MINERALOGY, GEOCHEMISTRY AND ORIGIN OF ZINC-LEAD-BARITE DEPOSITS IN NORTHERN THRUST ZONE, NORTHERN IRAQ

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Abstract

Four areas contain zinc - lead - barite deposits hosted by Cretaceous carbonate rocks are studied mineralogically, geochemically and genetically. These areas are Lefan, Lower Banik, Menin and Upper Banik, which are located northeast of Zakho city within Northern Thrust Zone, Northern Iraq.

The deposits occur as small veins, scattered patches to disseminated ore, characterized by simple mineralogy consists of sphalerite, galena, little quantity of pyrite as primary sulfides and barite as primary sulfate. Most of sulfides are altered to their secondary minerals by supergene solutions.

Paragenetic sequence of mineralization shows early and late sulfides generation deposited from hypogene solutions, and reveals reduction-oxidation potential fluctuation through nine stages of mineralization. The early generation of sulfides (sphalerite and galena) is characterized by replacement textures and high content of minor elements, while the late generation of sulfides is characterized by open space filling textures, and low content of minor elements.

Geochemistry of bulk ore revealed the average ore grade up to 44.4% ZnO, and 4.1% PbO in Lefan, 27.4% ZnO, and 2.7% PbO in Lower Banik, 9.1% ZnO and 1.2 PbO in Menin, 1.9% ZnO and 20 ppm of Pb in Upper Banik.

Fluid inclusions observed in barite contain heavy oil associated aqueous chloriderich fluids (13% - 15.5% wt equv. NaCl). Formation temperature of barite is suggested to be 50-60 °C.

The sulfur isotope composition (δ^{34} S) of early generation galena is 0.36 per mil. This value is close to the hydrothermal magmatic sulfur origin, but the sulfur isotope compositions (δ^{34} S) of late generation galena is 6.41 per mil. This value indicates that the hydrothermal magmatic fluids were partially mixed with oilfield brine connate waters. The sulfur isotope composition (δ^{34} S) of barite ranges from 16.64 to 24.23 per mil indicating high isotopic fractionation caused by descending meteoric waters which diluted the ascending ore-bearing fluids. This case led to precipitation of barite in oxidizing conditions. The Lead isotope compositions (204 Pb, 206 Pb, 207 Pb and 208 Pb) of galena revealed that lead was derived from the crust reservoir.

The elements (Zn, Pb, Fe, and Ba) may have originated from oilfield brine waters which may have partially mixed with hydrothermal fluids of magmatic origin supplying sulfur. These fluids may have been migrated upward as chloride and sulfide complexes along fractures and faults that they formed after crustal extension and rifting which took place by the effect of the Laramide Orogeny in the Upper Maastrichtian .

The studied zinc-lead-barite deposits could be classified as epithermal, epigenetic strata-bound of Mississippi valley type (MVT) deposits, lithologically and structurally controlled within Cretaceous carbonate host rocks.

Introduction

Several zinc – lead deposits have been reported in Iraq from the Northern Thrust Zone.

All of these deposits are hosted by sedimentary carbonate rocks of Permian – Cretaceous age. Although these deposits are known, but no mine

currently in operation. In this paper, four occurrences of zinc – lead – barite deposits (Lefan, Lower Banik, Menin and Upper Banik), about 25 km NE Zakho are studied (Figure-1). No detail previous work have been done, but some previous works on pyrite - lead – zinc deposits of Serguza have been carried out by[1,2,3];. All these works suggested the ore deposits to be epigenetic and concluded that the mineralizing fluids are hydrothermal solutions that were migrated upward from deep source, except [3] who concluded that the Serguza deposit is syngenetic stratigraphically controlled within the Triassic dolomite based on trace elements content in the ore minerals, dating of galena, and textures of country rocks. The aims of this paper are to describe the mineralogy and geochemistry of the ore deposits, in order to provide a model explains the source and ore genesis. Also via this paper we document the ore deposits by determination of their locations and extension on geological map, in addition to description of a new discovery of barite in Upper Banik locality.



Figure (1): Geological map of the area north – east of Zakho showing the studied areas, L= Lefan, BS=Lower Banik, BU= Upper Banik, M= Menin

Legend:

0= Basic Igneous Intrusion. 1 = Ore Shale Formation (L. Carboniferous). 2=Chia Zairi Limestone Formation (U.Permian).

