REE Geochemistry of Precambrian Shale-Hosted Barite-Galena Mineralization, a Case Study from NW Iran

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Abstract: The barite and the behavior of REE in its crystallo-chemical structure have been a major category of research done by scientists for a long time. There are various barite mineralization in Northwest Iran. These sediment-hosted resources as a type of tectonic-controlled-vein mineralization bear unconformity to their shale host rocks at Precambrian age (Riphean). The REE geochemical studies are carried out with the aims to investigate the behavior of REE in barite and galena crystal chemistries and to compare them with respect to their host rocks and some certain standards to reach the aims, Eu, Ce, La anomalies, chondorite normalized ratios, and other standards are used. REE evidences revealed discrepancy between barite-galena mineralization and host rocks. Barite crystallized at oxidized environment, but galena at reduction environment; moreover, barite originated from volcanic sources. Finally it seems that the mineralizations are formed under brine and hydrothermal fluid mixing condition.

Keywords: *barite; galena; geochemistry; mineralization; Precambrian; shale.*

Introduction

Barite is one of the useful mineral that has been long in the focus of geologists' attention, intriguing them with to study the behavior of the elements in its structure. In spite of many difficulties, such as the scarcity of rare-earth element and Y (REEs and Y) studies on barite and galena, numerous studies encourage us to follow this method of elucidating the source of hydrothermal fluids and material in element concentration in ore deposits ([1-5]).

During such studies, great attention must be paid to differences in the geochemical behavior of the REEs and Y, in hydrothermal fluids in accordance with Eh, pH, and temperature, in the interaction of fluids with the surrounding geological materials, and to the crystallographic characteristics of minerals to be precipitated ([6-10]). Based on the above mentioned works the REE-Y content of barite and galena may be lower than that in their parental hydrothermal fluids ([11-12]).

There are a number of shale hosted barite-galena mineralization in North-West of Iran (Morrow-Mishow Mountains) near Tabriz (Fig.1) ([13-14]). These deposits are epigenetically related to their Precambrian hosts (Kahar Formation with Riphean age) and the origin of their formation has not been clearly identified yet. These deposits are mainly of vein type. The current research based on the study of REE behavior in host rocks, barites and galenas, are trying to find a new horizons for understanding probable genesis of the studied mineralization.

Geological Setting

Based on the most recent structural zoning of Iran, the study area is located in the central Iran structural zone ([15]). Moreover, [16, 17] based on structural and sedimentary evidence, this region has been classified as central Iran zone, as well.

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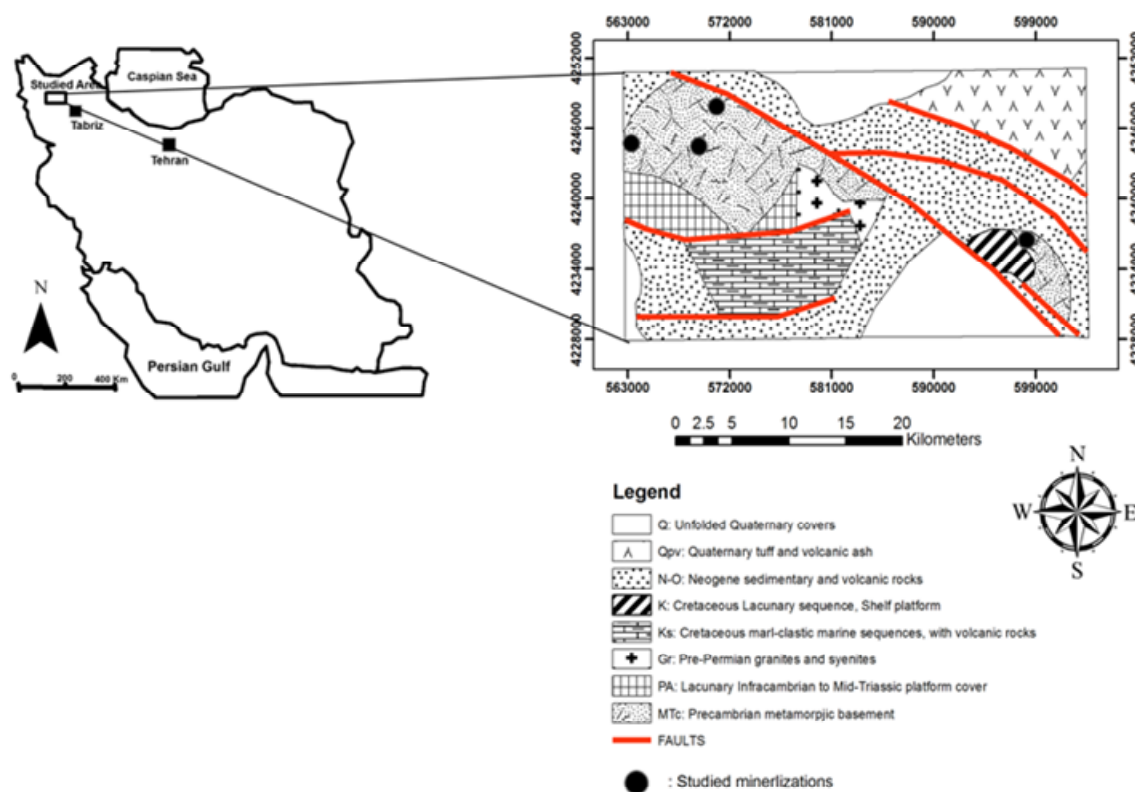
Figure 1 The simplified study area map in Iran map.

