PbO): the latter is found only by XRD. Among the clay minerals montmorillonite is predominant. It was found in the K^{lm}_1 unit, but also kaolinite was detected in some samples. Iron oxides and hydroxides are very scarce in this mine; they were found with manganese minerals in weathered zones. Mean Fe value both in depth and surface samples (657 samples) is 0.42%. The main gangue minerals consist of dolomite and calcite and rarely quartz.

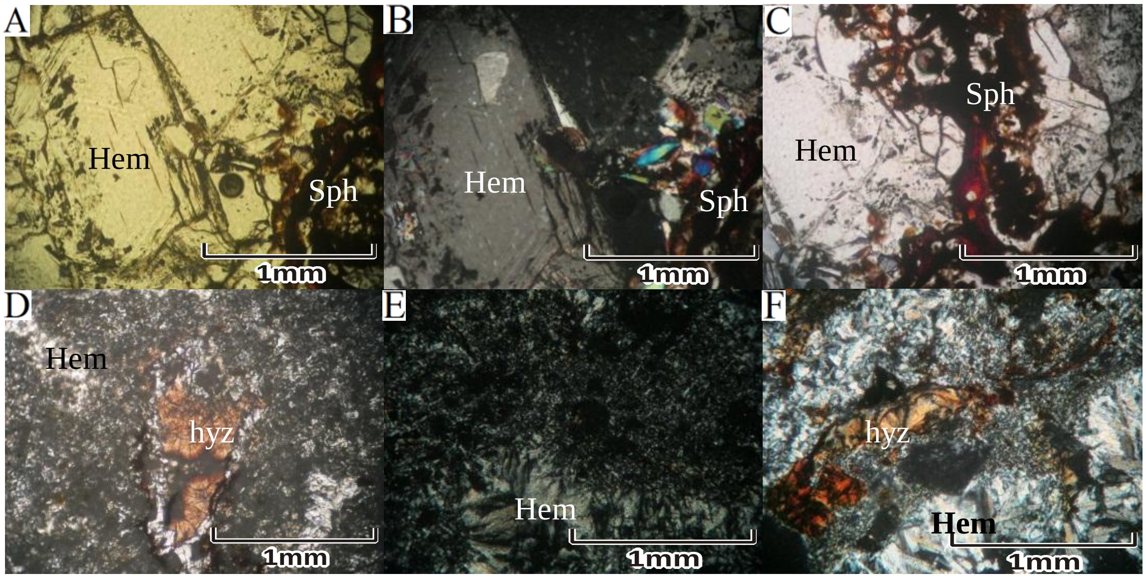


Fig.4. Microphotographs taken of Zn and Pb nonsulfide minerals from the mineralization of Chah-Talkh; A: direct replacement of sphalerite to hemimorphite (PPL); B: direct conversion of sphalerite to hemimorphite (XPL); C: residual sphalerite adjacent to hemimorphite (PPL); D: aggregates of fine radiating crystals of hydrozincite in the matrix of hemimorphite (PPL); E: aggregates of

fine radiating crystals of hemimorphite adjacent to cerussite (XPL); F: aggregates of fine radiating crystals of hydrozincite and aggregates of tabular crystals of hemimorphite replacing the carbonate host rock (PPL).

Hemimorphite

Hemimorphite is more abundant than smithsonite in many samples from the lower marly limestone (k^{lm}_1) unit. In this unit sphalerite is directly replaced by hemimorphite: in fact the sphalerite form has been kept during this process (Fig. 4). Hydrozincite replaces hemimorphite in turn. The latter mineral occurs as tabular crystals with radiating texture (under the microscope) and as massive cryptocrystalline aggregates

Smithsonite

Smithsonite is the most important supergene ore mineral in the veins in the lower dolomitic limestone (k^{ld}_1) unit; it is always found together with hydrozincite. The color of smithsonite ranges from milky white to beige. In many Samples this mineral occurs as cement of breccia clasts of micritic limestone. Other textures of smithsonite are earthy aggregates, carbonate replacements and open space filling in fractures and karstic cavities as combed veins. Smithsonite in aggregates is never completely pure and always occurs with hemimorphite and gangue minerals. In contrary smithsonite cements are more pure

Table 1
XRD qualitative analysis of the samples from the Chah-Talkh mine (S Iran)

sample	Mineral(s)	Host rock unit	sample	Mineral(s)	Host rock unit
CT-10-D	cc, qz	Klm1	**CT-83-D**	cc, qz	Kld2
CT-17-D	qz, san, mont,cc	Klm1	**CT-84-D**	cc, non,clc, qz	Klm1
CT-19-D	cc, qz, mont	Klm1	**CT-85-D**	cc, qz, clc, mos, rot	Klm1
CT-20-D	cc, hem, pir, clc	Kld1	**CT-86-D**	cc	Kld1
CT-22-D	sm, hyz	Kld1	**CT-112-D**	qz, mos, clc,cc	Kld1
CT-25-D	cc, qz, kaol	Klm1	**CT-115-D**	ce, sm, cc	Kld1
CT-42-D	cc, qz, mont	Klm1	**CT-201-D**	ce, qz, mas	Kld1
CT-55-D	sm, swe	Klm1	**CT-202-D**	hyz, sm	Kld1
CT-61-D	cc, mont	Klm1	**CT-203-D**	hyz, sm, cc	Kld1
CT-64-D	wi, hyz, cc	Klm1	**CT-204-D**	hyz, ce, qz, hem	Kld1
CT-79-D	cc, dol	Kld1	**CT-205-D**	hem, ce, hyz	Kld1
CT-81-D	cc, qz	Klm1	**CT-206-D**	hyz, sm	Kld1
CT-82-D	cc, qz, non	Klm1	**CT-207-D**	sm, ce, clc	Kld1

Mineral symbols are in order of abundance: cc calcite, ce cerussite, dol dolomite, sm smithsonite, hem hemimorphite, hyz hydrozincite, qz quartz, wi willemite, mont montmorilonite, kaol kaolinite, swe sweetit, pir pirophillite, clc clinochlore , mos moscovite, rot rotil, non nontronite, san sanidin, mas massicot.