3= Serwan Formation (Triassic). 4= Kurra Chine dolomite Formation (U.Triassic). 5= Sekanian dolomite. Sarki dolomite (L.Jurassic)
 6= Chia Gara, Barsarin, Neokelekan & Sargelu Formation (U & M Jurassic). 7= Sarmord Formation (L.Cretaceous). 8= Qamchuqa Formation (M.Cretaceous). 9= Bekhme limestone formation (U.Cretaceous). 10= Shiranish Formation (U.Cretacous). 11= Kolosh Clastic Formation (Paleocene). 12=Gercus Formation (L. Eocene). 13= Pele Spi Limestone Formation (U&M Eocene). 14= Anah Limestone Formation. 15= Injanh Formation (U.Miocene). 16= Bi Hassan Formation (Pliocene- pleistocene). /= fault

Geological setting

The oldest outcrop in the studied areas is the lower part of the Sarmord Formation (Hauterivian – Baremian) which comprises the neritic to deep water facies. The Qamchuqa Formation overlies Sarmord Formation and seems nonmineralized. Aqra – Bekhme Formation (U. Campanian – U. Maastrichtian) overlies Qamchuqa Formation and mainly consists of dolomitic limestone deposited in a reef environment between geosyncline and shelf area. Aqra – Bekhma Formation is conformably covered by deep basinal facies of Shiranish Formation which mainly consists of limestone. Shiranish Formation is the youngest formation in the Mesozoic [4], thus it appears on the top of the stratigraphic sequence. The upper surface of the Shiranish Formation seems erosional and unconformity separatal between U. Cretaceous and Tertiary. The zinc – lead – barite deposits in Lefan and Lower Banik mainly exist within Aqra – Bekhme Formation and partially within Shiranish Formation, while they occur within lower part of the Sarmord Formation in the Menin and Upper Banik. All ores are within Northern Thrust Zone in the northern margin of the passive Arabian Plate (Figure-2) The Arabian Plate collided with the southern active margin of the Anatolian Plate during Laramide Orogeny in the Upper Cretaceous. The sediments in geosyncline formed thrust sheets that have been stacked and folded as a result of the convergent movement and collision of these plates [5].



Figure (2): Geotectonic map of the Middle East (after Hempton, 1987).

Ore mineralogy

The ore mineralogy is relatively simple, domenanted by sphalerite and galena with very little quantity of subordinate pyrite. The common translucent minerals are barite and siderite. A few rhombic crystals of fluorite were distinguished in Lower Banik only. In thin sections, sulfides appear as cement material reacted with the boundary of the carbonate grains and filling porous space especially around dolomite grains. Replacement of carbonate by sulfides and barite is evident in hand samples. Sulfide textures provide more convincing evidence for replacement of carbonate. Sulfides replaced fossils such as rudist that are common in reef facies of Aqra - Bekhme Formation in Lefan and Lower Banik. The sulfides and barite have ability to replace carbonate [6]. Sulfides and barite textures suggest that the sulfides and barite replaced dolomite rather than calcite.

The optical properties and textural relationships revealed two generations of sphalerite (Figures 3 and 4). The crystals of early generation grew as dark brown in coarse grained aggregates, that they have high reflectance and deep red color of internal reflections in comparison with the late generation which is characterized by low

reflectance and mostly brown to yellow color of internal reflection. Also this generation commonly contains randomly dispersed inclusions of pyrite. Darker sphalerite colors generally indicate higher iron content [7]. The late generation sphalerite grew as pale brown fine grains deposted along cleavage cracks of barite. Three generations of galena are also identified. The second generation appears to be restrictive phase existed at Lefan only, thus this generation considered unimportant and negligted. The early generation galena is composed of coarse grains occur as anhedral masses to euhedral cubes which mostly replaced the early generation sphalerite along cleavage planes forming crystallographic control replacement which may have been later developed to the island shape texture (Figure-5). The late generation galena consists of fine grained aggregates deposited along cleavage cracks of barite (Figure-6) closely associated with the late generation sphalerite. Generally the early generations of both sphalerite and galena formed replacement textures, while the late generation mostly formed open space filling textures. Pyrite exists as fine grained anhedral to euhedral cubes. Some of the fractured grains display anisotropy. Early generations of sulfides contain textural evidence of deformation. Cataclastic texture in sphalerite and pyrite, slight anomalous isotropy in pyrite and curvature of triangle cleavage pits in galena, folding in barite give convincing evidences that the early generation was more affected by tectonic movement than late generation. Rose like shape is found in barite. This texture indicates low temperature [8 and 9]. The supergene solutions like meteoric waters, played role especially on the brecciated sulfides. Supergene alterations could be seen throughout the oxidized zone near the surface, in which moderate and extensive alteration of primary ores occur. Both partial and complete replacements are observed along grain boundaries and internal channel ways such as cleavage and fracture planes. Sphalerite is replaced by smithsonite, Galena is replaced by cerussite and anglesite, and pyrite is replaced by goethite.