In this area, the Kahar Formation of Precambrian (Riphean) age as the basement of the studied district is the host rock of barite-galena mineralization. It is assumed that the lower parts of Kahar Formation indicate pre-rift inter-cratonic facies. The middle and upper parts with autogenic silicate sediments exhibit continental (meanderic)-intermediate (deltaic) characteristics. In some parts the plat-formic carbonate deposits and volcano-plutonic facies are observable in Kahar Formation. The Kahar Formation of this area comprises shale-sandstone and some volcanic units ([18-20]). There are some tuff-rhyolitic out crops in Kahar Formation that seem to be related with late Precambrian alkaline magmatism ([15]).

Barite-galena mineralization
In the area under study, the barite-galena mineralization is formed as fault controlled space filling vein types. The veins are formed from barite as their main minerals, Pb-Cu sulfide mineralization, and their oxidized products (malachite, cerrusite and anglesite) as associated minerals. Barite consists of the euhedral-pheno-crystals (with 0.5-2cm length), drossy-space filling

aggregates and intensive impregnation with sulfide minerals and their oxidized products.

Galena as the main sulfide mineral in the studied area is reported for the first time in this paper. It is typically dispersed in barite masses as irregular aggregates of microcrystalline- xeno-hedrals, which are accompanied with calcite, cerrusite, anglesite and ankerite.

Chalcopyrite is another sulfide mineral in the studied case. Its xeno-hedral-dispersed aggregates were found in barite masses. The main part of them was altered to covellite and malachite. Pyrite as rare sulfide mineral occurs as oxidized -pyrite crystals. There are various field and microscopic evidence for post-mineralization deformation in this mineralization.

Analytical Methods
In order to conduct geochemical studies, 12 samples were chosen for analysis including 5 barites (AZB-01, AZB-02, AZB-03, AZB-04, and AZB-05), 2 galenas (AZG-01, AZG-02), 5 samples from the host rock (Kahar Formation) consists of 1 rhyolite AZ-06) and 4 samples of shales(AZ-07, AZ-08, AZ-09, AZ-10). The analysis of samples helps for better understanding the behavior of the

REE-Y in the mineralization and their host rocks, to assess the statistical correlations of the elements in the crystal chemistry of the studied barites and galenas, and to compare analytical data with various standards.

The samples were crushed and powdered for chemical analysis, while 100-200 micron grains of barite and galena were isolated from ore samples. For final isolation, heavy liquids and stereomicroscope were used. Trace and rare earth elements (REE) were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) techniques in ALS-Chemex company laboratories, Vancouver, Canada. The analytical precision of the method applied for each element was well above the limit requirement expected for research quality analysis.

