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Geochemical evaluation of the genetic relationship of Kısacık (Ayvacık, Çanakkale/Türkiye) epithermal gold mineralization using trace and rare earth elements

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Abstract

The Kısacık gold deposit is situated in the Biga Peninsula, Northwest Anatolia, Türkiye. The aim of this study is to investigate the genetic relationship between the Kısacık gold deposit and the surrounding rocks using trace element (TE) and rare earth element (REE) geochemistry. For this purpose, 48 samples directly and/or indirectly associated with the mineralization in the area were analyzed for major oxides, trace, and rare earth elements using inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS). Considering the laboratory conditions under which the analyses were performed, the limit of detection (LOD) values for metals varied between 0.01 and 0.04%, while those given in parts per million (ppm) varied between 0.002 and 0.1 ppm. In addition, the relative standard deviations (RSD) for all metals ranged from 0.38 to 5.52%. The results of the study revealed that the gold mineralizations in the Kısacık area have a compatible pattern with the Kısacık Volcanics and the Kuşçayırı plutonic rocks in the near vicinity of the area. The gold mineralizations in the Kısacık area are consistent with the TE and REE patterns of the upper continental and lower continental crust, as shown by comparison with spider diagrams normalized to different geological settings. The gold enrichments in the listvenites and silicified rocks in the area are also consistent with the TE and REE element patterns of these rock types. The results of this study support the conclusion that the gold mineralization in the Kısacık area is related to hydrothermal fluids that leached elements from the Kısacık volcanics. In addition, hydrothermal fluids from granitic rocks were also effective in the mineralization process. As a result, the gold mineralization in the Kısacık area is genetically related to both the upper continental crust and relatively the lower continental crust and is characterized as a multi-sourced and multi-process epithermal gold deposit.

Keywords: Kısacık epithermal gold mineralization, Trace-Rare Earth elements, Spider diagrams, Çanakkale, Türkiye

1. Introduction

Epithermal gold deposits are a type of gold mineralization that forms near the surface of the Earth due to the action of hydrothermal fluids. These fluids are heated by magmatic activity and can travel through fractures in rocks, dissolving and transporting minerals [1]. Trace elements (TEs) and rare earth elements (REEs) are often enriched in epithermal gold deposits, and their presence can provide valuable clues about the formation and potential richness of these deposits [2]. The geochemical behavior of TEs and REEs is an important factor in their association with epithermal gold deposits. These elements are typically found in minerals that dissolve easily in hydrothermal fluids, such as feldspars, micas, amphiboles, and pyroxenes. Once dissolved, TEs and REEs can be transported by hydrothermal fluids over long distances. During ore formation, hydrothermal fluids cool, and pressure drops, causing the dissolved minerals to precipitate and form new minerals. TEs and REEs are often incorporated into these newly formed minerals, leading to their enrichment in epithermal gold mineralization. TEs and REEs are also found in a wide variety of rocks, but they are particularly abundant in volcanic rocks. This is because volcanic rocks are formed from molten magma, which contains high concentrations of these kinds of elements. When hydrothermal fluids interact with volcanic rocks, they dissolve TEs and REEs and carry them away. These elements can then be transported to sites of epithermal gold deposition [3,4]. They (TEs and REEs) can be used to trace the movement of hydrothermal fluids through the rocks and to identify the different types of alteration that have occurred, including propylitic, argillic, and

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adularia-sericite alteration. This information can be used to better understand the formation of epithermal gold deposits and to identify potential exploration targets. The relationship between TEs and REEs, and epithermal gold deposits has several important implications for understanding of their genetic characteristics, and their exploration and evaluation. For example, the presence of these elements can be used to:

- Identify areas that have the potential to host epithermal gold deposits.
- Trace the movement of hydrothermal fluids and identify potential ore zones.
- Assess the potential richness of epithermal gold deposits.

By understanding the geochemical behavior of TEs and REEs, geologists can use these elements as valuable tools for exploring and evaluating epithermal gold deposits.

In addition to the factors discussed above, several other considerations are important when interpreting the relationship between TEs and REEs, and epithermal gold deposits. These include:

- The type of epithermal gold deposit (high-sulfidation, low-sulfidation, intermediate-sulfidation),
- The mineralogy of the deposit,
- The geological setting of the deposit.

So, trace and REEs are valuable indicators of epithermal gold deposits. Their chemical behavior, origin in rocks, and relationships with alteration in the field provide important clues about the formation and potential richness of these deposits.

