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Trace- and Rare-Earth Element Geochemistry of the Karalar (Gazipaşa–Antalya) Barite-Galena Deposits, Southern Turkey

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Abstract: The Karalar barite-galena deposits are typical examples of carbonate-hosted barite-galena deposits that occur widely in the central Taurides. Recent mining activity has been concentrated in the Büyük and Boyalık mine areas. The mineralisation occurs as ore veins along fault zones and as ore-filled breccia zones along the strongly deformed lower walls of limestone blocks in the Permian limestones of the Bıçkıcı Formation. These veins contain mainly barite (80–85%) and galena (10–15%), and lesser amounts of sphalerite, pyrite, fahlore, limonite, quartz and calcite as gangue minerals. Barite developed during an early episode of mineralisation and was mylonitised before the precipitation of other minerals. Trace-element geochemical studies show that Ba and Pb may have been derived from different sources: Ba is enriched in mudstones of the Ordovician Çakmak Formation, and Pb is enriched in limestones of the Permian Bıçkıcı Formation. The trends of the REEs–Y profiles and the plots of the values of barites and galenas on the Ce_N/Sm_N versus Ce_N/Yb_N diagram indicate that a seawater-dominated hydrothermal fluid supplied the barium and sulfate ions and deposited the barite, while a fluid mixture of seawater and a Tibetan-type (terrestrial) hydrothermal fluid was responsible for galena deposition. There is also a genetic relationship between galena and Permian limestone and dolomitisation processes.

Key Words: barite, galena, geochemistry, rare-earth element, Karalar, Antalya, Turkey

Karalar (Gazipaşa–Antalya) Barit-Galenit Yatağının İz ve Nadir Toprak Element Jeokimyası, Güney Türkiye

Özet: Karalar barit-galenit yatakları Orta Toroslarda yaygın olarak gözlenen karbonat yankayaçlı barit-galenit yataklarının tipik örneklerindendir. Güncel işletmeler Büyük ve Boyalık Ocak mevkilerinde toplanmıştır. Cevherleşmeler Permiyen yaşlı Bıçkıcı Formasyonu'na ait kireçtaşları içinde; kırık hatlarına bağlı damar tipi ve kireçtaşı bloklarının ileri derecede deforme olduğu alt kesimlerde ise breş dolgusu şeklindedir. Cevher damarlarında barit (% 80–85) ve galenit (% 10–15) hakim mineraller olup, sfalerit, pirit, fahler, limonit, kuvars ve kalsit gibi gang mineralleri çok az miktarda bileşime katılmaktadır. Baritler diğer minerallere göre daha önce oluşmuş ve milonitleşmişlerdir. İz element jeokimyası incelemelerinde baryum ve kurşunun farklı kökenlerden kaynaklandığı görülmüştür: Baryum Ordovisyen yaşlı Çakmakkaya Formasyonu'na ait çamurtaşlarında, kurşun ise Permiyen yaşlı Bıçkıcı Formasyonu'nda zenginleşmiştir. NTE–Y profillerindeki gidişler ile galenit, barit ve galenitlere ait değerlerin Ce_N/Sm_N'e karşılık Ce_N/Yb_N diagramındaki konumları, deniz suyunun hakim olduğu hidrotermal çözeltilerce baritlerin oluşturulduğunu; baryum ve sülfat iyonlarının sağlandığını, galenitlerin oluşumunda ise deniz suyu ile Tibet tipi (karasal) hidrotermal çözeltilerin karışımı şeklindeki hidrotermal çözeltilerin etkili olduğunu belirtmektedir. Ayrıca galenit oluşumu ile Permiyen yaşlı kireçtaşları ve dolomitleşme süreci arasında jenetik bir ilişki bulunmaktadır.

Anahtar Sözcükler: barit, galenit, jeokimya, nadir toprak elementler, Karalar, Antalya, Türkiye

Introduction

Carbonate-hosted barite deposits are widespread in the Gazipaşa region (Antalya, southern Turkey). Some contain galena and small amounts of other sulfide minerals. The most important deposits and prospects are located in the Karalar, Aydap, Yuları, Burhan Mahallesi, Kıcık, Endişegüney and Seyfe areas along the Mediterranean Sea coast (Figure 1).

The depositional styles, ore/host-rock relations, and mineralogical compositions of the deposits have been investigated by numerous geologists, and two different hypotheses have been proposed about their genesis: (1)

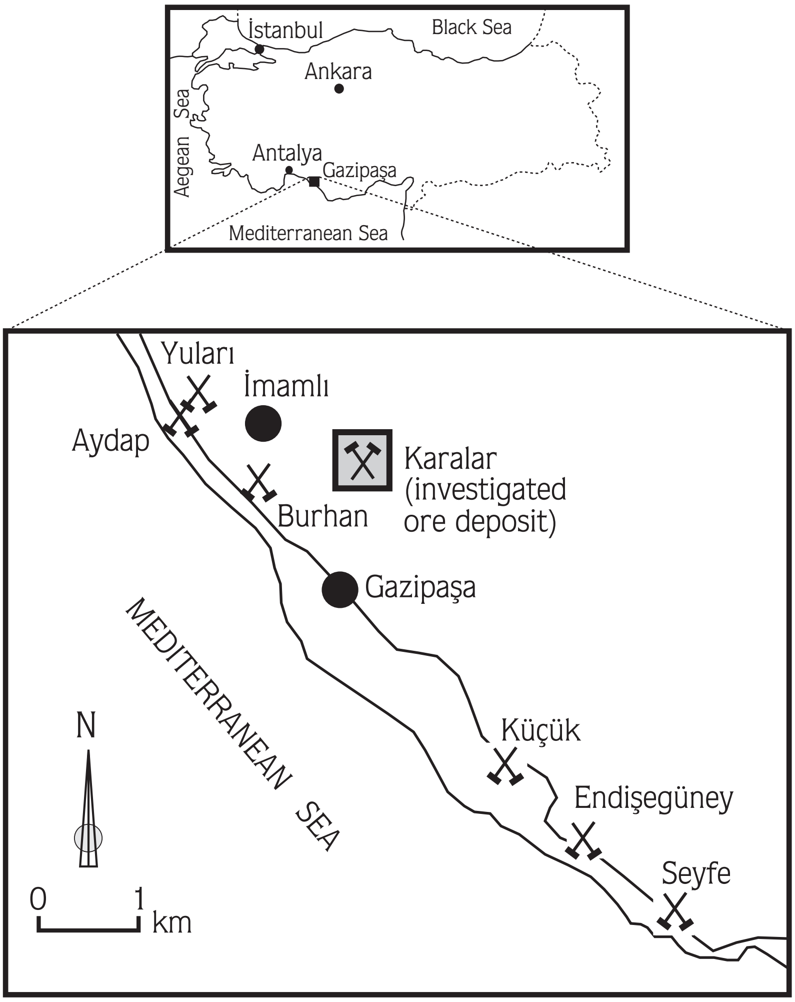

Figure 1. Map showing the location of the Karalar and neighbouring barite deposits.

the barite deposits formed by synsedimentary processes, being later affected by remobilisation, recrystallisation and deformation during post-depositional geological events, including diagenesis, regional metamorphism and tectonic movements. The thrust of this hypothesis is the occurrence of these deposits in the form of stratiform, strata-bound and/or vein-type bodies, typical of synsedimentary and epigenetic depositional processes (Striebel 1965; Şenel 1977; Sadıklar 1978, 1983; Sadıklar & Amstutz 1981; Ayhan 1979, 1981, 1982; Gülseren 1987; Çopuroğlu 1994); or (2) they occur mainly as vein-type deposits, produced through epigenetic hydrothermal processes (Barutoğlu 1942; Petrascheck 1966, 1967; Bilgisu 1976; Çöteli & Türk 1977; Remzi 1978; Gümüş *et al.* 1996).