Results

Results of trace-element analysis are given in Table 1. The trace element contents of the rock samples are in reasonable ranges compared to those of similar sedimentary rocks, while most of the trace-element values for the barite and galena separates are below the detection limits of the method applied. The REE results were normalized using the average C1 chondrite abundances of [21]. The distribution trends are shown as log-normalized REE abundances versus the atomic numbers of the REEs (Figure 2).

Tabe1 Geochemical analysis results SAMPLES

| TYPE	Rhyolite	SHALE				BARITE					GALENA	
Element(ppm)	AZ-06	AZ-09	AZ-10	AZ-07	AZB-08	AZB-03	AZB-04	AZB-05	AZB-01	AZB-02	AZG-01	AZG-02
Ce	56.3	59.7	55.1	63.5	73.7	0.5	0.7	<0.5	<0.5	<0.5	0.9	0.5
Dy	6.11	2.80	4.49	6.33	4.66	<0.05	0.06	<0.05	<0.05	<0.05	0.18	0.09
Er	3.91	1.72	2.43	3.24	2.80	<0.03	<0.03	<0.03	<0.03	<0.03	0.08	0.08
Eu	0.63	1.21	1.27	1.55	1.13	1.51	1.12	0.93	1.20	0.67	0.88	0.48
Gd	5.41	4.04	5.68	7.26	5.35	0.51	0.47	0.53	0.48	0.42	68	0.28
Ho	1.38	0.56	0.90	1.25	0.96	<0.01	<0.01	<0.01	<0.01	<0.01	0.03	0.07
La	26.5	31.6	27.3	30.1	35.6	1.2	1.2	1.2	1.3	1.0	1.3	<0.5
Lu	0.55	0.27	0.36	0.44	0.43	0.07	0.06	0.07	0.07	0.06	0.06	0.16
Nd	24.7	23.5	25.9	31.5	31.7	0.4	0.6	0.5	0.4	0.4	1.1	0.3
Pr	6.88	6.91	6.86	8.21	9.02	<0.03	0.07	<0.03	<0.03	<0.03	0.13	0.11
Sm	5.13	4.40	5.85	7.14	5.76	0.3	0.32	0.31	0.29	0.29	0.52	0.16
Tb	0.98	0.54	0.83	1.14	0.83	0.3	0.03	0.03	0.03	0.04	0.04	0.07
Tm	0.56	0.26	0.35	0.47	0.40	0.02	0.02	0.02	0.02	0.02	0.05	0.16
Y	35.0	14.7	24.6	32.1	24.1	0.7	0.9	0.7	0.7	0.7	1.4	1.4
Yb	3.72	1.74	2.26	2.85	2.68	0.18	0.20	0.21	0.21	0.16	0.23	0.23
La_N/Yb_N	4.80	12.24	0.74	7.12	9.18	4.49	4.04	3.85	4.17	4.21	3.81	3.37
Ce_N/Yb_N	3.91	8.87	0.57	5.76	7.11	0.71	0.90	0.61	0.61	0.80	1.01	1.29
Tb_N/La_N	0.24	0.11	0.19	0.24	0.14	0.16	0.16	0.16	0.15	0.26	0.20	0.91
Sm_N/Nd_N	0.63	0.57	0.69	0.69	0.55	2.30	1.64	1.90	2.23	2.23	1.45	1.64
Ce_N/Sm_N	2.64	3.27	2.27	2.14	3.08	0.40	0.52	0.38	0.41	0.41	0.41	0.75
Sm_N*Gd_N	549.51	351.9	657.9	1026.36	610.15	3.02	2.97	3.25	2.75	2.41	7.00	0.88
Eu/Eu*	0.36	0.87	0.67	0.65	0.62	11.80	8.83	7.01	9.83	5.86	4.52	6.93
Ce/Ce*	-0.006	-0.03	-0.03	-0.02	-0.02	-0.65	-0.52	-0.66	-0.68	-0.58	-0.48	-0.30
La/La*	0.98	1.11	1.06	1.00	1.01	-6.49	-13.88	-4.16	-7.04	-5.41	-8.92	0.94
∑LREE	114.38	121.7	115.1	133.31	150.92	2.13	2.57	2.23	2.23	1.93	3.43	1.41
∑MREE	19.64	13.55	19.02	24.67	18.69	2.41	2.01	1.86	2.06	1.48	2.33	1.15
∑HREE	8.74	3.99	27.74	7.00	6.31	0.3	0.31	0.33	0.33	0.27	0.42	0.5
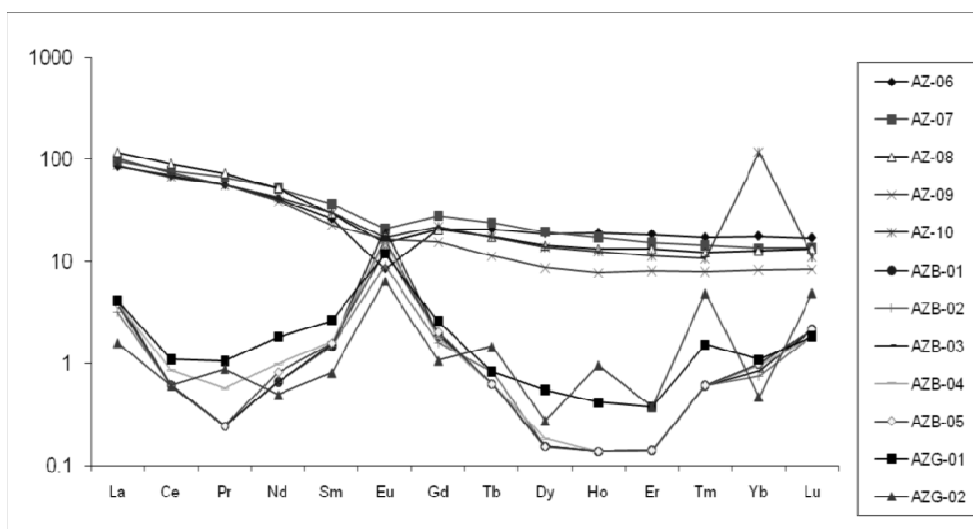
Figure 2 Chondorite normalized diagram (C1, [21]).