Anatolia's strategic location and rich natural resources were key factors in its emergence as a cradle of civilizations in antiquity. The Biga Peninsula, located in the northwest of Western Anatolia, has been one of the most important mining regions in the Anatolian geography, both today and in the past [5]. The rich mineral potential of the region has triggered numerous studies in the fields of general geology and mining geology [6,7, 8–15,16–21]. The region is characterized by a diverse array of mineral deposits, evidenced by numerous abandoned mine workings and ongoing mining operations. These deposits, encompassing copper, lead, zinc, iron, gold, tungsten, molybdenum, antimony, and mercury, reflect the region's complex geological history, shaped by multiple phases of granite intrusions and volcanic activities that have resulted in a variety of mineralization styles. Mineral exploration activities continue in the region, conducted by both the Turkish Geological Survey (MTA) and numerous domestic and foreign private companies. One of the most recent discoveries made under an MTA-led exploration project is the Kısacık gold deposit [14,22]. The Kısacık gold mineralization area is situated at Ayvacık-Çanakkale, Biga Peninsula, Northwest Anatolia (Türkiye).

The aim of this study is to contribute to the understanding of the genetic relationship of the Kısacık (Ayvacık, Çanakkale, Türkiye) epithermal gold deposit using TEs and REEs. To this end, the relationship between the deposit, wall rock, and source rock was investigated by using TEs and REEs patterns of the deposit, alteration, and surrounding rocks, as well as rocks that are thought to have influenced the potential mineralization process.

2. MATERIAL AND METHODS

2.1. Geological characteristics of the area

The Biga Peninsula, located in Northwest Anatolia, Türkiye, is home to a diverse array of geological units (Fig. 1) [15,22], including pre-Tertiary, Tertiary, and post-Tertiary rocks [23]. The pre-Tertiary units of the Biga Peninsula, Northwest Türkiye, were subdivided into three distinct tectonic zones by Okay et al. [23]: the Sakarya Tectonic Zone, the Ayvacık-Karabiga Zone, and the Ezine Zone, extending from northwest to southeast. The Sakarya Tectonic Zone is principally composed of the Kazdağ Group metamorphic rocks and the Karakaya Complex [24], overlying these metamorphic rocks and post-Triassic sediments. The Ayvacık-Karabiga Zone is characterized by an ophiolitic mélange, the Çetmi Ophiolitic Mélange. Eclogite blocks and Upper Triassic limestone blocks within the mélange are distinctive features of the Ayvacık-Karabiga Zone. The Ezine Zone comprises continental-derived rocks, including a Permo-Carboniferous sedimentary sequence, the Karadag Unit, metamorphosed under greenschist facies conditions, and an overlying ophiolite, the Denizgören Ophiolite, emplaced during the Permo-Triassic period in the western portion of the zone. Additionally, the Ezine Zone contains high-grade metamorphic rocks of sedimentary origin, the Çamlıca Mica schist [6,22,23].

The Tertiary and Post-Tertiary units in the region encompass magmatic and sedimentary rocks, commencing with middle Eocene neritic limestone. This is followed by Upper Eocene turbidites, interbedded andesite, and andesitic tuff, which concordantly overlie the neritic limestone. Volcanic rocks in the near vicinity of the study area were named Kuşçayır and Kısacık volcanics, respectively, based on their age differences. The older volcanics, which outcrop in the north, are named Kuşçayır volcanics, while the younger volcanics, which outcrop in the south, are named Kısacık volcanics. Eocene (?)/Oligo-Miocene calc-alkaline magmatism subsequently commenced in the region, marked by a disconformity plane [25–29]. Magmatic activity spanned