Our investigation has focused on the Karalar ore body and our field studies indicate that the deposits formed as epigenetic ore veins along fault zones in the limestone of the Permian Bıçkıcı Formation. Fluid-inclusion studies document the following conclusions (Gökçe & Bozkaya 2001, 2002): (1) the fluids contain considerable amounts of $CaCl_2$ and $MgCl_2$; (2) the fluid salinity varied during barite (16.0 to 11.0 % NaCl equiv.) and sulfide (9.7 to 4.6 % NaCl equiv.) crystallisation; and (3) homogenisation temperatures (T_h) were different during the crystallisation of barite (78.3 to 96.2 ºC), sulfide minerals (103.9 to 156.9 ºC) and quartz (121 to 138 ºC).

The present study documents the trace- and rare-earth element chemistry of the various lithologies and of barite and galena separates from the Karalar deposits. The chemical characteristics of the ore body and its possible implications for the origin of mineralisation and source(s) of element concentration in the ore- and mineral forming-fluids will be discussed.

In spite of many difficulties, such as the scarcity of rare-earth element and Y (REEs–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 (Graf 1977; Guichard *et al.* 1979; Morgan & Wandless 1980; Baar *et al.* 1985; Michard & Albarade 1986; Ruhlin & Owen 1986; Barrett *et al.* 1990).

During such studies, great attention must be paid to differences in the geochemical behaviour of the REEs and Y, in cold and 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 (Graf 1977; Guichard *et al.* 1979; Morgan & Wandless 1980; Baar *et al.* 1985; Michard & Albarade 1986; Ruhlin & Owen 1986, Barrett *et al.* 1990; Bau & Dulski 1994; Giese & Bau 1994; Bau *et al.* 1997; Möller 1998; Möller *et al.* 1998; Bau 1999; Bau & Dulski 1999; Möller & Dulski 1999; Paces *et al.* 2001; Möller 2002).

The foregoing literature review shows that the REEs–Y abundances of the precipitates may be lower than those of the mineral-forming fluid and the source rock, but the profiles of all three materials (source rock, fluid and precipitate) may be similar. In addition, the REEs and Y not only substitute in the crystal lattices of host minerals by replacing the main ions, but also may be trapped in fluid inclusions that represent the mineralising fluid. In particular, regarding the substitution of the REEs and Y into crystal lattices of barite and galena, replacement of the Ba^{2+} and Pb^{2+} ions is quite difficult, and it may be assumed that a major part of the REES–Y contents of these minerals come from fluid inclusions.

Geological Setting

The Karalar barite-galena deposits occur in the Upper Cambrian to Upper Cretaceous detrital and calcareous sediments of the Antalya unit, which is tectonically overlain by the Alanya unit – the metamorphosed equivalent of the Antalya unit. The Antalya unit only crops out in places where the Alanya unit is deeply eroded; this area is geologically known as the Alanya tectonic window (Özgül 1976, 1984).

In the study area, the Antalya unit consists of Ordovician detrital sediments, Permian limestones and Triassic detrital sediments of the Çakmakkaya, Bıçkıcı, Yöreme and Çamlıca formations (Ulu 1983; Gülseren 1987). Older rocks units are thrust over the clastic sediments of the Triassic Çamlıca Formation (Figure 2); conversely, we claim that the older units may have glided into the Triassic sedimentary environment during the deposition of the Çamlıca Formation.

Ore deposits of the study area crop out in two different mining areas: the Büyük mine and the Boyalık mine. In the Büyük mine, there are three different ore veins, all discordant to local bedding planes: (1) vein 1 (N85°W/35°SW), vein 2 (N70°W/85°NE) and vein 3 (N85°E/85°NW). The veins characteristically occur along fault zones that deform limestones of the Permian Bıçkıcı Formation (Figure 3). The thickness of the veins varies between 0.2 m and 2.5 m. In the Boyalık mine, the mineralisation developed as thin veinlets within slightly brecciated limestones that are the lowermost lithologies of the Bıçkıcı Formation along a tectonic contact (overthrust zone) between the Permian Bıçkıcı Formation and the structurally underlying Triassic Çamlıca Formation.

Ore Petrography

Microscopic and XRD investigations of the ore samples document that the ore deposits contain mainly barite (80–85%) and galena (10–15%), and small amounts of sphalerite, pyrite, marcasite, fahlore, limonite, quartz and calcite.

The macroscopic and microscopic characteristics of the deposits suggest that barite developed during an early episode of mineralisation and was later mylonitised prior to galena crystallisation (Figure 4a, b). Galena and other minerals are epigenetically related to barite. Galena formed along porous zones between brecciated barite crystals, and is particularly enriched in weakly mylonitised zones (Figure 4c). Quartz also crystallised along fissures in barite, forming comb texture (Figure 4d).