Because the profiles of barite and galena samples are quite similar, representative profiles for average values of the five barite and two galena samples were prepared. In addition, to estimate the environment of formation, the Eu, Ce, La anomalies, statistical correlations, normalizing to NASC, PAAS, seawater, upper crust, the La_N/Yb_N, Ce_N/Yb_N, Tb_N/La_N, Sm_N/Nd_N, Ce_N/Sm_N, La_N/Sm_N, Tb_N/Yb_N ratio values were also calculated and interpreted.

Finally, the profiles of barite and galena from this area were compared to those of hydrothermal fluids, precipitates, and barite occurrences in other areas. The plot of the calculated Ce_N/Sm_N and Ce_N/Yb_N values on an X-Y diagram shows the location of the possible source for mineralization and mineralizing hydrothermal fluids.

Eu anomaly

Based on diameter and electric value, the Eu^{2+}as, is most similar REE to Ba^{2+}ion. For the investigation of Eu behavior, the Eu anomaly is calculated with $Eu/Eu^*=Eu_N(Sm_N*Gd_N)^{1/2}$ formula. If $Eu/Eu^*>1$ the anomaly is positive, $Eu/Eu<1$ the Eu anomaly been negative ([22]; [23]). The obtained results show negative anomalies for rhyolites, shales, ad positive anomalies for barite-galenas. Positive Eu/Eu^* of Morow Mountains barites are higher than that in Mishow Mountains. Furthermore the Eu/Eu^* of barites are higher than that in galenas. The existence of Eu as a concentrated anomaly in barites is the result of similarities of ionic radius in Eu and Ba. The positive Eu anomaly may be caused under late metamorphic-sedimentary processes. The negative Eu existence is reasonable in sea formed barites with Ce positive anomaly.