Geochemistry

Zinc in nonsulfide ore at Chah-Talkh is present preferentially in smithsonite, hemimorphite and hydrozincite. Lead occurs in cerussite and minor massicot. Some galena and sphalerite remnants are disseminated in the matrix of nonsulfide ore. Chemical analyses of some nonsulfide minerals are shown in tables 2, 3 and 4.

The most important hole, among the 14 drilled in the Chah-Talkh mine, is the hole N. 8. In this hole the maximum amount of zinc is about 41%, found at 28 m in depth (sample BH8-15). The highest lead value is about 16% at 27 m in depth (sample BH8-14). The Ag content is below detection limit. The maximum value of As is greater than 10000 ppm in the sample BH8-14. However, in the metallographic analysis, no As minerals have been detected. The maximum Cd value is 2000 ppm in samples BH8-3 and 4 about 8 m below the surface. The Fe and Zn contents decrease with depth, while the Mn content increases with depth. The mineralized section of this drillhole goes from 8.5 m below surface 82.5 m in depth. The Zn and Pb grades at the depth of 82.5 m are 12.5% and 3% respectively. The total thickness of the ore interval is about 38 m (with more than 1% zinc). This drillhole reached a maximum depth of 119 m and did not reach the water table. The Pb/Zn ratio and the Fe content in this hole decrease with depth (Fig. 5).

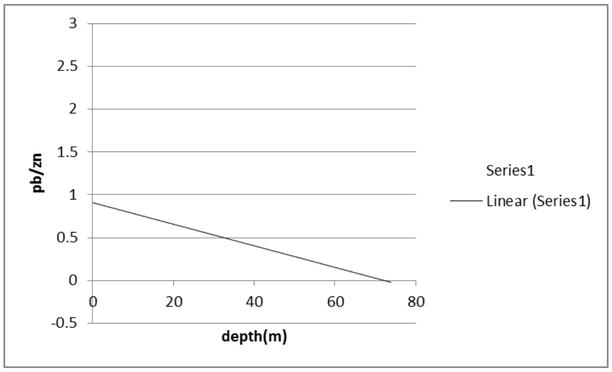


Fig.5: Inverse correspondence between Pb/Zn ratio and depth

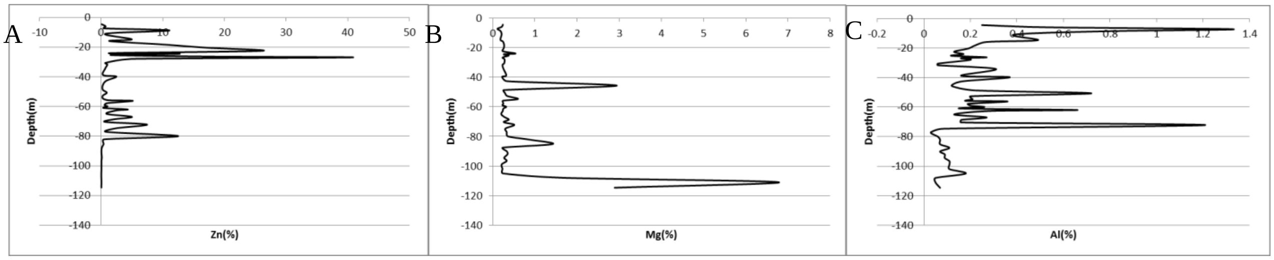
The chemical analyses of the samples from drillhole N. 8 are shown in Fig. 6.

Another interesting drillhole at Chah-Talkh is hole N. 5. In this hole the highest Zn grade is about 37% at a depth of 22 m (sample BH5-13) and the highest Pb grade is about 8% in the same sample. The maximum As value is 1339 ppm in sample BH5-16 at a depth of 24 m, and the maximum Mn value is 2393 ppm in sample BH5-18 at the depth of 27 m below the surface. The Fe, Cd and Zn contents decrease with depth.

The results of total chemical analyses (657 samples from depth and surface) show a direct correspondence between Zn and Pb contents and the Mg/Ca ratio and Al content. With the increase in Ca and Mg, the Zn, Pb and Cd values decrease (Fig.11).

The Late Cretaceous limestone equivalent of the host rock of Chah-Talkh deposit, was sampled in the north of Chah-Talkh area and analyzed. The average Zn and Pb content in the samples from this outcrop is about 11 ppm and about 5 ppm respectively. These values are lower than the general content of these elements in carbonate rocks (Zn 20 ppm and Pb 9 ppm) (Krauskopf, 1976).

An EPMA study carried out on some ore bearing samples revealed a few element maps (shown in Fig. 12, 13) and corresponding chemical analyses (Table 2, 3, 4). In these pictures zincite occurs as a cavity fills in the center of the image and around the cavity, and the host rock (dolomitic limestone) is replaced by Zn carbonates and hemimorphite. In the next stage Pb and Mn minerals replace on the margin of zincite (Fig. 12 D, F). In the other stage the host rock (dolomitic limestone) is replaced by Zn carbonates and silicates. Part of Zn carbonates in the cavity filling are replaced in the late stage by Zn carbonates and silicates similar to host rock but this replacement does not change the Pb and Zn minerals on the margin of zincite. The Zn content in the cavity is more than the wall rock. Fig. 13 shows a galena cube that is located in the Zn minerals texture. Microprobe analyses of some minerals from the Chah-Talkh mine are reported in table 2. Zn content of type1 smithsonite is about 42% but Zn content of type 2 is about 50%. Pb content of type 1 smithsonite is higher than in type 2. Ag and Mn content of type 1 and 2 smithsonite are low.