Figure (3): Early generation sphalerite (light gray) shows fractured grains cemented by barite, under reflected light (-), 200X.

Figure(4): Late generation sphalerite (light gray) along folded cracks of cleavage plane of barite, under reflected light (-), 100X.

Figure(5): Early generation galena (white) replacing early generation sphalerite (gray), reflected light (-), 50X.

Figure (6): Late generation galena (white) in the cleavage cracks of barite (gray), reflected light Light (-), 200X.

Mineralization and paragenetic sequence

The ore deposits at the study areas exhibit both lithological and structural controls. The ore occurrences are coarsely crystalline aggregates along extensional fractures, irregular anhedral masses, interstitial preexisting voids, veinlets, veins and disseminated sulfides deposits are the common types of the ore in the studied areas. The main ore deposits occur at Lefan and Lower Banik, while they are less at Menin and Upper Banik. Generally sphalerite is the most abundant mineral in the primary ore. These ore deposits are hosted by folded dolomitic limestone of lower part of Sarmord Formation and of Agra -Bekhme Formation. The primary ore minerals consist of sphalerite, galena and little amount of pyrite. Barite and siderite are the abundant gangue minerals. Barite is mostly associated with the ore minerals, but sometime it presents as individual mineral especially in the Upper Banik where barite prevails. The sulfides and sulfates have been affected by tectonic deformation, since then and later they cut by secondary calcite veinlets.

Microtextures and microstractures linked with the field observations were used to carefully analyse and decide the order of mineral deposits. The systematic relative chronological order of the minerals of the zinc – lead – barite deposits revealed two generations of sphalerite, three generations of galena, and four generations of Ore minerals exhibit complex barite. paragenesis in which multiple episodes of deposition, oxidation and replacement are evident. The depositional alternation of the sulfide minerals (sphalerite, galena, and pyrite) with the sulfate (barite) actually reflects fluctuation of the reduction-oxidation potential through nine stages of mineralization (Figure-7) as follow:

- 1- First stage: First generation barite deposited as veins within highly calcareous dolomite of the lower part of Sarmord Formation at Upper Banik.
- 2- Second stage: Very little quantity of fine grained pyrite deposted as scattered grain within carbonate host rocks. Some of this pyrite occurs as inclusions in the sphalerite.
- 3- Third stage: This stage is represented by the early generation of sphalerite which is characterized by coarse grains and dark brown to black color. This generation exists at all study areas, but it is mostly abundant at Lefan and Lower Banik.

- 4- Fourth stage: Coarse grained aggregates of galena deposited in Lefan, Lower Banik and Menin clearly represent this stage of mineralization. Galena replaces early sphalerite grains along their cleavage planes forming islands shape like texture. This stage of mineralization is considered as the first generation of galena. Barite, pyrite, sphalerite and galena in all stages from first stage to fourth stage are deformed and brecciated.
- 5- Fifth stage: This stage is represented by the brown barite which contains mumerous tiny angular fragments of early generation sphalerite. This barite is considered as a second generation barite. This generation was accomplished by the white barite which is considered as the third generation. It has platy grains cemented brecciated grains of the early generation sphalerite.
- 6- Sixth stage: A very little quantity of small grains of galena intruded in between early generation sphalerite and third generation barite. This is considered as a second generation of galena. Because of the limited and restrictive distribution of this generation, which occurs at Lefan only, it condidered as an unimportant phase.
- 7- Seventh stage: columnar bands of white barite crosscut the second and third generations barite represent the fourth generation. This type mostly exists at Lefan and Lower banik.
- 8- Eighth stage: In this stage the sphalerite exists again but as disseminated grains of light brown color scatted along cleavage cracks of barite. This type seems to be a late generation sphalerite which mostly exists at Lefan and Lower Banik.
- 9- Ninth stage: Galena repeated itself again in different feature. This stage displays fine grains of galena deposited along cleavage cracks of barite in association with the late generation sphalerite.

	mineralization stages					ė.				
minerals& events	1	2	3	4	5	6	7	8	9	10
	oxidation	idation reduction		oxidation		reduction				
barite	1	- 3	x 1	_	2.3		4			
pyrite	1 2 A		1	1. 20 K					1	
sphalerite			1	1000	· · · ·			2		
galena	1. 1. 1. 1.			1		2	1.14		3	
brecciation					1 1				1.1	
secondary calcite									_	
time						المحمد المحمد الم		-		

Figure(7): Paragenetic sequence of minerals.