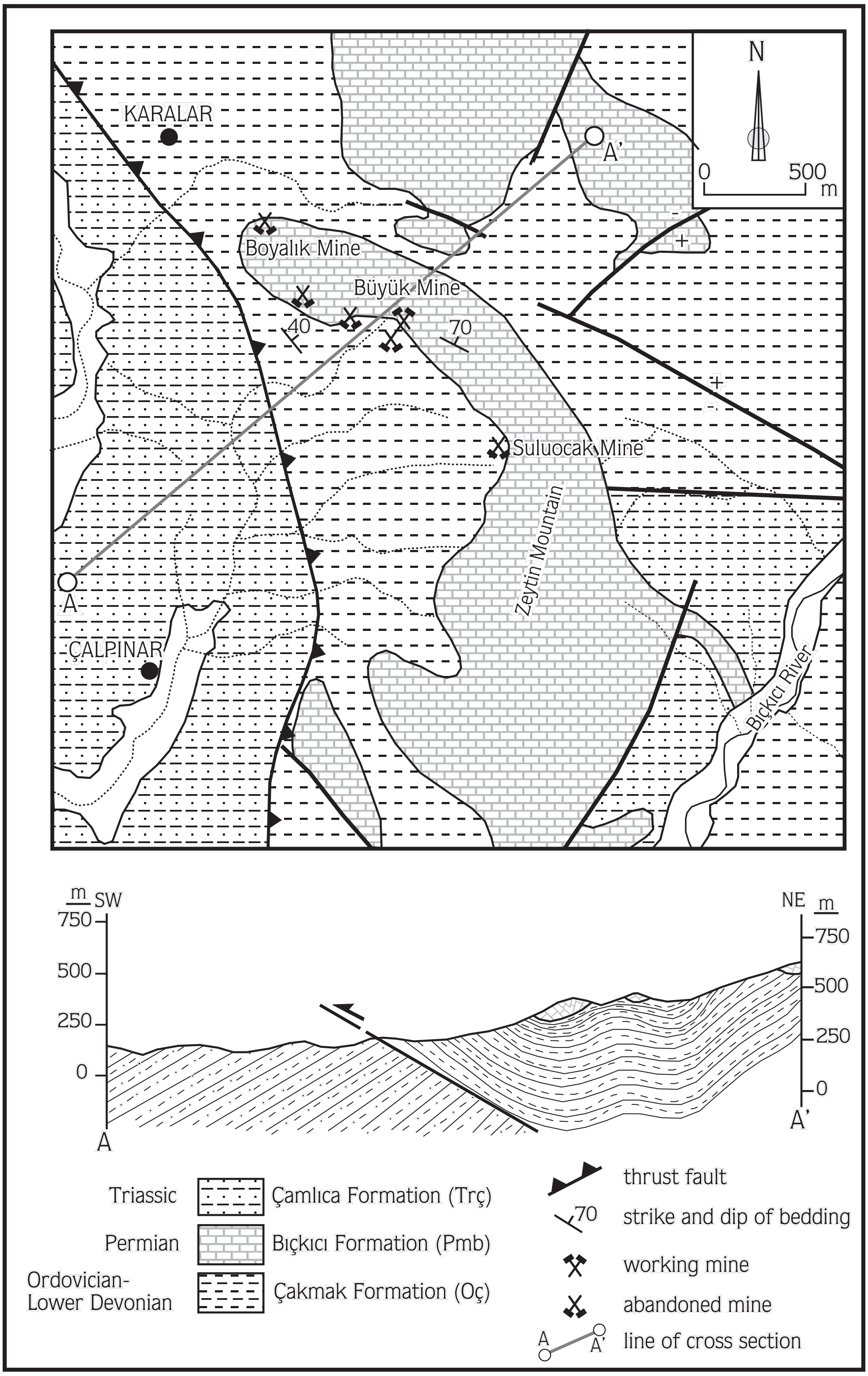

Figure 2. Geological map of the Karalar area (modified after Ulu 1983).

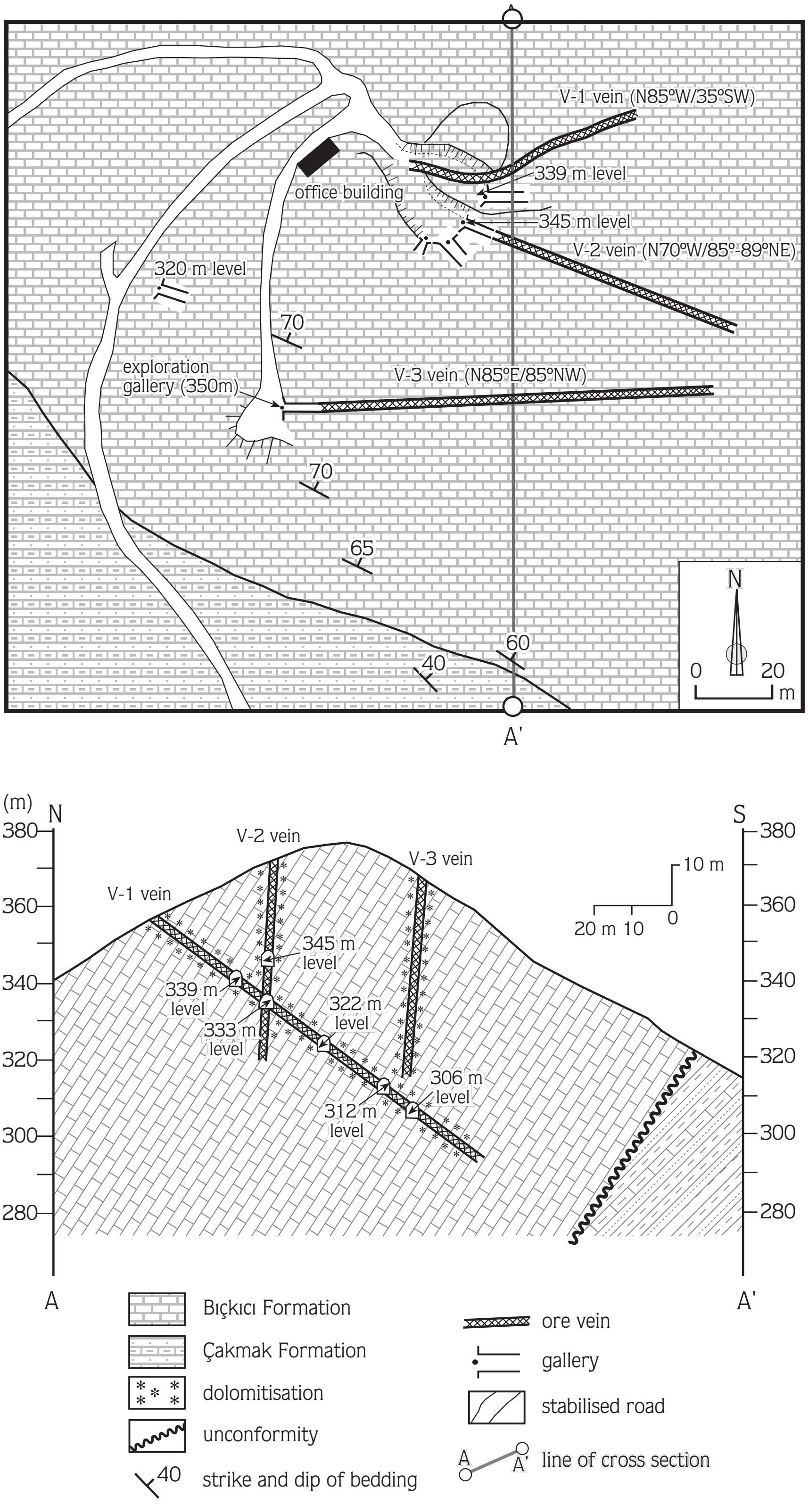

Figure 3. Geological map and cross section of the Büyük Mine area.