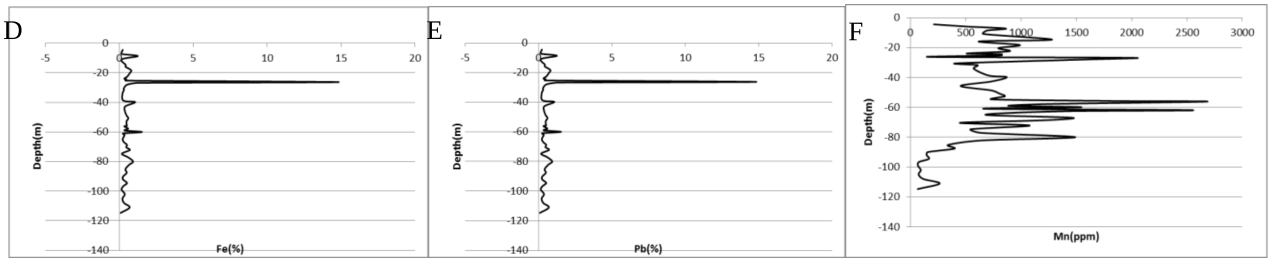


Fig.6. Variations of elements with depth in drillhole N. 8.

Table 2: Chemical analyses (EPMA) of smithsonite from the Chah-Talkh deposit.

smithsonite									
	CT-231			CT-264				CT-231	
Element (%)	Type 1			Type 1			Elements	Type 2	
Mg	0.41	0.44	0.36	0.38	0.42	0.36	Mg	0.5	1.98
Al	0.68	1.19	1.38	1.4	1.44	1.47	Ca	0.24	0.02
Si	0.07	0.07	0.07	0.08	0.08	0.1	Mn	0	0
S	0	0.1	0.1	0.15	0.18	0.13	Fe	0.04	0
Ca	0.08	0.32	0.33	0.34	0.34	0.35	Cu	2.33	0.16
Ti	0	0.33	0	0	0	0	Zn	50.58	50.03
Mn	1	0	0	0	0	0	As	0	0
Cu	1.31	0.19	0.07	0	3.44	2.33	Ag	0	0
Zn	40.09	40	42.14	40.31	42.65	40.88	Cd	0.33	0.23
Ag	0.03	0	0	0	0	0	Au	0.5	0.06
Ba	0	0.32	0	0	0	0	Pb	0.07	0.02
Pb	2.95	1.09	1.18	1.22	1.14	1.31	S	0	0.02
Total	46.62	44.07	45.62	43.9	49.68	46.94	Total	54.6	52.54

Table 3: Chemical analyses (EPMA) of hemimorphite and hydrozincite from Chah-Talkh deposit.

	hemimorphite			**Hydrozincite**						**hydrozincite**				
Element (%)	CT-231			CT-231			CT-231			CT-264				
Mg	1.64	0.24	0.52	0.38	0.38	0.61	0.58	0.52	1.51	0.8	0.72	0.61	0.62	0.59
Ca	0.02	0.58	0.03	0.01	0.02	0.02	0.02	0.08	0.06	0.09	0	0.03	0.02	0.02
Mn	1.41	0.58	0	4.5	0	0.22	0.92	5.9	0.75	0	0	0	0	0
Fe	0.07	0.09	0.13	0.17	0	0.03	0.12	0.87	0.04	0	0	0	0	0

Cu	1.92	0	0	1.25	1.07	0.01	0	0	0	0.15	0.06	0	0.15	0.29
Zn	53.97	54	54.05	61.67	59.77	61.35	56.94	56.19	56.67	64.24	63.15	62.87	60.63	60.27
Ag	0	0.01	0.03	0	0	0	0	0	0.01	0	0.03	0.02	0	0.02
Cd	0.19	0.21	0.2	0.12	0.13	0.22	0.22	0.42	0.26	0.25	0.18	0.28	0.14	0.11
Au	0.61	0.53	0.02	0.3	0.43	0.26	0.11	0	0.02	0.35	0.17	0.12	0.2	0.28
Pb	0	0.05	0.09	0.04	0.11	0.02	0	0.05	0	0.11	0.18	0.05	0.17	0.2
S	0	0.11	0.01	0	0	0.02	0.02	0	0.02	0	0	0	0	0
Total	59.84	56.4	55.08	68.44	61.91	62.74	58.94	64.02	59.35	65.99	64.5	63.98	61.93	61.77

Table 4: Chemical analyses (EPMA) of zincite from Chah-Talkh deposit.

Elements (%)	**zincite**			**Zincite**			**Zincite**			**zincite**			**zincite**		
	CT-231			CT-231			CT-231			CT-231			CT-231		
Mg	0.13	0.09	0.13	0.08	0.14	0.13	0.11	0.4	0.13	0.13	0.11	0.12	0.11	0.08	0.13
Ca	0.02	0.02	0.01	0.03	0.03	0.02	0.02	0.03	0.01	0.04	0.03	0.02	0.02	0.02	0.03
Mn	0.98	0.2	3.74	0.1	0.05	4.34	0.46	0.54	0.07	1.57	0.33	0.08	5.19	0.9	0
Fe	0.14	0.02	0.21	0.03	0.01	0.18	0	0.01	0.01	0.12	0.02	0	0.22	0.03	0
Cu	0	0	0	0.07	0.13	0.02	0.05	0	0.04	0	0.01	0.21	0	0.33	0.04
Zn	68.7	69.13	70.78	68.24	67.73	71.81	68.49	65.91	66.96	69.1	68.77	68.72	70.82	68.79	69.45
As	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ag	0	0	0.01	0	0.02	0.03	0.02	0	0	0	0.03	0.01	0.04	0.01	0.05
Cd	0	0	0.06	0.02	0.01	0	0	0.01	0	0.02	0	0	0	0	0
Au	0.15	0.27	0.3	0.25	0.23	0.25	0.24	0.24	0.25	0.15	0.22	0.28	0.33	0.36	0.29
Pb	1.45	1.54	1.39	1.49	1.47	1.28	1.45	2.27	1.4	1.19	1.5	1.44	1.19	1.44	1.47
S	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total	71.56	71.27	76.64	70.32	69.82	78.06	70.85	69.41	68.87	72.32	71.03	70.87	77.92	71.95	71.46