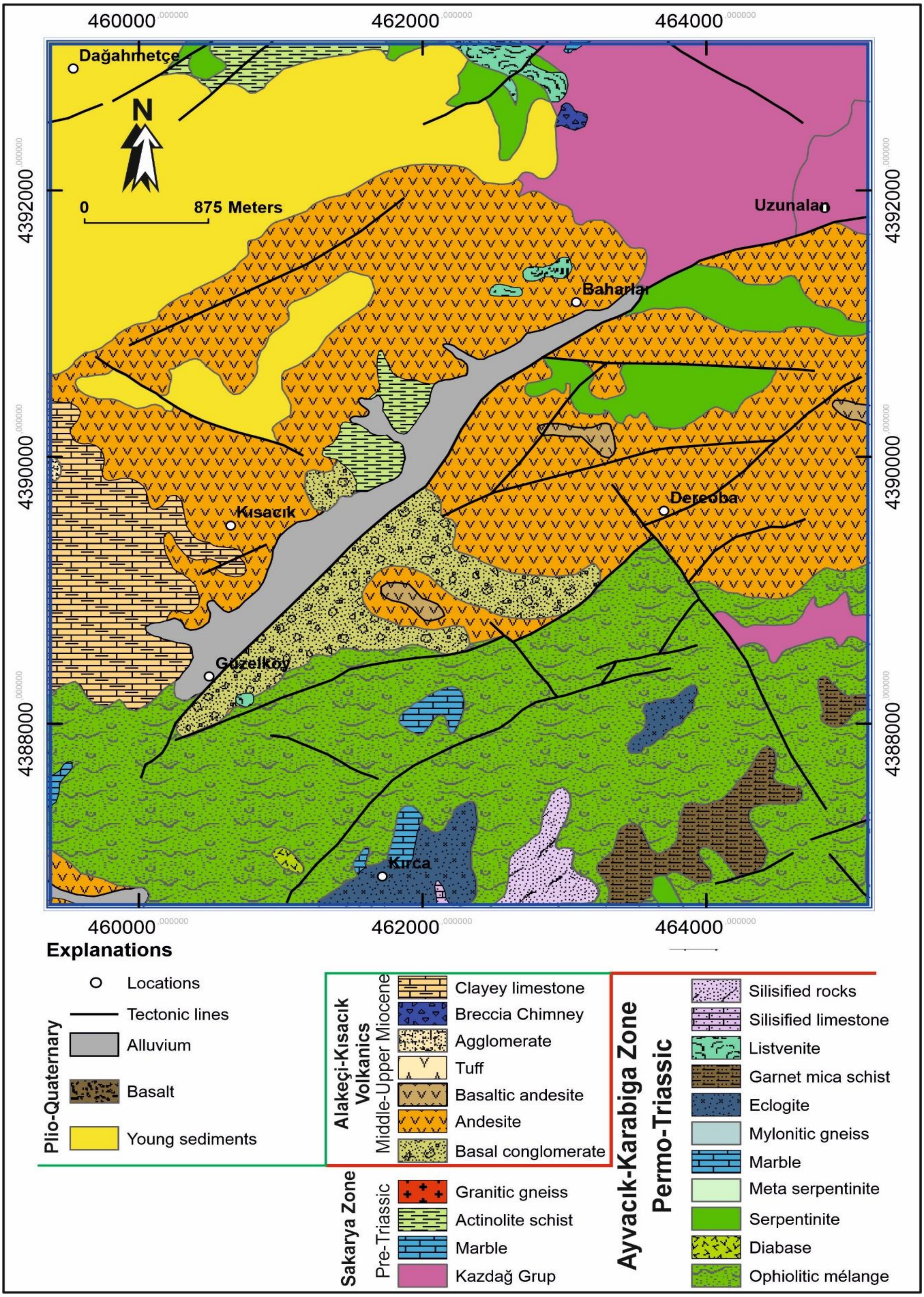

Figure 1. Geology of the study area

the Eocene (?)/Oligocene to Upper Pliocene Quaternary (?) period, encompassing plutonic and volcanic rocks along with their associated pyroclastics [22,30]. Notably, dacite, andesite, rhyolite, and acidic tuffs are exposed, often interbedded with sedimentary rocks containing coal in some areas. Sedimentary rocks, primarily lacustrine and terrestrial clastics, are found in Upper Miocene-Pliocene age terrains, and Quaternary alluvium is also present.

Granitic rocks are present outside the study area, in its northern part. Volcanic rocks, collectively known as the Kısacık volcanics [22], occur within the study area and exhibit varying degrees of alteration, including hematization and silicification. These rocks predominantly comprise andesite, latite, rhyolite, basaltic andesite, ignimbrite, basaltic trachyandesite lavas, and pyroclastic rocks. Lateral transitions between these volcanic rocks and fluvial conglomerates, as well as lacustrine sedimentary rocks, are observed. Geochronological studies by Siyako et al. [26] and Genç [29] indicate that these volcanic rocks belong to the Early-Middle Miocene period. Basalt, the youngest manifestation of magmatism in the region, is found in the western vicinity of the study area.