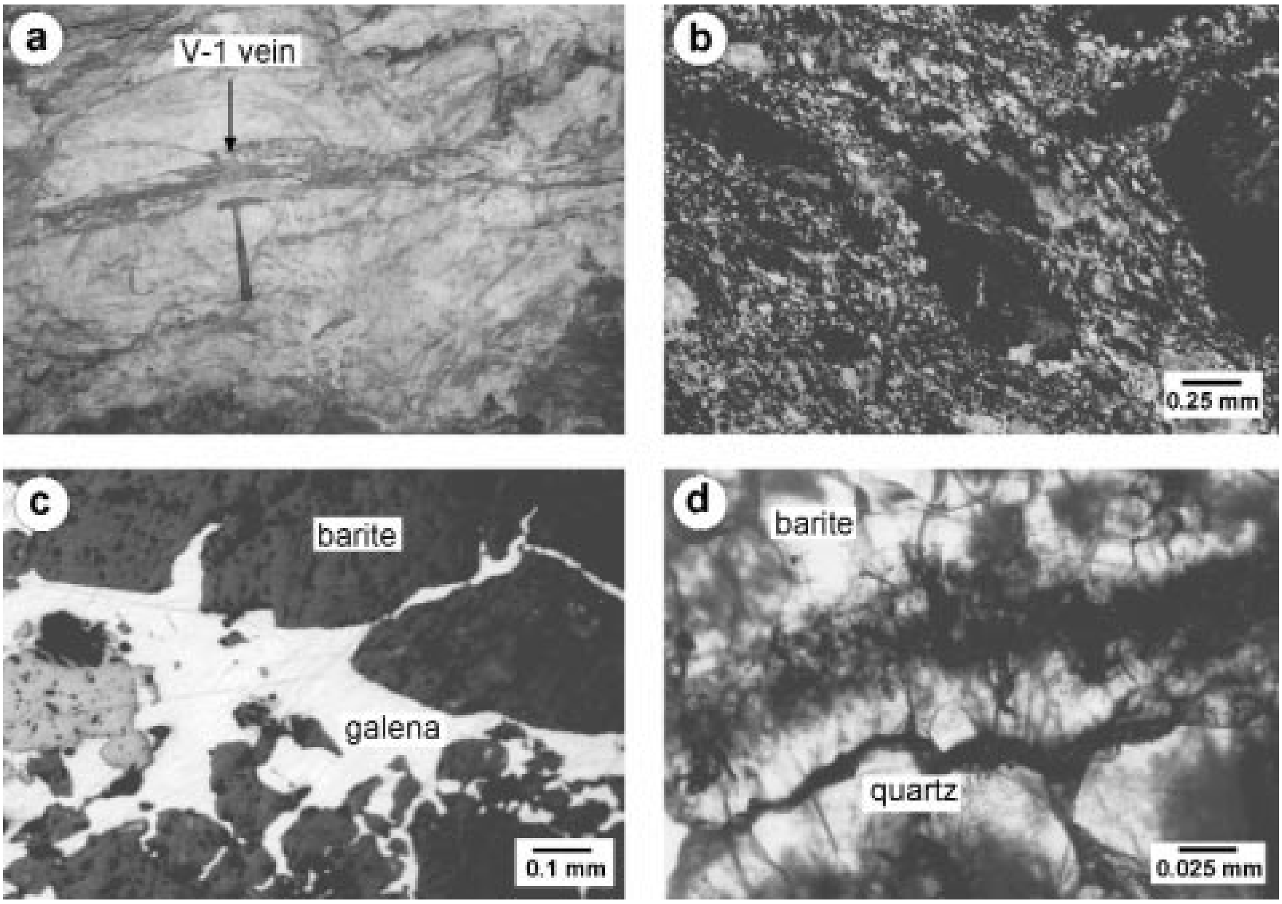

Figure 4. Various petrographic views from the investigated deposits and samples: **(a)** macroscopic view from the V-1 ore vein; **(b)** mylonitized barites and porphyroblastic texture (Sample No: GK-38, thin section, crossed nicols); **(c)** galena occurences along porous zones and fissures among the barite crystals (Sample No: GK-47, polished block, single nicol); **(d)** Quartz veinlets cutting across the barite crystal (plane polarized light).

Trace- and Rare-Earth Element Geochemistry

Analytical Methods

Representative rock samples from the surrounding lithological units (limestones of the Ordovician Çakmak and Permian Bıçkıcı formations, dolomitised zones in the Permian Bıçkıcı Formation and, mudstones of the Ordovician Çakmak and Triassic Çamlıca formations) were crushed and powdered for chemical analysis, while 100–200 micron grains of barite and galena were liberated from ore samples and were separated using heavy liquids or by hand-picking using a stereomicroscope.

Trace and rare earth elements (REE) were analysed by ICP-MS at Activation Laboratories Ltd. in Canada. The analytical precision of the applied method (4B2-res) for each element is within the limits expected for research-quality analyses.

Analytical Results

Results of trace-element analyses are given in Table 1. The trace-element contents of the rock samples are in reasonable ranges compared to similar sedimentary rocks, while most of the trace-element values for the barite and galena separates are below the detection limits of the applied method.

Trace-element (excluding REEs) distributions of the surrounding rock units are plotted on lithologic unit versus elemental contents diagrams (Figure 5) to elucidate the potential source rocks for the Cu, Zn, Pb and Ba concentrated in the ore veins.

Table 1. Trace-element and REE contents of samples from the study area (Oçm– mudstone of the Ordovician Çakmakkaya Formation; Oçl– limestone of the Ordovician Çakmakkaya Formation; Pmbl– limestone of the Permian Bıçkıcı Formation; Trçm– mudstone of the Triassic Çamlıca Formation; Pmbd– dolomitic zones in limestone of the Permian Bıçkıcı Formation; galenas and barites from ore veins) and chondrite values used in normalisation (values of La to Lu, after Boynton 1984; Y value, after Taylor & McLennan 1985).

	Sample No	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
1	GK-18 (Oçm)	58.7	113	13.0	45.2	6.77	1.22	6.22	0.92	5.46	1.16	3.39	0.470	3.27	0.466	33.8
2	GK-26 (Oçl)	27.4	49.0	5.68	20.0	3.66	0.787	3.34	0.49	2.94	0.60	1.73	0.249	1.68	0.256	18.7
3	GK-30 (Pmbl)	6.29	11.6	1.64	6.68	1.35	0.299	1.33	0.20	1.07	0.22	0.64	0.091	0.60	0.085	6.9
3 rep	GK-30 (Pmbl)	6.29	11.7	1.66	6.41	1.38	0.265	1.36	0.20	1.07	0.22	0.66	0.091	0.58	0.085	7.3
4	GK-16 (Trçm)	44.4	85.0	9.51	34.4	7.04	1.55	7.41	1.22	7.76	1.70	5.06	0.737	5.06	0.769	49.1
5	GK-31 (Pmbd)	2.31	5.0	0.69	3.07	0.67	0.078	0.68	0.08	0.48	0.10	0.26	0.034	0.24	0.035	3.0
6	GK-42 (galena)	0.15	0.2	0.03	0.13	0.03	<0.005	0.03	<0.01	<0.02	<0.01	<0.01	<0.005	0.01	<0.002	<0.5
7	GK-50 (galena)	0.14	0.2	0.03	0.10	<0.02	<0.005	0.02	<0.01	<0.02	<0.01	<0.01	<0.005	<0.01	<0.002	<0.5
8	GK-70 (galena)	0.11	0.2	0.03	0.14	0.03	<0.005	0.04	<0.01	<0.02	<0.01	0.01	<0.005	<0.01	<0.002	<0.5
9	GK-42 (barite)	0.15	0.2	<0.02	0.19	0.05	<0.005	0.05	<0.01	<0.02	<0.01	<0.01	<0.005	0.10	0.008	1.5
10	GK-50 (barite)	0.15	0.2	<0.02	0.16	0.04	<0.005	0.05	<0.01	<0.02	<0.01	<0.01	<0.005	0.08	0.006	1.4
11	GK-70 (barite)	0.18	0.3	0.02	0.17	0.05	<0.005	0.05	<0.01	<0.02	<0.01	<0.01	<0.005	0.07	0.008	1.4
(*) chondrite x 1000		310	808	122	600	195	73.5	259	47.4	322	71.8	210	32.4	209	32.2	2.10