Zn content of hemimorphite from sample number 231 is quite close to ideal hemimorphite (which contains about 54% Zn). Au content of hemimorphite is higher than other minerals (up to 0.61%). Ca, Mg and Mn content are low. Zn content of hydrozincite from sample number 264 (about 60% to 64%) is more than sample number 231 but hydrozincite from sample number 231 shows high Mn and Fe content. Au, Cd and Ag in hydrozincites are traces. Zincite occurs as cavity and fracture fill (Fig. 12) and shows high Zn content in the range from 67 to 72 wt. %. Mn content can reach up to 5.2 wt% and Pb content can reach to 2.27% with traces of Ca, Mg, Cd and Au.

To evaluate of Zn and Pb content of Permian metamorphic units (shale and schist) that are located below the carbonate host rock in Chah-Talkh, 4 samples (CT-33, 34, 35, 36) were sampled in the nearest outcrops of these units 4 km east of ChahTalkh mine. The average Zn and Pb contentsin the metamorphic rocks are about 320 ppm and 215 ppm respectively.

Isotopic Geochemistry

The results of the carbon and oxygen isotope measurements in metallic carbonate minerals has been used to investigate the approximate temperatures and genesis of nonsulfide Zn ores (Gilg et al., 2008). Smithsonite in Chah- Talkh deposit occurs as disseminated grains intergrown with other minerals such as hydrozincite and hemimorphite: a condition that renders separation very difficult. For this reason hydrozincite, that is very similar to smithsonite in its isotopic characteristics (Boni et al. 2003), was sampled for measurement of carbon and oxygen isotopes. However, even though the published data on hydrozincites (Gilg et al., 2008) suggest that the oxygen isotope fractionation factors for this mineral and water are similar to those of smithsonite, further studies are still required.

Table 5: Carbon and Oxygen isotope data of hydrozincite samples from Chah-Talkh deposit

Sample ID	**normalized δ^{13}C vs.**	**normalized δ^{18}O vs.**

	VPDB	NSMOW
CT-2221	-7.03	9.65
CT-2261	-8.57	14.99
CT-2211	-4.91	15.15
CT-2232	-7.95	10.66
CT-2262	-8.68	7.57
CT-2233	-7.79	14.60
CT-2212	-4.88	7.80
CT-2222	-6.84	11.65
CT-2231	-9.32	14.27
CT-2213	-5.25	14.19

The results of the oxygen and carbon isotope measurements on 10 hydrozincite samples are presented in table 5. The $\delta^{18}O$ values range from 7.57 to 15.15 per mil and the $\delta^{13}C$ values between -4.88 and -9.33 per mil. This range in $\delta^{18}O$ and $\delta^{13}C$ values point to multiple sources for the fluids that had been responsible of oxidation of primary sulfide (Gilg et al. 2008). Comparing the results of the oxygen and carbon isotope measurements in Chah-Talkh to the published parameters of rocks and waters from different geological environments (Fig. 7), it can be observed that the $\delta^{18}O$ values of our hydrozincites is located in the range of detrital rocks, metamorphic rocks and metamorphic waters (Hofez, 2004). Since to locating of Chah-Talkh deposit in Sanandaj-Sirjan zone and abundance of metamorphic rocks around of this deposit (fig. 1), relation between $\delta^{18}O$ values and thus rocks and metamorphic waters is justifiable and we can suggest that metamorphic water have been effective in nonsulfide mineralization. In the other hand, high temperature can reduce $\delta^{18}O$ value too. Therefore this reducing in oxygen isotope value can be consider due to increasing temperature during formation or crystallization of hydrozincite that can uphold metamorphism source of temperature.

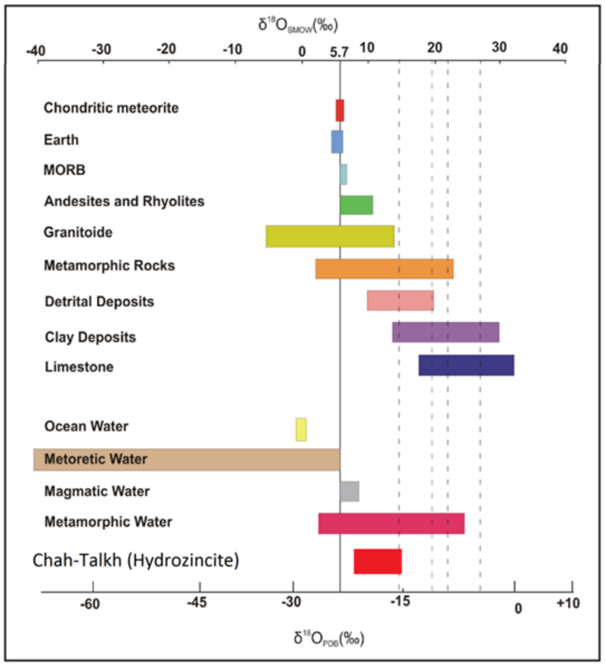


Fig 7: $\delta^{18}O$ value of Chah-Talkh hydrozincite in comparison with $\delta^{18}O$ values in different geological environments (Amiri and Rasa, 2006).