Known anomalous areas in the study area and its vicinity have been identified in the lisvenitic zones north of the Kısacık ore field and in the veins and fractures of altered volcanic rocks in the southern part of the field. Hydrothermal alteration is widespread in the volcanic rocks in the Kısacık epithermal ore field and its vicinity.

A few samples from the Kısacık area analyzed for heavy mineral geochemistry by Pehlivan et al. [31] yielded Au values ranging from 60 ppb to 1100 ppb. In the study conducted by the principal investigator during his doctoral dissertation at the Kısacık gold field, the volcanic rocks were found to be extensively cut by capillary silica veins. Sericitic hydrothermal alteration was widespread in the volcanic rocks of the ore field, and hematitization and limonitization accompanied this alteration and mineralization.

In a study of the Kısacık gold ore field conducted by the corresponding author, Vural [22], it was determined that the formation temperatures of the orebodies ranged from 190 °C to 290 °C based on fluid inclusion studies. The salinity was found to be 0-7% NaCl equivalent, and sulfur isotope values were mostly close to zero. Therefore, it was proposed that the gold mineralization in the field is of the epithermal type.

2.2. Sampling and analytical procedure

As part of the mine geology study of the area, a detailed geology and mine geology map of the area was prepared. Observations were carried out to reveal the details of the mine geology of the area, and rock samples were collected for geochemical purposes, considering the sections where alteration and silicification are present. In addition to geochemical samples, petrographic samples were collected to reveal the geology and lithology of the area, XRD samples to identify alteration, and ore microprobe samples to identify ore minerals. Petrographic studies were used to determine the rocks in the area, thus revealing the geology of the area. The results of these studies in detailed will be presented in a separate mine geology study of the region.

To elucidate the genetic relationship between the orebodies and the mineralization in the area, a total of 48 samples were collected from both orebodies and associated rocks (host rock, wall rock, and associated rocks). These samples were ground at the Gümüşhane University Central Laboratory and the MTA Laboratory before being sent to the ACME Analytical laboratory (Vancouver, Canada) for whole-rock major oxide, trace element (including heavy metals), and rare earth element (REE) analyses. Major oxide and trace element (including heavy metals) analyses were performed using inductively coupled plasma-atomic emission spectrometry (ICP-AES), while rare earth element (REE) analyses were performed using inductively coupled plasma-mass spectrometry (ICP-MS) at ACME Analytical Laboratories (Vancouver, Canada). The laboratory is accredited, and all analyses were conducted in accordance with international standards. To ensure the accuracy and sensitivity of the analyses, routine procedures were followed, and a t-test was performed to confirm that the certified values used during the analysis and the values obtained were statistically indistinguishable ($p \leq 0.05$) [32].

For major and trace element/heavy metal analyses, approximately 0.2 g of powdered sample was mixed with 1.5 g of $LiBO_2$ and analyzed after dissolving it in a solution containing 5% HNO_3. For rare earth element analysis, approximately 0.25 g of powdered sample was dissolved in four different acids and analyzed.

After the acidic solutions of the samples solubilized by the wet digestion method were obtained, they were measured in ICP-AES and ICP-MS devices. The measured values were converted into ppm and % units with the help of the formulas given in Equation 1 and Equation 2.

$$ppm = \frac{C \times V}{m} \quad (1)$$

$$\% = \frac{ppm}{10000} \quad (2)$$

ppm: part per million (mg/kg)

C: Concentration measured in mg/L by ICP-AES and ICP-MS

V : Final volume completed after wet digestion (mL)

m : Mass of sample weighed for wet digestion (g)

Table 1. The analysis results of the samples from the study area (1)