	Sample No	Hf	Ta	W	Tl	Cu	Zn	Ga	Ge	As	Rb	Sr
1	GK-18 (Oçm)	4.6	1.6	20.5	1.49	<10	42	33	2.0	<5	243	38
2	GK-26 (Oçl)	4.2	0.9	113	0.64	11	<30	12	1.0	<5	92	168
3	GK-30 (Pmbl)	0.9	0.2	14.3	0.31	32	<30	3	<0.5	<5	13	168
3 rep	GK-30 (Pmbl)	0.9	0.2	14.2	0.32	34	<30	3	<0.5	<5	14	176
4	GK-16 (Trçm)	22.8	2.3	437	0.75	<10	38	16	1.3	<5	63	26
5	GK-31 (Pmbd)	0.2	0.1	265	0.08	39	<30	2	0.5	<5	4	74
6	GK-42 (galena)	<0.1	<0.1	0.3	1.32	<10	41	<1	<0.5	<5	<2	11
7	GK-50 (galena)	<0.1	<0.1	0.5	2.08	<10	41	<1	<0.5	<5	<2	6
8	GK-70 (galena)	<0.1	<0.1	0.4	3.97	<10	<30	<1	<0.5	<5	<2	4
9	GK-42 (barite)	<0.1	<0.1	0.2	<0.05	<10	<30	<1	<0.5	<5	<2	5010
10	GK-50 (barite)	<0.1	<0.1	0.3	<0.05	21	<30	<1	<0.5	<5	<2	5840
11	GK-70 (barite)	<0.1	<0.1	<0.2	<0.05	<10	<30	<1	<0.5	<5	<2	4340

	Sample No	Zr	Nb	Mo	Ag	In	Sn	Sb	Cs	Ba	Pb	Bi	Th	U
1	GK-18 (Oçm)	161	20.4	<2	<0.5	<0.1	4	0.9	14.1	1470	12	5.12	16.9	3.14
2	GK-26 (Oçl)	158	10.3	<2	<0.5	<0.1	2	1.4	3.7	364	14	1.37	9.34	1.31
3	GK-30 (Pmbl)	30	2.3	<2	<0.5	<0.1	<1	0.3	0.4	666	24	1.07	2.49	0.55
3 rep	GK-30 (Pmbl)	32	2.4	<2	<0.5	<0.1	<1	0.3	0.4	685	24	1.05	2.49	0.54
4	GK-16 (Trçm)	896	26.4	<2	<0.5	<0.1	3	0.6	3.6	173	20	1.25	17.3	4.03
5	GK-31 (Pmbd)	5	0.6	<2	0.6	<0.1	<1	0.9	0.2	1020	18	0.47	0.63	2.32
6	GK-42 (galena)	<1	<0.5	<2	<0.5	<0.1	<1	<0.2	<0.1	1000	>10000	7.83	<0.05	<0.05
7	GK-50 (galena)	<1	<0.5	<2	<0.5	<0.1	<1	0.2	<0.1	404	>10000	9.74	<0.05	<0.05
8	GK-70 (galena)	<1	0.7	<2	<0.5	<0.1	<1	3.4	0.1	389	>10000	14.7	<0.05	<0.05
9	GK-42 (barite)	<1	0.5	<2	<0.5	<0.1	<1	<0.2	<0.1	>100000	10	0.90	<0.05	<0.05
10	GK-50 (barite)	<1	<0.5	<2	<0.5	<0.1	<1	<0.2	0.1	>100000	<5	0.71	<0.05	<0.05
11	GK-70 (barite)	<1	<0.5	<2	<0.5	<0.1	<1	<0.2	<0.1	>100000	132	0.47	<0.05	<0.05

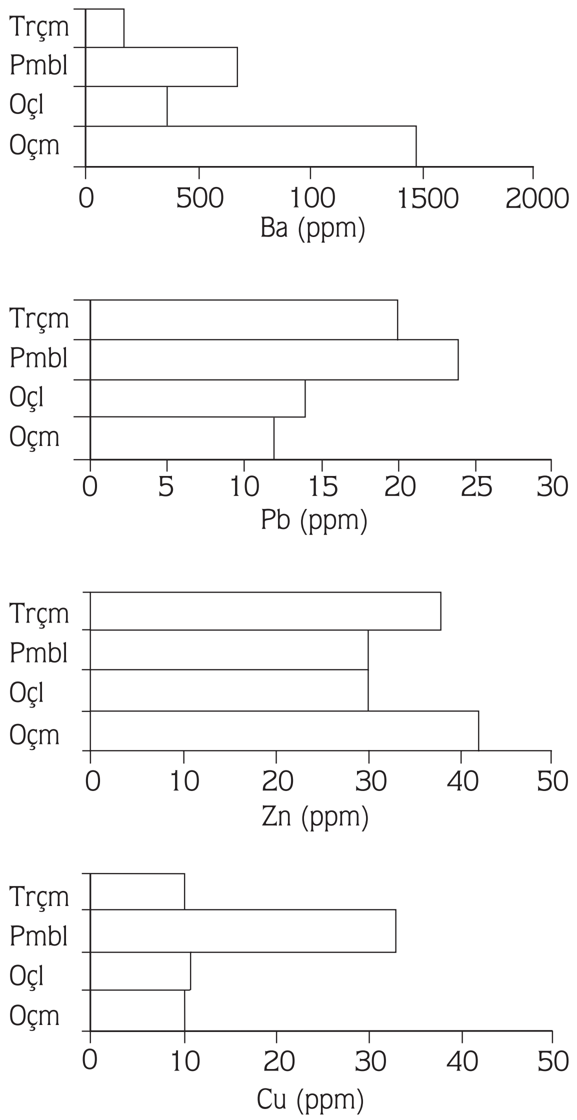

Figure 5. Graphical presentation of trace-element distribution in the lithological units.

The REE results were normalised using the average C1 chondrite abundances of Boynton (1984). The distribution trends are shown as log-normalised REE abundances versus the atomic numbers of the REEs (Figure 6). Because the profiles of the barite and galena samples are quite similar, representative profiles for average values of the three barite and galena samples were prepared. Although Eu values of barite and galena are below detection limits, they are extrapolated as indicating negative Eu anomalies (marked with (?) on Figures 6–8).

In addition, to estimate the environment of formation, the profiles of barite and galena from the study area were compared to those of hydrothermal fluids, precipitates and barite occurrences in other areas (Table 2; Figures 7 & 8). The plot of calculated Ce_N/Sm_N and Ce_N/Yb_N values on an X–Y diagram show the location of the barites and galenas in relation to the possible source materials and mineralising hydrothermal fluids (Figure 9).

Discussion

The major components of the ore veins, Ba and Pb, do not show parallel enrichment. Ba is enriched in mudstones of the Ordovician Çakmak Formation whereas Pb is enriched in limestones of the Permian Bıçkıcı Formation. If the metals were leached from the surrounding rocks by hydrothermal fluids, Ba might have been leached from mudstones of the Ordovician Çakmak Formation whereas Pb from the limestones of the Permian Bıçkıcı Formation.