The $\delta^{13}C$ values of hydrozincite samples in Chah-Talkh range from -9.32 to -4.88 per mil and have an average value of -7.12 per mil. In fig. 8 the $\delta^{13}C$ values of Chah-Talkh are compared to $\delta^{13}C$ in different geological environments. As shown in fig. 8 $\delta^{13}C$ value of hydrozincite in Chah-Talkh fall within the range of atmospheric CO_2 and limestone that in attending to situation of deposit in carbonate rocks and near the surface, this subject is expectable. These values are comparable to the range of $\delta^{13}C$ values in Sardinia deposits.

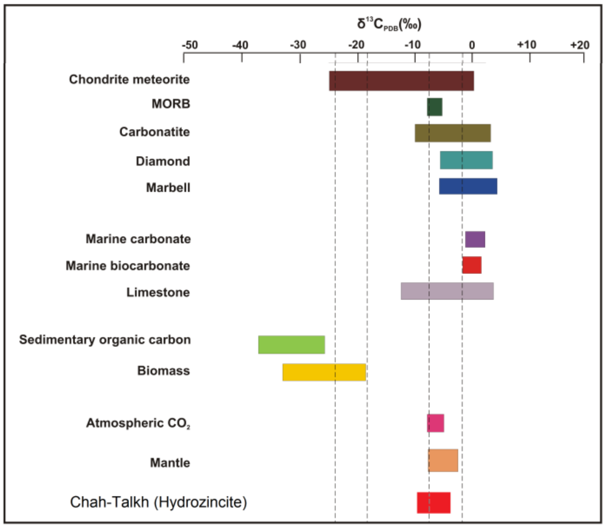


Fig 8: δ^{13}C value of Chah-Talkh hydrozincite in comparison with δ^{13}C values in different geological environments (Amiri and Rasa, 2006).

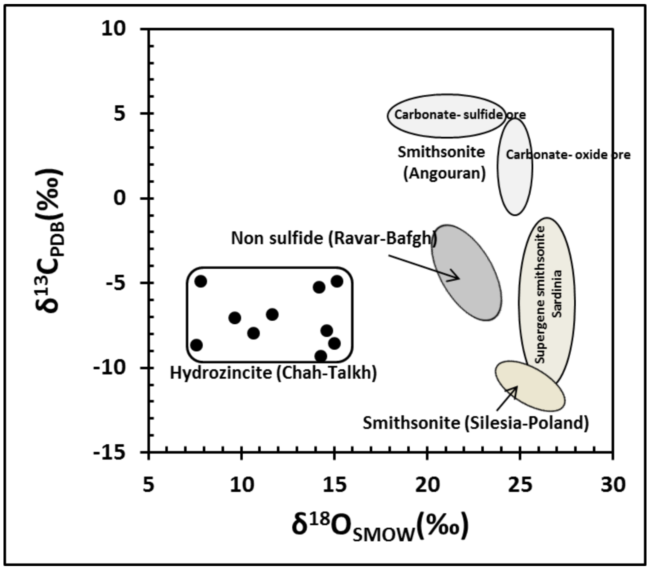


Fig.9: Stable oxygen and carbon isotope composition of hydrozincite from Chah-Talkh in compare to the values in Ravar-Bafgh area (Amiri and Rasa, 2008), Angouran, Sardinia (Gilg et al. 2003) and Silesia (Coppola et al. 2009).

In fig. 9 the oxygen and carbon isotopic values in Chah-Talkh are compared with the values in Angouran and Sardinia. As shown in fig. 10 δ^{18}O values in Chah-Talkhwere compared with different deposit across the world. If we consider that each unit per mil decrease in δ^{18}O value be indicate 4°C are increasing in formation temperature (Ghasemi et al. 2004), in attending to average of 18 per mil decreases in δ^{18}O values in Chah-Talkh toward Sardinia, this points to very lower than δ^{18}O values in Sardinia and Angouran. temperature formation of hydrozincite in Chah-Talkh is about 70°C higher than hydrozincite in Sardinia district. Therefore, attending to this hypothesis, temperature formation of hydrozincite in Chah- Talkh is about 80 to 100° C. This suggests that both meteoric water and metamorphic water have been role in oxidation of primary sulfide.

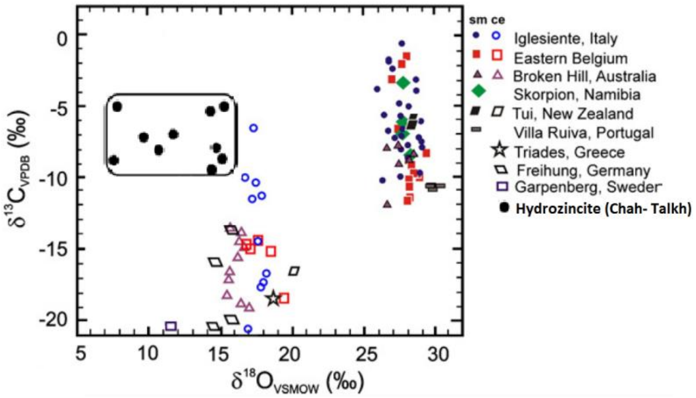


Fig.10:Carbon and oxygen isotope composition of smithsonites (sm) andcerussites (ce) from supergene oxidation zones of several Pb–Zn deposits in compre with these values in Chah-Talkh hydrozincite (Gilg et al. 2008).

Discussion

Nonsulfide Zn-Pb mineralization in Chah-Talkh deposit has many characteristic of typical supergene carbonate hosted nonsulfide Zn-Pb deposits. In this deposit there is no sulfide zone at depth and neither drillholes that recently carried out up to 134 m in depth, don't cut sulfide zone. This is notable neither drillholes don't reach to water table, too. Sulfide minerals (sphalerite, galena & pyrite) as relict fine grain occur in the matrix of nonsulfide minerals. It seems that depth of water table is a significant factor in generation of high Eh conditions and intensive weathering of entire sulfides. The arid climates and limited availability of meteoric water and deep to very deep water tables provide the best conditions for the preservation of nonsulfide deposits and protect the nonsulfide ore from subsequent dissolution (Reichert, 2007). Boni (2003) believed that many of the oxide deposits of supergene type, are located between latitudes 15° and 40° N and this may reflect particularly favorable climatic conditions conducive to formation of secondary zinc minerals. Therefore the latitude of Chah-Talkh deposit location (about 29° N) could be having a role in formation of nonsulfide mineralization.