Analyte	K_2O	TiO_2	P_2O_5	Cr_2O_3	Ba	Sum	Ni	Rb	Sr	Y	Zr	Nb	Cs	La	Ce
Unit	%	%	%	%	*ppm*	%	*ppm*	*ppm*	*ppm*	*ppm*	*ppm*	*ppm*	*ppm*	*ppm*	*ppm*
Sample/ LOD	**0.01**	**0.01**	**0.01**	**0.0001**	**1.0**	**0.01**	**20.0**	**0.1**	**0.5**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**
Kıs20	3.35	0.13	0.03	0.001	271.7	100.01	1.8	96.1	50.1	12.7	77.9	10.6	3.4	29.2	52.2
BayG-1	4.37	0.21	0.06	0.001	1251	99.81	13.2	168.8	614.1	6.4	187.4	10.4	1.8	37.9	76.9
BayG-2	2.80	0.59	0.18	0.001	622.2	99.89	4.8	97.5	557.2	21.1	117.8	6.4	3.0	27.5	54.1
BayG-3	2.80	0.61	0.15	0.002	434.7	99.95	6.1	106.2	342.9	21.1	127.2	6.4	8.2	24.3	47.9
Kusvol-1	1.44	0.68	0.15	0.001	400.2	99.80	15.2	43.9	391.2	21.7	114.1	5.9	2.2	16.1	29.7
Kıs21	2.82	0.76	0.19	0.002	630.0	99.91	11.2	101.3	174.1	24.3	92.9	11.2	9.9	31.8	57.6
Ter1	0.28	0.04	0.21	0.076	46.3	100.0	35.8	9.9	176.7	2.6	11.3	3.4	3.5	2.8	7.7
Kusvol-2	1.94	0.48	0.14	0.003	378.7	99.81	17.1	62.3	384.4	14.6	114.5	4.9	3.2	18.9	37.2
Lis1	0.34	0.03	0.01	0.253	92.0	99.90	1227.1	10.5	71.7	1.7	6.7	0.9	1.4	1.7	3.1
Kıs1	2.93	0.11	0.02	0.001	191.4	100.0	2.3	83.1	25.8	11.7	67.8	7.8	3.8	21.1	36.2
Kıs4	5.98	0.50	0.10	0.002	487.4	99.95	8.7	190.0	23.4	18.7	131.2	7.9	12.2	20.9	42.9
Lis2	0.05	0.01	0.01	0.131	50.5	99.86	410.1	2.4	662.1	0.9	0.8		1.0		0.9
Kar1	0.17	0.01	0.01	0.001	145.1	100.0	12.1	13.5	20.5	3.7		2.6	8.1	0.8	1.5
Kar2	1.96	0.44	0.15	0.001	591.4	99.78	5.7	80.6	426.6	17.4	133.3	7.5	7.8	27.1	50.2
Kar3	0.14	0.01	0.11	0.001	259.3	99.91	21.3	0.7	357.2	0.4	3.0	1.5	0.3	2.1	4.3
BayG-4	2.51	0.60				99.55								28.7	
Kusvol-3	3.00	0.80				99.25	20.1								
Kusvol-4	3.22	0.78				99.07	20.2								
Kusvol-5	2.90	0.80				98.20	20.3								
Kusvol-6	2.95	0.88				99.09	19.2							36.7	
Kıs21	4.66	0.45				99.66	9.1								
Kıs22	3.39	1.11				99.07	39.4								
Kıs23	3.22	1.06				98.44	24.3								
Kıs24	3.36	0.81				98.43	20.2							71.5	
BayG-5	5.49	0.26				100.3								63.3	
BayG-6	3.02	0.67				100.4								34.2	
BayG-7	3.06	0.81				100.3								35.1	
BayG-8	3.29	0.52				99.32	5.0								
BayG-9	2.80	0.55				99.03									
Kıs2	2.85	0.10	0.04	0.002	228.2	100.0	8.0	86.0	71.6	9.2	49.0	5.0	3.6	14.2	26.3
Kıs3	1.38	0.17	0.11	0.001	106.0	100.0	0.2	56.6	42.3	7.6	57.7	3.5	9.4	11.8	23.5
Kıs5	1.82	0.11	0.04	0.003	200.3	100.0	7.5	62.6	72.0	3.6	30.6	3.7	7.5	4.7	10.1
Kıs6	5.38	0.37	0.15	0.001	988.9	99.87	2.7	147.8	68.0	24.6	176.0	10.1	3.2	41.3	79.8
Kıs7	0.04	0.01	0.02	0.120	26.9	100.0	633.1	1.1	133.4	0.5	1.3	1.6	0.5		
Kıs8	0.03		0.01	0.113	22.1	99.96	643.2	0.7	120.7	0.4	1.4	1.7	0.4	0.6	0.3
Kıs9	4.77	0.52	0.25	0.012	1114.3	99.81	37.3	166.5	453.8	14.2	216.1	9.8	3.3	45.5	77.9
Kıs10	5.80	0.57	0.16	0.010	657.2	99.79	8.0	293.3	165.6	19.7	271.2	18.2	50.3	53.5	89.6
Kıs11	3.30	2.31	0.50	0.022	1607.1	99.63	17.0	163.6	318.2	35.5	437.8	20.0	20.7	103.6	203.8
Kıs12	2.95	0.16	0.03	0.012	267.3	99.96	2.5	82.7	27.2	13.3	87.8	12.6	4.1	21.7	33.3
Kıs13	5.58	0.48	0.14	0.009	532.4	99.88	2.5	173.7	248.3	22.6	180.8	15.7	6.2	43.2	73.6
Kıs14	6.39	0.44	0.07	0.009	946.3	99.88	4.8	184.2	146.0	22.7	179.5	9.4	6.1	32.7	62.3
Kıs15	2.14	0.17	0.03	0.021	117.2	99.95	22.4	69.2	34.0	12.8	94.9	11	4.0	25.9	44.6
Kıs16	2.83	0.77	0.18	0.003	747.4	99.84	10.8	97.2	157.6	21.9	94.3	11.8	8.8	31.4	52.2
Kıs17	2.03	0.12	0.03	0.003	202.1	99.98	7.1	58.5	63.6	3.2	33.1	3.8	6.5	5.1	9.3
Kıs19	3.26	0.13	0.03		241.2	99.96	1.7	85.9	42.1	10.9	74.6	10.1	2.6	27.6	43.3
Lis3	0.04	0.02	0.04	0.320		99.93		26.9	0.4	1.2	0.3	1.4	102	0.4	
Lis4	0.08	0.03	0.02	0.254		99.94		39.5	0.6	5.2	0.2	0.8	18.2	1.7	0.2
Lis5	0.01	0.01	0.02	0.142		99.95	1.3	16.2	0.3	3.3	0.9	1.3	11.1	0.7	