Host rocks and their alteration

Host rocks are typical dolomitic limestons dominanted by medium to coarse grained calcite and dolomite. These carbonate rocks were developed in a sedimentary basin located on the northern passive margin of the Arabian Plate. In comparison with time of mineralization, the carbonate country rocks have undergone the following changes:

1- Premineralization changes: Many favorable premineralization changes made carbonate country rocks more receptive to the ore bearing fluids. The dolomitization is the most abundant chemical change took place in the limestone. The dolomitized limestones are generally more permeable than undolomitized ones [10]

Simple recrysatallization and restricted silisification also participated in increasing permeability, because such these the changes make the country rocks more responsive for deformation. Because the ores are epigenetic and they formed later than the country rocks, therefore all these changes are considered essential factors of ground preparation. The dolomitization, recrystalization, silicification and fractures formed the secondary or superimposed permeability. In addition, the reef limestone of Agra - Bekhme Formation had also guided ore localization due to their structural features that influenced porosity and permeability. Such permeability is considered primary or intrinsic as permeability.

2- Symmineralization changes: These alterations resulted from direct mineralization processes and are marked by recrystalization of the dolomite grains and sideritization. Dolomite grains lying close and in contact with the invading fluids seem to be larger than those lying far away. This means that the alteration was restricted to the vicinity of the veins and did not extend more than a few centimeters into the wall rocks. The typical hydrothermal alteration may extend a few kilometers wide [11]. sphalerite may have been Iron-rich dissolved and repricipitated releasing Fe ions to the solution which reacted with CO_3 forming siderite. The silicification processes resulted from mineralizing fluids is not clear and it is locally restricted to Menin and Upper Banik.

Geochemistry of bulk ore

The highest contents of ZnO and PbO are found in Lefan (44.4%, 4.1%) respectively. These contents decrease toward Lower Banik (27.4%, 2.7%), Menin (9.1%, 1.2%) and Upper Banik (1.9%, 0.002 ppm) respectively. The deficiency of the base metals toward Upper Banik may due to depletion of the base metals in solution during mineralization. Obviously these deposits are rich in iron which is a minor element in sphalerite and a major constituent in siderite. The BaO content in Upper Banik (47.5%) appears to be the highest content in the study areas (Table-1). The CaO and MgO contents represent remnant dolomitic limestone hosting the ores. The bulk ores are deficient in K_2O and Na_2O .

Generally, the positive correlation between base metals and trace elements should be noted. The

Cd, Fe and Mn have clear positive correlation with Zn, while Ag is correlated with Pb. These relations indicate that elements such as Cd, Fe and Mn are present in sphalerite, but Ag is present in galena. In general The Co content is less or more than Ni in pyrite of sedimentary and of some hydrothermal origin, but many hydrothermal pyrite contains higher Co (Fiesher, 1955). The Co contents in the bulk ore are more than that of Ni at Lefan , Lower Banik and Upper Banik, while they are less at Menin (Table-1). Zinc, Pb and Fe are plotted on the ternary diagram illustrated in Figure-8. Samples appear to have occupied the Mississippi Valley Type (MVT) field approximately [12].

The distribution of samples in the triangle seems similar in Lefan, Lower Banik and Menin (Figures 8 a, b and c respectively), but it differs from Upper Banik (Figure-8d), this difference may be attributed to the depletion of lead in the mineralizing fluid in Upper Banik. According to the similarity of major and trace elements behavior, the studied deposits are considered to have same source.

oxides (%) and	Lefan	Lower Banik	Menin	Upper Banik	
trace elements	elements (21 samples) (15 samples)		(17 samples)	(20 samples)	
(ppm)					
Fe ₂ O ₃ (ranges)	3.32-18.0	1.05-20.12	0.51-5.61	0.09-3.35	
(averages)	8.3	10.6	2.8	1.3	
CaO	1.26-30.6	10.88-29.71	20.59-38.0	0.33-20.11	
	5.2	19.9	29.4	9.3	
MgO	0.06-3.2	1.91-6.83	12.2-20.91	0.01-6.73	
	1.0	4.0	14	2.58	
ZnO	20.15-53.21	18.02-39.1	1.99-16.62	0.25-3.95	
	44.4	27.4	9.1	1.9	
PbO	1.99-7.64	0.09-4.6	0.03-2.97	0.001-0.02	
	4.1	2.7	1.2	0.002	
BaO	0.33-25	0.001-3.11		35-65	
	4.1	1.0		47.5	
K ₂ O	0.001-0.03	0.71-0.005	1.91-0.02	0.22-0.003	
•	0.01	0.1	0.82	0.03	
Na ₂ O	0.001-0.05	0.002-0.09	0.002-0.06	0.001-0.2	
	0.01	0.01	0.02	0.05	
L.O.I	25.5-35	23.0-35.35	34.3-42.5	31.7-38.0	
	31.1	30.6	38.1	34.9	
I.R	0.4-2.6	1.02-3.33	1.09-3.51	0.4-3.0	
	1.4	2.3	2.4	1.7	
Ag	110-452	10-39	10	10	
0	323	22			
Cd	320-1100	366-880	35-820	10-115	
	831	579	222	71	
Ni	15-120	10-39	10-300	10-29	
	68	19	39	11	
Cr	33-100	63-170	10-130	10-120	
	59	99	70	52	
Cu	80-198	190-780	75-200	10-39	
	144	458	122	21	
Mn	120-850	205-760	35-210	20-150	
	360	385	125	78	
Co	60-175	30-105	10-35	10-30	
(1979)	111	72	23	15	