The host rock in Chah-Talkh is dolomitic limestone and dolomitic marly limestone that distribution of ore minerals in this unites is relatively difference. The results of XRD analyses (table 1) show that main minerals in selected samples from marly limestone unit (k^{lm}_1) are calcite and clay minerals (kaolinite and montmorillonite) and main ore in this unit is hemimorphite. The main ore mineral in dolomitic limestone unit (k^{ld}_1) is hydrozincite. This suggests that probably some of SiO_2 employed in generation of hemimorphite derived from clay minerals in marly limestone units. Takahashi believed that the change in pH is the principal control on the precipitation of secondary zinc minerals from the metal bearing solution. In waters with average pH values between 7 and 8 percolating through carbonate rocks, smithsonite is the least soluble zinc mineral, followed by hydrozincite, and then by hemimorphite (Boni & Large, 2003). Therefore abundant of hemimorphite in marly limestone may be reflect of difference of pH value in these two units. Nonsulfide mineralization in Chah-Talkhhas direct correspondence with fracture zone and dolomitization of host rock and seems that this fractures act as channels for solutions.

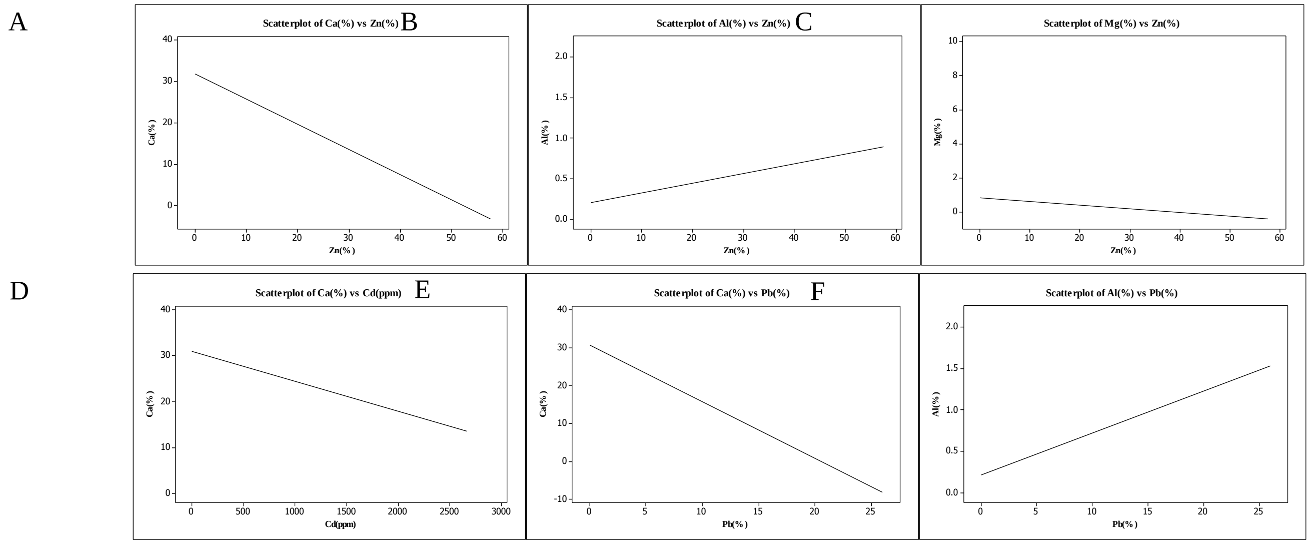


Fig. 11: Relationship between elements contents in total geochemical analyses.

In addition Zn and Pb content in total geochemical analyses (from surface and depth samples) show an inverse correlation with Ca and Mg content (Fig. 11). Balassone et al. (2007) is believed that this might be due to the replacement of dolomitic host rock first by primary and then by secondary Zn minerals. However with increases of Zn and Pb minerals in each sample (in high grade) the host rock volume (dolomitic limestone) decreases. Cd content is followed of Zn and Pb content too. There is a direct correspondence between Al and Zn content that may be due to of replacement of part of mineralization in marly limestone unite (klm1). However in many of nonsulfide Zn deposits such as Mehdi-Abad (Ghasemi et al. 2008), and Dare-Zangir (Iran) Zn mineralization (nonsulfide) have relation with shale or marly unites. Thus probably clay minerals play a role in precipitation of nonsulfide or primary sulfide Zn minerals. In Chah-Talkh deposit the main part of mineralization hosted by marly limestone, too.