[2], believed that the positive Eu anomaly can be caused under the conditions that Eu^{3+} changes to Eu^{2+} in reduction status. If the ore-forming fluid is the final remain of a magmatic differentiation, the late fluids are dense in Eu, K, Ba, Sr. It is worthy to mention that two elements Eu^{2+} and Sr^{2+} are similar to Ba^{2+} that leads to their involvement in barite structure. This event may occur in conditions without any exchange of energy. The positive Eu anomaly indicates the suitable barite property to concentrate Eu. Eu positive anomaly and the difference of the above-mentioned rates between the various samples can indicate mixing of two fluids, high oxygen fugacity, and the oxidized ore forming condition for barites ([24]).

Ce anomaly

According to [24], [3], the Ce anomaly was calculated for barites, galenas and shales by $Ce/Ce^*= log [Ce_N/(2/3La_N+1/3Nd_N)]$ formula. All the results show negative anomaly, whereas this rate in shales and rhyolites are more than that in barites and galenas. The low intensity of the negative Ce anomaly in galenas can demonstrate the reduction tendencies of galena ore forming fluids and the reduction tendencies of ore forming conditions.

The negative Ce/Ce^* in Morow mountains is more than that in Mishow mountains which can show high oxygen fugacity of ore-forming environment at Morow mountains in comparison to Mishow mountains. This phenomenon represents

the oxidation and the Ce remobilization from the original environment. On the other hand, the lack of correlation between Ce and Eu may indicate the effect of various factors on their distribution in the mineralization masses and processes. Finally, the high Ce/Ce* negative anomaly can indicate the oxidation status for seawater environment ([24]).

La anomaly

[25] stated that La anomaly is calculated by La/La* = La $(3Pr_N-2Nd_N)$ formula. The obtained results illustrate low positive La/La* for shales and high negative La/La* for galenas and barites of Morow-Mishow mountains. There is a significant statistical correlation between Ce and La anomalies. La can intrude into mobile parts during the flow of hydrothermal fluids from wall rocks. Consequently, there is a notable La deficiency in wall rocks. The La might also migrate from wall rocks as a result of formation of some complexes with F ([5]).

Chondorite normalized patterns

Some ratios of chondorites normalized ratios such as La_N/Yb_N, Ce_N/Yb_N, Tb_N/La_N, Sm_N/Nd_N, Ce_N/Sm_N, La_N/Sm_N, Tb_N/Yb_N are used in REE-Y geochemistry.

Generally, in all of the studied samples (except in altered shales), there are $La_N/Yb_N>1$ status. La_N/Yb_N in rhyolites, barites and galenas are similar, but the ratios in the shales of Morow Mountains have threefold of that than other samples. La_N toYb_N in in altered shales of Morow Mountains is <1. The rich content of the discussed ratio (>1) indicates higher concentration of LREE. The ratio of below one in shales is interpreted with as La depletion and probably LREE deficiency in comparison with HREE. The high concentrations of LREE indicate they can act as the preparing of carrier complexes in parental fluids.

The ratio of Ce_N toYb_N is >1 in all the samples, except in the altered shales. This fact may reveal the high amount of the LREE concentration in comparison to HREE. Finally, the observable anomaly in the altered shale demonstrates LREE movement and the HREE concentration.

The ratio of Tb_N/La_N in all samples is less than one. As indicated by [5] in their experimental investigations, the primary deposited phases are rich in LREE but the later phases are rich in HREE. The value of Tb_N/La_N indicates the differentiation rate in deposition environment.

The La_N/Sm_N of all samples is more than one, which display the LREE concentration in comparison to HREE concentration. This event can lead to high concentration of Ce and Tm in hydrothermal fluids.

The low values of La_N/Yb_N, Ce_N/Yb_N, and La_N/Sm_N in altered rocks indicate the depletion of altered rocks from REE. If the values of La_N/Yb_N, Ce_N/Yb_N, and Tb_N/Yb_N are more than one, this indicates LREE concentration. The ratio of less than one is a sign of HREE concentration. The acidic pH and high SO_4^{2-} contents in hydrothermal fluids, is an evidence of the REE depletion. The concentrations of REE in oceanic barites are higher than in the other autogenetic minerals ([11]; [12]; [26]).