Table (1): Ranges and averages of major and trace	
elements in bulk ore at the study areas.	

----: not analysed

L.O.I: Loss on ignition at 1000°C.

I.R: Insoluble Residue in Aqua Regia

Figure (8): Pb-Fe-Zn ternary diagram of the zinc – lead - barite deposits in Lefan (a), Lower Banik (b), Menin (c) and Upper Banik (d).

Geochemistry of sulfides

Major and some trace elements of both generations of sphalerite and galena were analysed in almost pure hand picked minerals by atomic absorption technique. In the early generation sphalerite, the Fe ranges from 6.0 to 10.7%, Cd ranges from 236 to 2800 ppm and Mn ranges from 115 to 510 ppm, while in the late generation they appear low and range (2.1-2.3%), (120-215 ppm) and (80-125 ppm) respectively (Table-2). The high content of minor and trace elements in the sphalerite may reflect the nature of the original fluid from which the sphalerite was formed.

The Ag content in early generation galena varies from 200 ppm to 1260 ppm. It is relatively higher than its content in the late generation that ranges from less than 5 to 90 ppm. The high Zn and Fe content in the early generation galena are due to the contamination by the remnants of the early generation of sphalerite during hand picking process. The content of the minor and trace elements in minerals has been suggested as a generally applicable geothermometry [13].

The high content of Fe, Cd and Mn in early generation sphalerite and high content of Ag in early generation galena indicate that the first generation phase is relatively of higher temperature than the later generation.

There are positive correlations between Fe content and dark color in sphalerite. Darker sphalerite colors generally indicate higher iron content, but this correlation is by no means consistent and is especially unreliable if iron contents are below 5% (Craig and Vaughan, 1981). The low content of Cu in sphalerite is consistent with the ore petrography and confirms no chalcopyrite inclusions in sphalerite.

Generation	Area	Zn%	Fe%	Cd	Mn	Cu	S%
				ppm	ppm	ppm	
Early	Lefan	59.3	6.0	236	115	<5	32.5
Early	Lefan	54.0	10.7	2800	470	50	32.6
Early	Lower Banik	54.7	9.8	2450	510	10	32.3
Late	Lefan	63.3	2.3	120	80	25	32.3
Late	Lower Banic	62.6	2.1	215	125	<5	31.8

 Table (2): Concentration of major, minor and some trace elements in sphalerite.

Generation	Area	Pb%	Ag ppm	Ni ppm	Zn ppm	Fe ppm	S%
Early	Lefan	84.9	1260	68	3100	360	13.2
Early	Lower Banik	84.5	200	55	2900	210	13.0
Late	Lefan	83.9	<5	<10	n.a	>10	12.9
Late	Lower Banik	83.7	90	<10	900	129	12.9

Table (3): Concentration of major and some trace elements in galena.

Fluid inclusions

Fluid inclusions were studied in two paragenetic stages of barite in ordrer to characterize the origin of the mineralizing fluids. These barite samples were selected for microthermometry (Table-4) which was carried out at the University of London. The liquid phase of inclusions consists of oil with water rim and sometime specks of asphaltene are present. The vapor bubbles suggested oil was giving off gas as heterogenous trapping. The oil inclusions contain variable density by which the oil is considered heavy to very heavy oil (Table-4). The salinity of liquid phase was estimated to range from 13 to 15.5 wt% equiv. NaCl. The formation temperature of barite is estimated as very low temperature of about 50 to 60 °C. The presence of oil and brine aqueous solutions as primary inclusions evidently refers to the oilfield brine connate water as the important source of the mineralizing fluids.

Table-4: Results of the fluid inclusions analyses in barite.