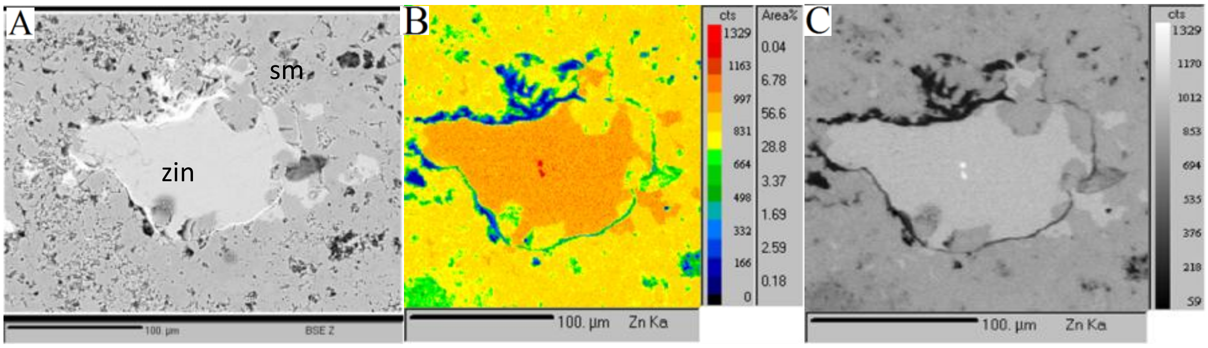
Results of chemical analyses of depth samples from drillhole number 8 (Fig.6) represent that distribution of some elements such as Mn and Mg follow of mineralization zones. Direct correspondence between Zn mineralization and Mg content is due to occurring of Zn nonsulfide minerals in dolomitization zones. In addition Fe content in Chah-Talkh is relatively lower than other Zn nonsulfide deposits. Inverse correspondence between Pb/Zn ratio and depth is due to more mobility of Zn into Pbin supergene conditions and leaching of Zn in surface toward depth of veins. Thereupon in the veins near the surface cerussite is main ore and toward depth Zn minerals increases.

EPMA map elements of zinc sample (Fig.12) indicate that before of mineralization there was some cavity in the host rock. It seems that these cavities formed due to dolomitization or dissolution of host rock. First solutions that start to precipitate their content in these cavities have been high *f*O2 (Fig. 12-B) and precipitate Zn oxide minerals (zincite) in the cavity. Precipitation of Mn oxides on the margin of zincite in the next stage of mineralization shows high *f*O2 conditions, at which Fe and Mn oxides are stable (Balassone et al., 2007). Presence of Pb together Mn in this stage is probably due to negative charge of manganese sols and absorption of Pb ions in sols (Krauskopf, 1976). Mn value of zincite is lower than of standard level (about 6% Mn) that indicate *f*O2 is high and in this condition Mn oxides are stable and Mn concentration is very low in the circulating fluids and consequently in the precipitated zincite. Production of zincite in this stage is probably due to absence of carbonate ion and lowing of *f*CO_2 in fluids. In next stage dolomitic host rock is replaced by smithsonite and hemimorphite in so far as part of zincite in cavity replaced by smithsonite but Mn and Pb minerals around of primary zincite are unchanged. Replacement of zincite by smithsonite shows that *f*CO_2 in fluids increases (due to dissolving of carbonate host rock). Fig 6 show EPMA elements map of a galena that surrounded by zinc minerals and protects primary shape of galena cube. As content in the galena is more than of Zn content. Zn content of galena is below 1% (table 6). However part of mineralization in this deposit is direct replacement type and other part is wall rock replacement type and filling karstic cavities and is comparable to nonsulfide mineralization in southwest Sardinia (Boni et al., 2003).

Table 6: Chemical analyses (EPMA) of galena crystal in Zn ores.

Elements	Galena		
S	11.39	12.63	12.24
Fe	0	0	0
Cu	0.66	0	0.73
Zn	0.95	0.5	0.81
Pb	86.86	84.96	86.45
V	0.01	0	0.01
Al	0.28	0.94	0.03
Total	100.15	99.03	100.27

Hitzman et al. (2003) believed that in absence of pyrite and marcasite doesn’t form large amounts of acidic solutions and zinc can’t migrate in long distance. Therefore weathering can’t form distal supergene wall-rock replacement deposits. In Chah-Talkh deposit in low Fe conditions (about 0.4 % Fe in total analyses) Zn minerals precipitated as direct replacement and wall-rock replacement in adjacent of primary sulfide veins.



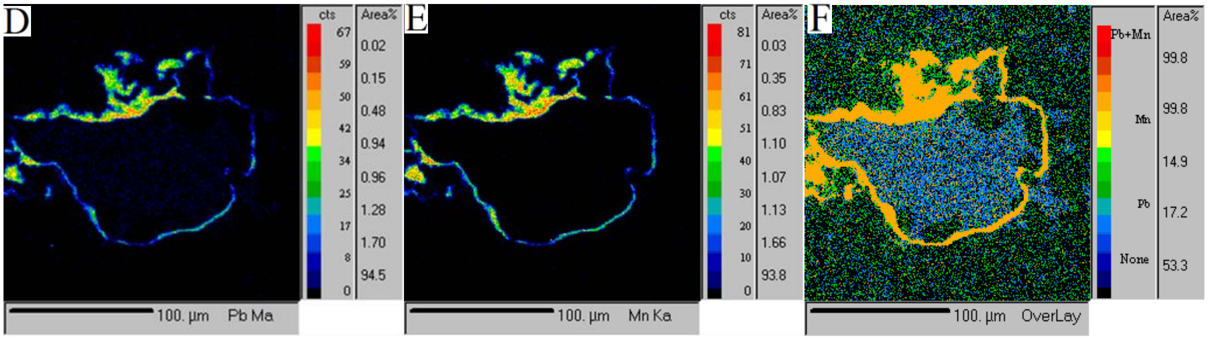


Fig. 12: EPMA element maps of ore bearing sample; A: electron microscope image (BSE) of Zn mineral; B , c: distribution of Zn in center of cavity and matrix; D, E, F: distribution of Pb and Mn in section and overlay of these elements.