Standard Normalizing diagrams

The obtained results were normalized to Chondorite (C1) ([21]), North American Average Shale Composits (NASC form [27], Crustal Continental Average ([22]), Standard Sea water form 900m depth [27] and Post Archean Average Sedimentary rocks (PAAS from [28]). In all diagrams, the distribution trends are shown as log-normalized REE abundances versus the atomic numbers of the REE.

- Normalizing to Chondorite: As maintained by [2], depending on the ionic radious of the main cation in barites (Ba^{2+}), REE frequencies in barites are various. All of the samples are normalized according to [21] C1 chondorite abundances (Fig. 2). All of the shales and rhyolites as mineralization host rocks represent normalizing patterns similar to each other and rich in chondorite. Therefore, there is a slight negative tendency from LREE to HREE, which intensifies in Eu position. The decrease of Eu in rhyolite is more than that in shales.

Regarding Yb, it can be noted that the altered shales in Morow Mountains which hosted the studied mineralization samples possess higher concentrations of HREE than that of fresh shales (AZ-07, AZ-08, AZ-10). This may have been brought about due to LREE mobility which leads to concentration of HREE and deficiency of LREE in alteration processes). But in the case of the other elements, the variation rates including a falling trend for LREE down to Eu point, followed by the rising continuation with a negligible dip up to the end of HREE. Generally, the pattern of chondorite-normalized data indicates a similarity between sedimentary host rocks of barite-galena mineralization. The similarities of LREE in spider diagrams of both samples can be interpreted in the light of their genetic similarities [11,12].

The barite and galena curves are characterized by some sinus variations and two sorts of deficiencies i.e. Pr-Nd-Sm in LREE and Dy-Ho-Er in HREE. There are two important issues regarding these curves; First, the disproportion between host rock and its mineralization and second, the relative HREE concentration in the galenas with regard to barites. Both barites and galenas have positive Eu, negative La, and Ce anomalies that indicate Eu concentration and La and Ce (LREE) deficiencies in barites and galenas. Eu concentration in barites (based on the former discussion) may be interpretable with Eu^{2+} - Ba^{2+} replacement that might occur in high Eu concentrations. Additionally, some similarities between REE normalized curves in barites-galena mineralization of Morow and Mishow mountains may bear testimony their unique origin.

- Normalizing to NASC: The shales, barites, and galenas were normalized to North American Shale Composites ([27]) (Fig. 3). The shales were observed to have similar dispersion patterns and conformity - despite the Morow Mountains altered shale with Yb concentration- with NASC trends. In this case, the barites and galenas have obvious deficiencies, the high notice ability of which reveals high negative Ce-Pr and low positive Eu anomalies. In addition, there is a lack of correspondence between galenas and barites pertaining to Pr-Nd (LREE) and Tm-Yb (HREE) patterns. However, as far as other factors are concerned they look like each other.

The distribution of normalized values on the Ce_N/Sm_N versus Ce_N/Yb_N diagram ([26]) shows that the values of the studied barite and galena separates are very close to that of seawater (Fig. 4). The studied samples accumulated near seawater and volcanic rocks points in diagram, which indicates some probable similarities to sea water and volcanic rocks.
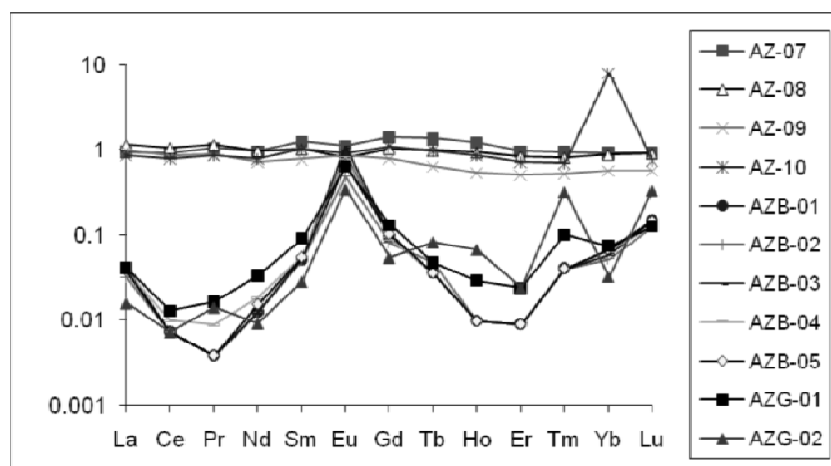