The REE profiles of samples from the surrounding lithologic units are subparallel with only minor differences (Figure 6). Ordovician (GK-18) and Triassic (GK-16) mudstones have high REE abundances. Ordovician (GK-26) and Permian (GK-30) calcareous rocks show patterns/trends similar to those of the mudstones, but with lower total REE contents. Representative samples from dolomitic zones in the Permian limestone (GK-31) have low REE abundances and more pronounced negative Eu anomalies than the other rock units. Simply, the profiles with negative Eu anomalies and the LREE sections of these profiles are negatively sloped, while the HREE sections are relatively flat – as is common in sediments (McLennan 1989).

The REE abundances of the barite and galena separates are quite low compared to those of the surrounding rocks; in fact, the abundances of Eu, Tb, Dy, Ho, Er and Tm are below the detection limits of the applied analytical method.

The REEs–Y profiles of the average values of the three barite and galena samples are characterised by negative Eu anomalies, however the profiles are not similar to each other. The difference in the shapes of the barite and galena profiles indicates that these two minerals formed from hydrothermal fluids with different compositions.

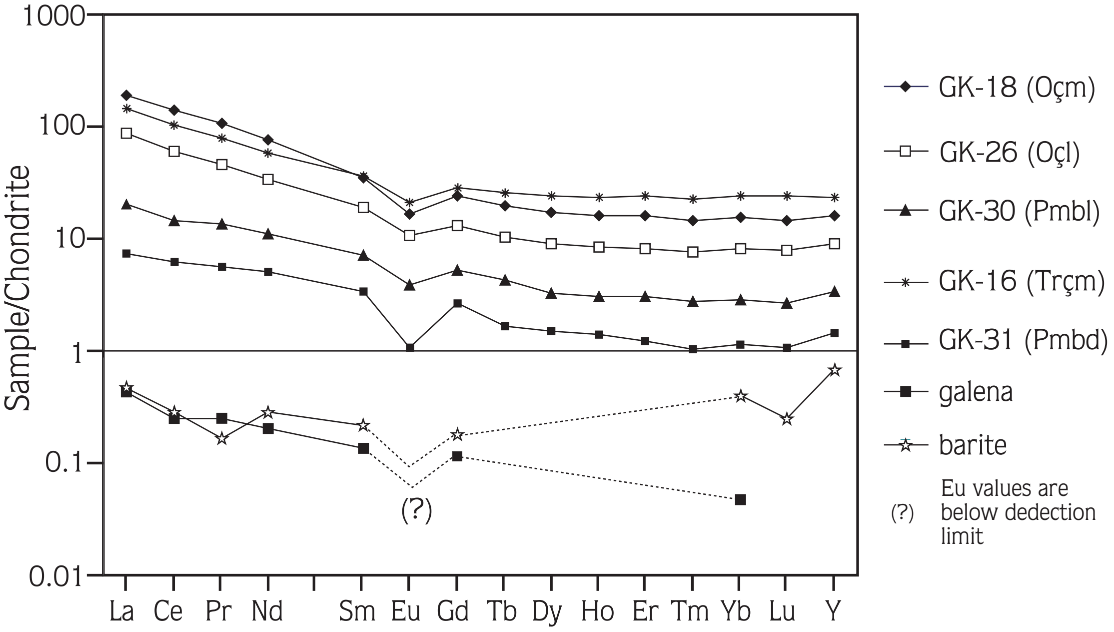

Figure 6. Chondrite-normalised rare-earth element distributions of galena and barite from the Karalar deposit and of surrounding rock units. Oçm– mudstone of the Ordovician Çakmakkaya Formation; Oçl– limestone of the Ordovician Çakmakkaya Formation; Pmbl– limestone of the Permian Bıçkıcı Formation; Trçm– mudstone of the Triassic Çamlıca Formation; Pmbd– dolomitic zones in limestone of the Permian Bıçkıcı Formation; galena and barite from ore veins.

Table 2. REE contents of various barite occurences and hydrothermal systems.

Elements	Seawater (1)	MB2 (1)	MB9 (1)	CB3 (1)	Tibet Average (2)	Bulgaria Average – 1 (2)	Bulgaria Average – 2 (2)	EPR 21 Average (2)	Salton Sea (3)	Chondrite x 1000 (4)
La	3.1	13	143	75	–	–	–	–	–	310.0
Ce	1.2	3.5	309	103	62.5	21.4	46.3	331.5	706	808.0
Pr	0.64	–	12.5	–	–	–	–	–	–	122.0
Nd	2.5	–	–	–	21.5	8.9	16.8	102.5	226	600.0
Sm	0.43	0.38	7.4	0.98	4.65	1.75	3.2	19	22.6	195.0
Eu	0.12	0.1	1.7	0.45	0.3	0.55	0.4	32.5	305	73.5
Gd	0.65	–	–	–	3.5	3.75	2.4	25	25	259.0
Tb	0.14	–	–	–	–	–	–	–	–	47.4
Dy	0.82	0.54	14	1	3.2	5.95	2	19.2	17.3	322.0
Ho	0.22	0.18	5.7	–	–	–	–	–	–	71.8
Er	0.68	–	18	–	2.2	4.1	1.2	11.7	10.6	210.0
Tm	0.15	–	–	–	–	–	–	–	–	32.4
Yb	0.63	–	26	–	2.2	4.2	1.25	13.3	9.33	209.0
Lu	0.17	–	–	–	–	–	–	–	–	32.2
Y	–	–	–	–	–	–	–	–	–	–

References
(1) Guichard *et al.* 1979
(2) Michard & Albarede 1986
(3) Michard 1989
(4) Boynton 1984

Barite Samples
MB2: pelagic barite (central Pacific)
MB9: deeply buried (diagenetic) barite (northeast Pacific)
CB3: hydrothermal vein barite (Sterling, Colorado, USA)

Hydrothermal Fluid Samples
Average of the Tibet AH-9 & AH-35 values
Average of the Bulgaria–1 BU–14 & BU-13 values (pH<7.5)
Average of Bulgaria–2 BU-26. BU-04 BU-21 values (pH>7.5)
EPR21– Average of the East Pasific Rise; 21°N–SW 1149–2.1157–2