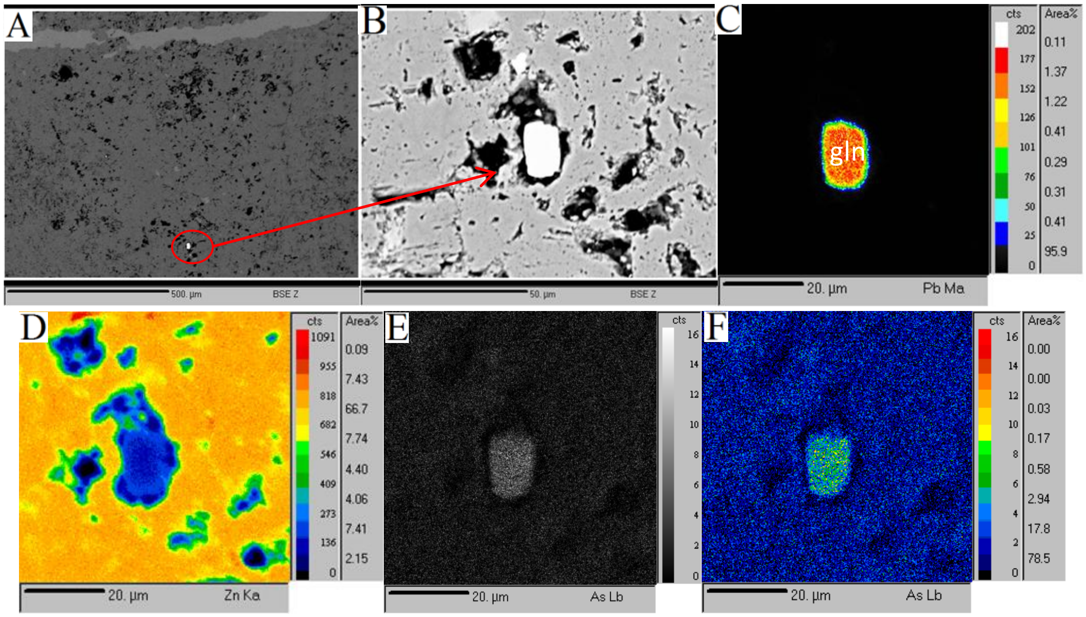


Fig.13: EPMA element maps of ore bearing sample. A, B: electron microscope image (BSE) of Pb mineral (galena);

Pb content in the smithsonite only in one sample (CT-231) is more than 2% that may indicate direct replacement of sphalerite by smithsonite (Balassone et al., 2007). Time of weathering and nonsulfide mineralization is unclear but Sanandag-Sirgan zone influence of Laramid orogeny has been out of sea in Paleocene (Agha nabati, 2004). Therefore from Paleocene to recent time have been favorite conditions for weathering of primary sulfide.

Attending to absence of igneous rocks around of Chah-Talkh deposit, two hypotheses was performed for primary source of Zn and Pb in Chah-Talkh deposit: 1- late cretaceous host rock 2- Permian shiest and shale. The results of chemical analyzes from carbonate rocks equivalent of host rock show that mean of Zn and Pb content is lower than mean of Zn and Pb content in carbonate rocks but results of analyzes of shale and shiest show enrichment of these samples from Zn and Pb. The Zn content is four orders (320 ppm) more than from mean of Zn content in shales. Attending to about 500 m thickness of metamorphic rocks (sabzehei et al.,1997) and with hypothesis of leaching of 50% of Zn content in this unit and concentration of this zinc in carbonate rocks, 4 km^2 area of shale and shiest unit (2 km^3) is enough to preparation Zn content for generation of this deposit. Therefore it seems that Permian metamorphic rocks have high potentials for Zn source in Chah-Talkh deposit but for determine of Zn and Pb sources, suggest that isotopic study of Pb must be done in this deposit.

Conclusions

The instances such as epigenetic dolomitization and brecciation of host rock and ores, morphology, texture, existing of clay minerals in host rock and simply mineralization suggest that type of primary sulfide ore probably was MVT. Concentration of nonsulfide zinc ores in Chah-Talkh is intensively reacting of locally fracturation system (NW-SE). The paragenesis of minerals in high pH and Eh condition is influence of lack or presence of clay minerals. In presence of clay minerals main ore is hemimorphite and sphalerite conversion to hemimorphite directly. In absence of clay minerals main ore are hydrozincite and smithsonite. Presence of clay minerals caused that fluids no dispersed in the host rock and precipitate their content in cavities and fracture zones. Different types of smithsonite that revealed in Sardinia and Irish deposits, don’t recognize in Chah-Talkh deposit. Zn and Pb content show an inverse correlation with Ca and Mg. This might be due to the replacement of dolomitic host rock first by primary and then by secondary Zn minerals. Zn and Pb content show direct correlation with Al content that is due to deposition of ore in marly limestone.

The results of EPMA analyses on ore bearing zones suggest that in first stage of weathering, Zn oxides (zincite) deposit in center of cavities in high fO_2 conditions. In next stage Pb and Mn bearing solutions beginning to precipitation of their content on the margin of zincite. In the last stage fCO_2 begin to increase and host rock and part of previously Zn oxides replaced by Zn carbonates (smithsonite). This subject suggests that at first, weathering begin influence of meteoric water (increase in fO_2 value) and in continue metamorphic water play effective role in weathering (increase in fCO_2 value). The absence of sulfide zone into depth 134 m below surface is due to high altitude of deposit relation to around area, deeping of water table, arid climate in this area, situation at suitable latitude and circulation of metamorphic water. It seems that the source of Zn and Pb is Permian shale and shiest unites.

The results of oxygen and carbon measurements on hydrozincite samples indicate that the range of $\delta^{18}O$ value in Chah-Talkh is large spread (7.58 per mil) that is owing to mixing of at least two waters in forming of Zn carbonates. In addition the average of $\delta^{18}O$ value in Chah-Talkh is □ 12 per mil that is very lower than $\delta^{18}O$ value in other nonsulfide Zn deposits (□ 27 per mil). This value suggests that ore forming temperature of oxide ores in Chah-Talkh is very higher than other deposits. This point combined with situation of $\delta^{18}O$ value in the range of metamorphic water, confirm that both metamorphic and meteoric water act as fluids responsible of weathering. Situation of Chah-Talkh in arid climate indicate that there is not favorable condition for deep weathering just by supergene processes, which confirm the effect of metamorphism water in weathering of primary sulfides.

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