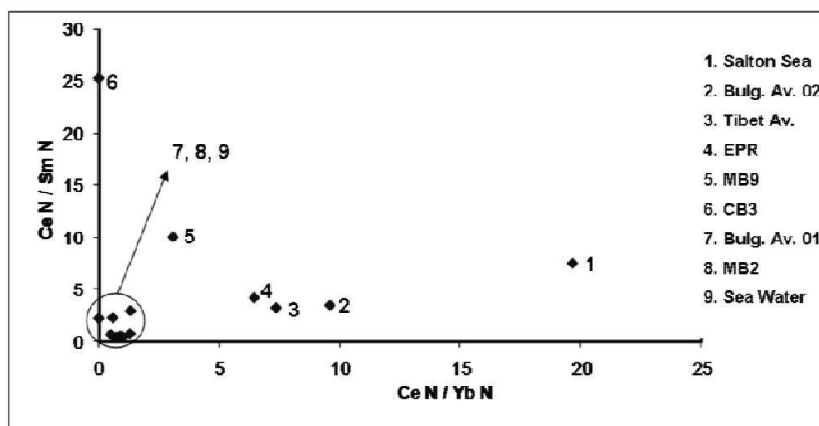**Figure 3** North American Shale Composite normalizing diagram (from [27]).

Figure 4 Ce_N/Yb_N-Ce_N/Sm_N normalized data. The studied case samples are located into circle with 7, 8, 9 standard data (C1, after [1, 21, 29, 31]).

This data can show the leaching of Ba and Pb from volcanic rocks (Rhyolites in this case) by seawater (according to average 1535 ppm Ba Clark in study area rhyolites). The existence of similarities between our data and sea water may attribute the origin of SO_4^{2+} in barites to sea water. Moreover, close distance of galenas and barites in this diagram can indicate their similar source. Finally, their proximity to Bulgarian average hydrothermal fluid sample (pH<7.5), can manifest that their probable genesis may have been formed from a pH<7.5 hydrothermal fluid, which is differ from seawater and its produced barites ([26,11,12]).

To investigate the formation system and locality, the studied barites besides REE data of seawater, pelagic barites of central Pacific ocean (MB2), deeply buried diagenetic barites of North Pacific (MB9), hydrothermal vein barites of Sterling district of Colorado (USA) (CB3) ([1]), Tibetan average hydrothermal (geothermal) fluid samples pH<7.5, Bulgarian average hydrothermal (geothermal) fluid pH>7.5 & pH<7.5, hydrothermal fluid average of the East Pacific rise 21° N-SW (EPR21) [30], and Salton Sea ([29]) are normalized to C1 chondrite ([21]) and they are compared in Fig. 5.

[31] Stated that the distribution of REE in Atlantic and Pacific depends on seawater oxygen content, water chemistry, opal and calcium carbonate frequencies, and depth of sea water, micro-organisms, and the ability of above mentioned materials for REE-ions exchange by their chemistry.

REE deficiency of the Tibetan and Bulgarian average fluids flowing to sea water and oceanic

hydrothermal fluids depend on the pH and alkalinity of the above mentioned fluids. Like EPR21 and Salton Sea, the barites and galenas of the studied areas show intensive deficiency of Eu, but there are not any similarities between EPR21 and Salton Sea with the studied case host rocks with reference to, concerning, regarding REE distribution patterns. Despite the little similarities between MB2 and the studied case, the UCC, PAAS, NASC, sea water, Tib. Av. and Bulg. Av. 1&2 are bearing the most resemblance to the studied shales.