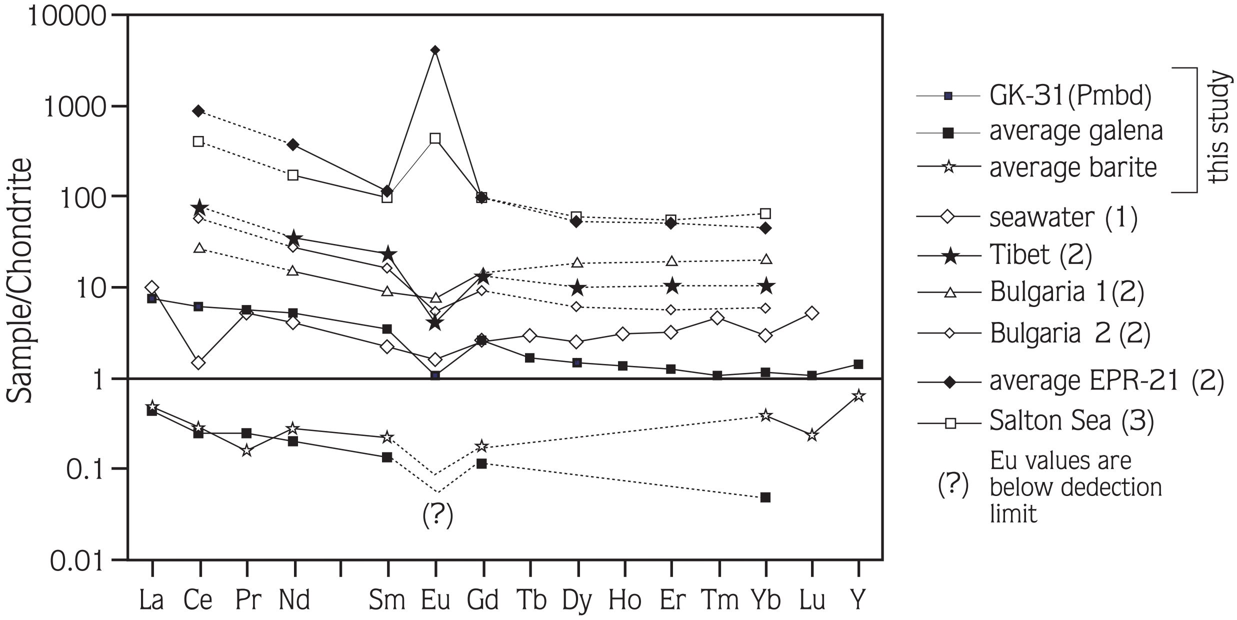

Figure 7. Comparison of the rare-earth element distributions of galena and barite of the Karalar area with various hydrothermal fluids: (1) after Guichard *et al.* (1979), (2) after Michard & Albarade (1986), (3) after Michard (1989). See Figure 6 for symbols and abbreviations.

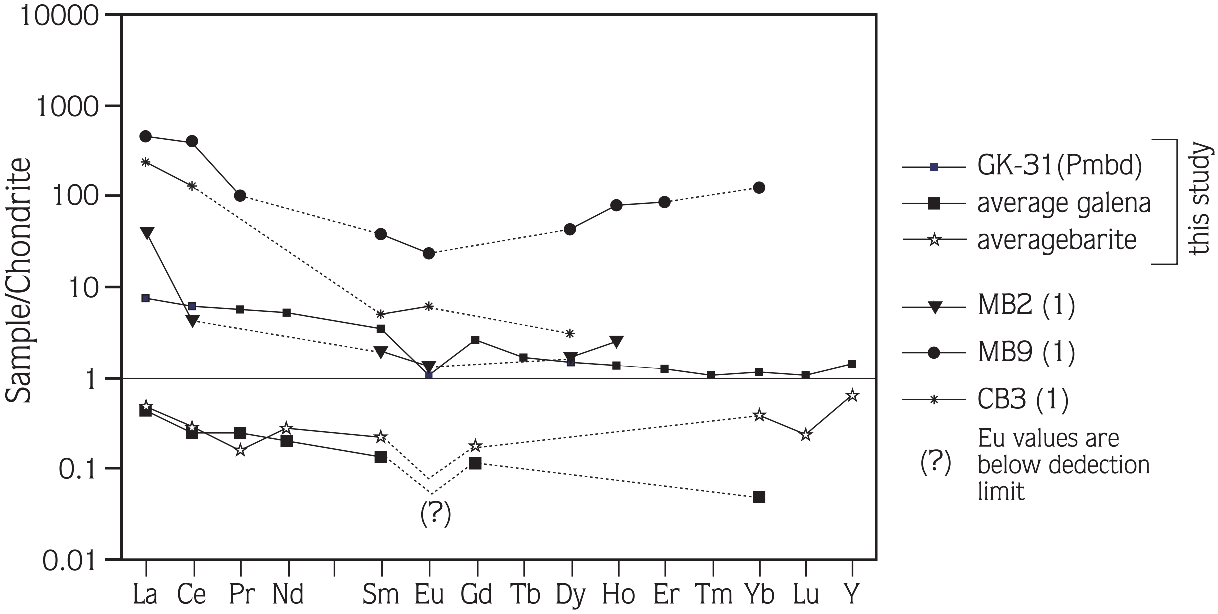

Figure 8. Comparison of rare-earth element distributions of galena and barite of the Karalar area with the various barite occurences; (1) after Guichard *et al.* (1979). See Figure 6 for symbols and abbreviations.

The REEs–Y profile of the average values of the three galena samples is similar to that of the dolomitised zones (GK-31) in Permian Bıçkıcı Formation (Figure 6). This similarity indicates a genetic relationship between dolomitisation and galena mineralisation; most probably the two processes occurred at the same time and possibly with involvement of the same hydrothermal fluid.

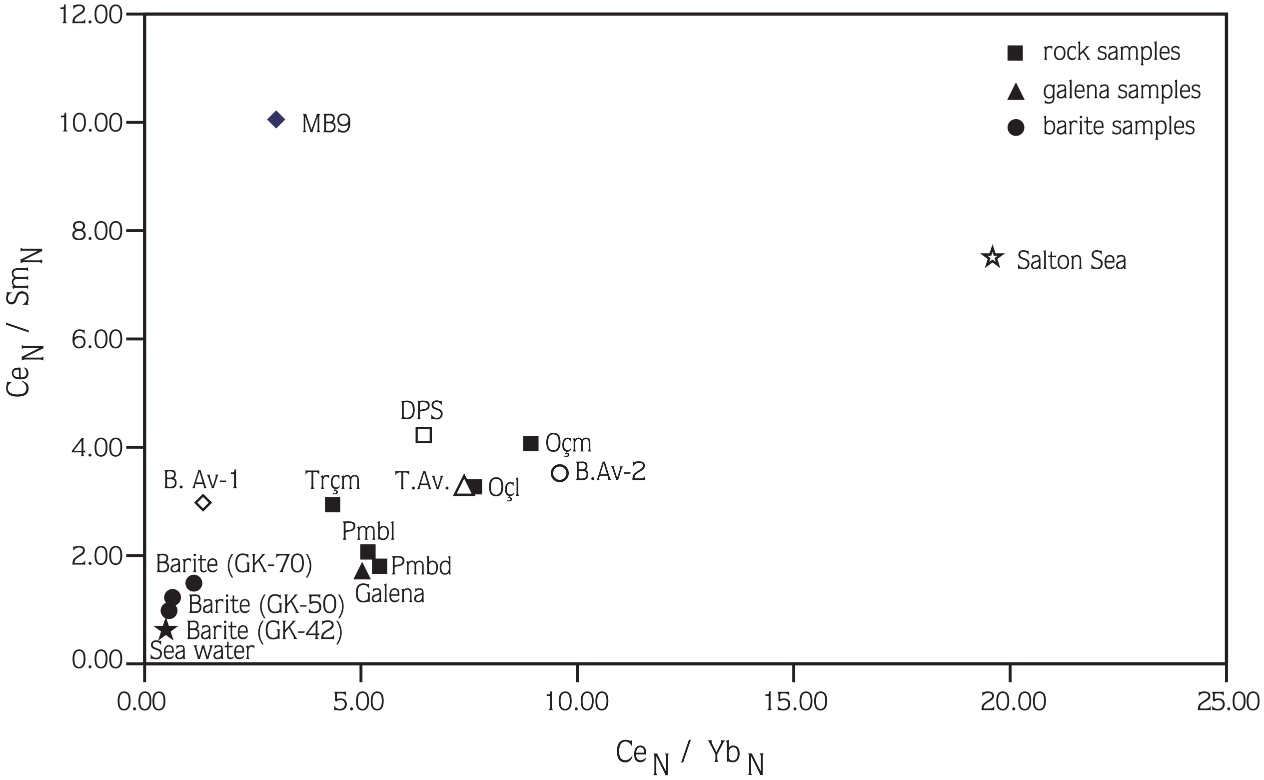

Figure 9. Plot of barite and galena of the Karalar deposits and similar occurences on a Ce_N/Sm_N versus Ce_N/Yb_N diagram. See Figure 6 for symbols and abbreviations.