Generation	Fluid inclusions	°API gravity	Salinity Wt%	Formation
× +			equev. NaCl	temperature °C
1 st generation	Oil and water	5-19	13.0	50-60
2 nd generation	Oil and water	11-20	15.5	50-60

Lead and sulfur isotopes

Lead isotopes in galena and sulfur isotopes in galena and barite were carried out on optically pure minerals separated from the ores. The analyses were carried out at the Czech Geological Survey in Prague. The lead isotopes ratios in both generations of galena are relatively homogenous (Table-5). This may indicate that lead was derived from same source in both generations [14 and 15]. The two stages method has been applied to obtain the model ages. The results show that the early generation galena has 120 Ma., while the late generation has 30 Ma. In both early and late generation of galena, δ^{34} S values range from +0.36‰ to +6.41‰ (Table-6). The sulfur isotopes values of sulfides around zero per mil have been interpreted by Spiro and Puig [16] as indication of magmatic source. The value +0.36‰ indicates hydrothermal solution of magmatic origin, while the value +6.41‰ indicates either different source or different mechanism affecting the sulfur species of magmatic source. However the sulfur isotopes value in early generation indicates magmatic origin, but in the late generation it indicates isotopic fractionation caused by partial mixing

between hydrothermal solutions and oilfield brine connate water.

In barite, δ^{34} S values ranges from +16.64‰ to + 24.23‰ (Table-6). These values appear slightly higher than those values of Upper Carboniferous and Permian sulfates published by Nielson[17] and may suggest that sulfur in barite was derived from connate waters diluted by descended meteoric water. Data of sulfur isotopes are concordant with those of marine syngenetic origin, but the field occurrence features of barite and the fluid inclusions results led us to suggest the barite forming solution derived from oilfield brine connate water. The high δ^{34} S values in barite are attributed to the isotopic fractionation between connate water (original trapped sea water) with adjacent rocks and meteoric water for long time.

Lead isotopes	Early generation	Late generation
²⁰⁶ Pb/ ²⁰⁴ Pb	18.625 ± 0.089	18.535 ± 0.062
²⁰⁷ Pb/ ²⁰⁶ Pb	0.8406 ± 0.0024	0.08405 ± 0.002
²⁰⁸ Pb/ ²⁰⁶ Pb	2.0855 ± 0.0055	2.0861 ± 0.0063
²⁰⁷ Pb/ ²⁰⁴ Pb	15.6568	15.5786
²⁰⁸ Pb/ ²⁰⁴ Pb	38.8424	38.6658
Age	120 Ma.	30 Ma.

 Table (5): Lead isotopes composition in galena.

Table (6): Sulfur isotopes composition in galena and barite.

Mineral	generation	δ ³⁴ S‰ CDT
galena	Early generation	0.36
galena	Late generation	6.41
barite	1 st generation	16.64
barite	2 nd generation	24.23

Discussion and conclusions

The origin of lead – zinc – barite occurring in sedimentary and not associated with magmatic activities still remains a problem. Objective criteria are needed to solve it. Some of these criteria are lead isotope, sulfur isotope and fluid inclusions. In order to introduce a discussion on the ore genesis, all the resulted data from the field work, mineralogy and geochemistry are used for concluding ore genesis model.

Source of fluids

The aqueous solutions beside hydrocarbons as constituents of fluid inclusions, the salinity13 -15.5 wt% equiv. NaCl, the gravity 5 -20° API, and the very low temperature of barite formation (50 -60°C) refer to oilfield brine connate water participated as a major source of mineralizing fluids. The homogeny of lead isotopes ratios obviously suggested that lead was derived from single source. The oilfield brine waters are clearly potential Zn, Pb, and Ba forming solutions[18 and 19]. The sulfur isotope values around 0 per mil have been interpreted by [16 and 20] to indicate a magmatic source of the sulfur. Depending on the sulfur isotopes composition in galena, the δ^{34} S value (+0.36‰ CDT) suggests magmatic origin, but the variation in the other sample of galena (+6.41‰ CDT) led us to suggest magmatic fluids and oilfield brine water were partially mixed. In barite the +16.64‰ CDT to + 24.23‰ CDT values are close but higher than those in the Upper Carboniferous and Permian sea water[17]. The Lower Cretaceous seawater sulfate values are around 16 per mil [21]. These values of δ^{34} S in barite have been interpreted by Grandia [22] as consistent with mixing of a metal rich brine

with small amount of ³²S enriched sulfur and a sulfur-rich fluid with $\delta^{34}S$ close to the marine sulfate of Upper Cretaceous and Lower Paleocene age. However, this case is not necessary to suggest a syngenetic marine origin barite, because field observations of barite provided deposits to be epigenetic and they never coeval sea water. The relative high values of $\delta^{34}S$ in barite ascribe to the isotopic fractionation that happened between mineralizing fluids and each of adjacent rocks meteoric waters that diluted and the mineralizing fluids. The dilution processes by meteoric water oxidized further reduced sulfur. According to above, the base metals (Zn and Pb) and Ba were driven from oilfield brine connate water, while the sulfur isotopes variation between galena and barite can best be explained by the mixing of two sulfur reservoirs with different isotopic composition. The increase of trace elements concentration in the early generations of both sphalerite and galena relative to the late generations do not mean they came from different sources, but this fluctuation may reflect the depletion of the trace elements in the remnant mineralizing fluids consequent to their precipitation during early mineralization