The frequencies of REE in the studied barite-galena are lower than those in their host rock. Furthermore, there are not complete similarities between the barites, galenas and host rock regarding REE frequencies and distribution patterns. According to field, microscopic, and stable isotope assessments ([13]) the galenas are formed after the barites. The difference of galenas-barites REE pattern may be the result of the differentiation of ore forming fluid chemistry in a mineralization period.

During the barite formation (early phase of mineralization), some REE ions must have accumulated in barites chemistry. Therefore, and the ore forming fluids can show REE deficiency. There is also a differentiation in hydrothermal fluids. The galenas are formed from differentiated remains of ore forming hydrothermal fluids which their REE frequency variations can be interpretable with the hydrothermal fluid differentiations. Finally, there are not any similarities between oceanic- diagenetic and pelagic barites and the barites in the studied areas (Fig. 5).
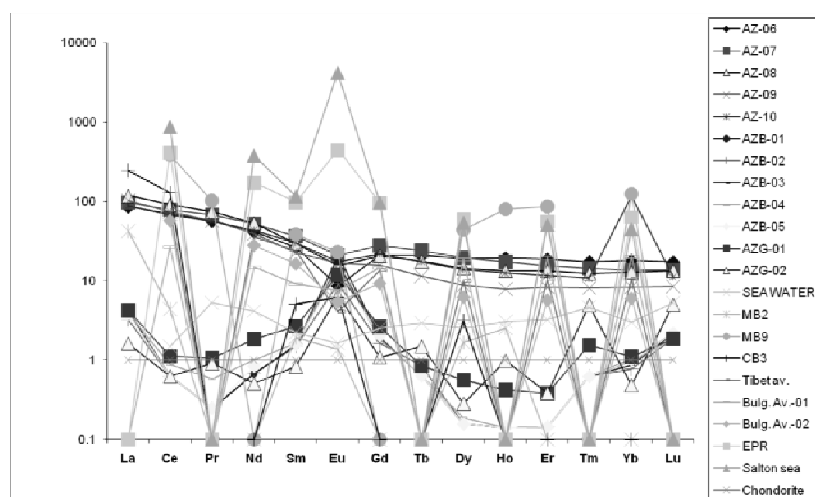

Figure 5 Normalized data to chondrite.

Conclusion

There are a lot of barite- galena reserves in North-West of Iran (especially in in Morow- Mishow Mountains). The field, microscopic, geochemical and isotopic evidences demonstrate that these reserves have Riphean- age, fault-controlled-space- filling- vein- type. They are host- rock-discordant (epigenetic), strata- bound and non-stratiform deposits.

The assessments show that the studied samples contain large amounts of LREE than HREE. The host rocks and their same age volcanics are assumed to be the origin of Ba & Pb. The average Ba content of shales in the host rocks of this case (shales) is 490 ppm.

Same age rhyolites of Kahar Formation (effusive equivalents of Doran granite as Mahabad-Qaradash series) as one of the acidic volcanism in the studied area with 1535 ppm average Ba, are the second probable barium sources (sources of barium). REE assessments revealed that the volcanics, especially acidic volcanics were more reasonable to have prepared the mineralized barium than shales. The previously discussed $Ce_N/Sm_N - Ce_N/Yb_N$ model diagram and Eu anomaly similarities between barites and volcanic rocks, emphasize that barium must have been derived from volcanic rocks.

The absence of Zn and spreading of Pb in this case can be justified with by their frequencies (low concentration) in rhyolites as Ba-Pb sources. As discussed above, barites are formed in an oxidized Eh and in later stages, besides the reduction of the hydrothermal fluids, the galena and other sulfide minerals are formed. Finally, in meteoric-crustal conditions, malachite, diegenite and other secondary minerals are formed in oxidized conditions.

The investigation of REE show some similarities between ore- forming fluids and sea water, as well as the pelagic barites (central pacific), but they reveal some variations with Average of the East Pacific Rise and diagenetic barites. The application of $Ce_N/Sm_N - Ce_N/Yb_N$ diagram suggests, a polygenetic origin for ore formation processes and ore- forming fluids which bear some similarities to Bulgarian average hydrothermal (geothermal) fluid (pH<7.5) and some similarities to sea water.

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