The REEs-Y profiles of the various hydrothermal fluids and precipitates show different profiles (Figure 7). The REEs-Y composition of seawater is characterised by negative Ce and Eu anomalies, and it has been pointed out that it shows some variations with depth, alkalinity, oxygen, opal and calcium-carbonate contents, input from rivers and hydrothermal vents, and adsorptive scavenging by settling particles (Baar *et al.* 1985; Elderfield 1988). The REEs-Y profiles of hydrothermal sediments around the East Pacific Rise (Michard & Albarede 1986) and hydrothermal fluids from Salton Sea vents (Michard 1989) are characterised by positive Eu anomalies; this constitutes the main difference from other occurrences (Av. EPR-21°N and Salton Sea on Figure 7). Submarine hydrothermal solutions from the EPR-21°N exhibit a significant enrichment in most of the REEs relative to seawater. The patterns are nearly parallel, with pronounced LREE fractionation (Ce/Yb ~ 30) and a positive Eu anomaly (Eu/Eu* ~ 10). In addition, an REE investigation of hydrothermal sediments from the East Pacific Rise at 19°S revealed an REE pattern for the hydrothermal sediments that approaches to that of seawater (with increasing palaeo-distance from the rise crest), and shale-normalised REEs patterns are similar to that of seawater, with the conclusion that the REEs in the hydrothermal component are derived from the interaction of seawater with MORB basalts (Ruhlin & Owen 1986).

The studies of Michard and Albarade (1986) on Bulgarian and Tibetan hot springs and continental geysers showed that hydrothermal solutions from Tibet contain very low total REEs, patterns nearly parallel to those of shales, with LREE enrichments, rather flat HREE distributions and prominent negative Eu anomalies. The REE contents of hydrothermal fluids from Bulgaria are comparable to those with higher pH and lower alkalinity from Tibet; in comparison, the LREEs are markedly less enriched and the HREE less depleted in two samples with lower pH value and higher alkalinities.

When we compare the REEs–Y profile of the average values of the three barite samples with the hydrothermal fluids and precipitates summarised above, it differs from those of the Salton Sea and East Pacific Rise sediments (in being characterised by positive Eu anomalies), but is similar to that of sea water (Figure 7). This similarity may indicate that the barite was deposited by seawater-bearing hydrothermal fluids. It is very difficult to compare the REEs–Y profile of the average values of the three galena samples with any of the hydrothermal fluids plotted on Figure 7.

In addition, the REEs–Y profiles of barites deposited in various environments show different patterns (Figure 8). MB-2, MB-9 and CB-3 barites represent pelagic, deeply buried (diagenetic) and hydrothermal barites, respectively. The profile of the barites from the study area is not similar to those of any mentioned barite occurrences (Figure 8).

The distribution of normalised values on the Ce_N/Sm_N versus Ce_N/Yb_N diagram shows that the values of our barite separates are very close to that of seawater, while the values of our galena separates plot in an area between seawater and Tibetan-type (terrestrial) hydrothermal fluids (Figure 9). These results indicate that barite and galena formation developed from hydrothermal fluids with different characteristics. It may be assumed that barite was deposited by seawater-derived hydrothermal fluid, while galena was deposited by a hydrothermal fluid which was a mixture of seawater and terrestrial fluid, similar to Tibetan hydrothermal fluids.

On the same diagram, the location of barite and galena relative to possible source materials also indicates that the materials which formed these two minerals were derived from different sources. The proximity of galena to limestone of the Permian Bıçkıcı Formation and dolomitised zones in the same unit suggests a genetic link between galena formation and the dolomitisation process/Permian limestone. The proximity of barite to seawater and the distance from other possible source materials suggests that Ba^{++} and $SO_4^{=}$ in the barites were possibly derived from seawater.

Conclusions

Ore-host rock relationships and petrographic studies show that the studied deposits are vein-type deposits – discordant with the bedding surfaces of the host limestones – that developed epigenetically along fault and overthrust zones. These observations point to a mode of ore formation totally different from that of typical stratiform and strata-bound type occurrences as documented in some earlier studies (Striebel 1965; Şenel 1977; Sadıklar 1978, 1983; Sadıklar & Amstutz 1981; Ayhan 1979, 1981, 1982; Gülseren 1987; Çopuroğlu 1994).

The results of our trace-element study suggest that Ba and Pb were derived from different sources. If the metals were leached from the surrounding rocks by hydrothermal fluids, Ba may have been leached from mudstones of the Ordovician Çakmak Formation, whereas Pb may have been leached from limestones of the Permian Bıçkıcı Formation.

Although it is unwise to rely unequivocally on the REEs–Y profiles, it may be argued that the hydrothermal fluids which produced the Karalar deposits were different from those of the Salton Sea and East Pacific Rise sediments, and from pelagic and diagenetic barites. However, they may have been similar to seawater, and this slight similarity may indicate that the barite was deposited by seawater-bearing hydrothermal fluids. In addition, the close similarity of the galena profile to dolomitised limestone suggests a genetic relationship between galena mineralisation and dolomitisation.

The scatter plots of the barite (close to seawater) and galena (in an area between seawater and Tibetan hydrothermal fluid) in different areas on the Ce_N/Sm_N versus Ce_N/Yb_N diagram support the possibility that these minerals formed by hydrothermal fluids with different characteristics; barite formed from seawater-bearing hydrothermal fluids while galena formed from a mixture of seawater and Tibetan-type (terrestrial) hydrothermal fluids.

The locations of barite and galena on the same diagram also indicate that the materials which yielded these two minerals were derived from different sources. The proximity of galena to limestone of the Permian Bıçkıcı Formation and dolomitised zones in the same unit suggest a genetic relationship between galena and dolomitisation processes/Permian limestone. The close proximity of barite to seawater and the great separation from other possible sources suggests that Ba^{++} and $SO_4^{=}$ to produce barite possibly were derived from seawater.

These results suggest that the galena-bearing barite deposits of the Karalar area are vein-type deposits and that barite and galena developed from hydrothermal fluids having different characteristics; it is reasonable to suggest that seawater dominated barite deposition while a mixture of seawater and Tibetan-type (terrestrial) hydrothermal fluid was available during galena deposition. Ba was either concentrated from seawater or leached from mudstones of the Ordovician Çakmak Formation, and Pb was probably leached from limestones of the Permian Bıçkıcı Formation. Barite was deposited during the early stages of mineralisation while galena was deposited during the later stages of mineralisation.

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