Mechanism of fluid movement

movement and of The ascent the mineralizing fluids require a reasonable driving force. This force may coeval with the Laramide Orogeny which is possibly linked to the plate margin tectonic, therefore it is reasonable to conclude that the rifting took place during a time span of the Upper Cretaceous. The absolute age of early generation galena is close to the time at which the Laramide Orogeny started. The emplacement of the deep water facies of Shiranish formation over shallow water facies of Agra - Bekhme Formation and east - west trend of ores extend provide reliable evidence of crustal extension and rifting they happening. The bending of the north margin of the Arabian Plate beneath the Anatolian Plate during subduction produced two types of forces. Extension force in the upper part of the plate and compression force in the lower part of the plate. The extension axis is perpendicular, while the displacement axis is parallel to the plate motion. The Arabian Plate moved relatively due north with slightly anti clockwise direction, therefore east - west trend of the ores distribution was found preferred. The ore carrying fluids were moved and migrated upward and up dip as chloride and sulfides complexes. The chloride

complexes are good media for transporting Zn and Pb [23]. Then sphalerite, galena and pyrite were naturally precipitated under reduced conditions. The descending meteoric water may have diluted the ascending mineralizing fluids.

This dilution added oxygen to the fluids, from then barite precipitated. The ability and oxidation state of sulfur are obviously important factors for determining whether or not sedimentary brines could be a potential barite forming solutions. Many subsurface brines are clearly potential barite-forming solutions [18]. The precipitation of barite from brine water has been recorded from most of the oil producing areas [24, 19 and 25]

According to the mineral species of both ore and gangue minerals, field observations and textures, the zinc – lead – barite deposits of the studied localities may be classified as epithermal, epigenetic, strata-bound of Mississippi Valley-type deposits (MVT).

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References

- Akif, A. and Venecek, M., 1972, The role of geological environments in the location of ore occurrences in Northern Iraq (Kurdistan). IGC24th proceeding. Montreal, Canada. Mineral Deposits, sect 4, pp.131-136.
- 2. Al-Qaraguhli, N. and Lange, H., **1978**, Geochemical and mineralogical investigation of pyrite–sphalerite–galena deposits in the Duri-Serguza area, Northern Iraq. Journal of the Geological Society of Iraq, vol. XI, pp. 46-66.
- Al-Bassam, K. S., Hak, J. and Watkinson, D. H., 1982, Contribution of the origin of the Serguza lead – zinc – pyrite deposits, Northern Iraq. Mineralium Deposita. Springer- Verlag, vol. 17, pp. 133-149.
- 4. Buday, T. and Jassim, S. Z. ,**1987**, *The Regional Geology of Iraq*. Vol. 2, Tectonism,Magmatism and Metasomatism.

Kassab, I. M., and Abbas (eds.). D. G. Geol. Surv. Min. Invest. , lib. Published, Baghdad, Iraq. 352p.

- 5. Numan, N. M. S., **2001**, *Cretaceous and Tertiary Alpine subductional history in Northern Iraq.* Iraqi of Earth Science, vol. 1, no. 2, pp. 59-74.
- Kelly, K. D., Dumoulin, J. A., Jennings, S.,2004, *The Anarraq Zn-Pb-Ag and barite deposits, Northern Alaska*. Evidence for replacement of carbonate by barite and sulfides. Econ. Geol., vol. 99. pp. 1577-1591.
- Craig, J. R., and Vaughan, D. J., 1981, Ore Microscopy and Ore Petrography. John Wiley and Sons. New York, 406p.
- 8. Ayhan, A., **2001**, *Stratiform barite deposits between Sarkikaraagac (Isparta) and Huyuk (Konya) in Sultandag region*, Turkey geochemistry, vol. 61, pp. 54-66.
- 9. Paradis, S., Chi, G., and Lavoie, D.,2004, Fluid inclusions and isotopes evidence for the origin of the Upton Ba-Zn-Pb deposits, Quebec Applachians, Canada. Econ. Geol.,vol.99, pp.807-817.
- 10. Guilbert, J. M., and Park, C. F., **1986**, *The Geology Of The Deposits*. Freeman and company .New York. 985p.
- Beaudoin, G. Roddick, J.C. and Sangster, D. F., 1992, Eocene age for Ag-Pb-Zn vein and replacement deposits of the Kokanee Range, Southeastern British Colombia. Canadian Jour. Earth Sci., vol, 29. pp3-14.
- Yilmaz, A., Unlu, T., and Sonmez, I. S., 1992, An approach to the origin of Keban lead-zinc mineralizations, Elazaq. Turkey: A preliminary study. Research and Exploration Bull., Ankara. no.114, pp.27-50.
- Philip, M.and Paul, B. JR., 1971, Distribution of some minor elements between coexisting sulfide minerals. Econ. Geol., vol. 66, pp. 140-163.
- Bjerkgard, T., Cousens, B.L., Franklin, J. M.,2000, The Middle Valley sulfide deposits, North Jaun Fuca Ridge : Radiogenic isotope systematics. Econ. Geol.vol. 95. pp. 1473-1488.
- Ayuso, R. A., Wooden, J. L., Foley, K. N.,Seal, R. R., and Sinha, A. K., 2005, U-Pb zircon age and Pb isotope geochemistry of gold deposits in the Carolina State Belt of South Carolina. Econ. Geol.,vol. 100, pp.225-252.

- Spiro, B., and Puig, A., **1988**, *The source of* sulfur in polymetallic deposits in the Cretaceous magmatic arc, Chilian Andes. Jour. of South America, earth sciences ,vol. 1.pp. 261-266.
- 17. Nielsen, H., **1968**, *Sulfur isotope in nature*. *In: Jager E. and Hunziker, J.C.*(eds.) 1979, Lectures in isotope geology . Berlin, Heidlberg, New York. pp. 329
- Barnes. H. L., **1979**, *Geochemistry of Hydrothermal Ore Deposits* (2nd ed.). John Wiley and Sons. New York. 797p.
- 19. Collins A. G. **1975**, Geochemistry of Oilfield Waters. Developments of Petroleum science. Elsevier scientific published company. New york.pp. 496.
- Gu, X. X., Schulz, F., Vavtar, J., Liu, M., and Liu, X. M., 2003, Sulfur isotope geochemistry of Woxi W-Sb-Au deposits. South China: Implications for ore genesis . Goldschmidt Conferent Abstract. ,p. A127.
- Lieben, F., Moritz, R. and Fontbte, L.,2000, Mineralogy, geochemistry and age constraints on the Zn-Pb skarn deposits of Maria Christina, Quebrada Galena, Northern Chile. Econ. Geol., vol. 95, pp. 1185-1196.
- Grandia, F., Cardellach, E., Canlas, A., and Banks, D., 2003, Geochemistry of the fluids related to epigenetic carbonate hosted Zn-Pb deposits in the Maestrad Basin, Eastern Spain: Fluid inclusions and isotope (Cl, C, O, S, Sr) evidences. Econ, Geol, , vol, 98, pp. 933-954.
- Leach, D.L., Hofstra, A., Seifert. T. and Zak, K., 1999, Silver- lead- zinc veins: A descriptive model. Mineral deposits: Processes to processing, Stanley et al., (eds). Balkama, Rotterdam, ISBN 90 5809 0681. pp. 923-926.
- 24. Weintritt. D. J. and Cowan, J. C., **1967**, Unique characterstics of barium sulfate scale deposition: J. Petrology Tech. pp. 1318-1394.
- Leach, D. L., Bradley, D., Lewchuk, M. T.,Symons, D. T. A., de Marsily, G., and Brannon, J., 2004, Mississippi Valley type lead- zinc deposits through geological time : Implications from recent age dating research: Mineralium Deposita, vol. 369, pp. 711-740.
- 26. Anderson, G. M., **1973**, The thermal transport and deposition of galena and

sphalerite near 100° C. Econ. Geol.,vol. 68, pp. 480-492.

- Ayhan, A., 2000, Genetic comparison of lead - zinc deposits of Central Taurus. In: Tekeli, O. and Concu, Glu, M. C.(eds.) Geology of Taurus Belt proceeding, pp335-342.
- 28. Hempton, M. R., **1987**, *Constraint on Arabian plate motion and extentional history of the Red Sea. Tectonics*. Amercan Geophysical Union, vol. 6, no. 6, pp. 687-705.
- 29. McCarthy, M. J. and Smith, J. S., **1954**, *Geological investigation for NE Zakho region.National Company for Mineral, internal report.*