Table 2. The analysis results of the samples from the study area (2)

Analyte	Hf	Ta	Au	Pb	Th	U	Lu	Yb	Tm	Er	Ho	Dy	Tb	Gd	Eu	Sm	Nd	Pr
Unit	*ppm*	*ppm*	*ppb*	*Ppm*	*ppm*	*ppm*	*ppm*	*ppm*	*ppm*	*ppm*	*ppm*	*ppm*	*ppm*	*ppm*	*ppm*	*ppm*	*ppm*	*ppm*
Sample /LOD	**0.1**	**0.1**	**0.5**	**0.1**	**0.2**	**0.1**	**0.01**	**0.05**	**0.01**	**0.03**	**0.02**	**0.05**	**0.01**	**0.05**	**0.02**	**0.05**	**0.3**	**0.02**
Kıs20	3.1	1.1	3.6	7.1	27.1	3.5	0.27	1.74	0.22	1.32	0.36	1.75	0.24	1.39	0.27	2.10	13.9	4.70
BayG-1	5.5	1.2	0.8	11.3	30.3	4.5	0.11	0.62	0.09	0.61	0.22	1.12	0.23	1.57	0.73	3.31	22.4	6.83
BayG-2	3.3	0.6	1.5	6.6	14.9	3.4	0.32	2.13	0.30	2.12	0.69	3.41	0.64	3.75	1.21	4.62	23.3	5.87
BayG-3	3.7	0.6	4.1	9.4	10.3	3.4	0.35	2.22	0.31	2.27	0.70	3.65	0.63	3.86	1.04	4.10	20.1	5.20
Kusvl1	3.0	0.6	1.3	2.6	9.1	2.6	0.36	2.26	0.32	2.25	0.81	3.86	0.61	3.63	1.07	3.43	15.5	3.86
Kıs21	2.5	0.7	106.5	9.7	7.0	1.0	0.42	2.61	0.38	2.66	0.87	4.21	0.72	4.31	1.16	4.31	21.9	5.94
Ter1		0.4	9470.5	22.0	0.9	2.1	0.04	0.25		0.28	0.11	0.46	0.09	0.44	0.16	0.60	4.0	1.15
Kusvl2	2.8	0.5	4.5	8.8	7.5	2.8	0.22	1.53	0.23	1.45	0.51	2.44	0.44	2.60	0.94	3.10	16.2	4.08
Lis1			20.8	1.2	1.8	0.6	0.03	0.17		0.17		0.25	0.04	0.20		0.20	1.0	0.32
Kıs1	2.4	0.7	14.1	4.9	18.6	3.5	0.22	1.43	0.20	1.19	0.36	1.66	0.25	1.26	0.32	1.62	10.1	3.14
Kıs4	3.8	0.6	6922.8	38.7	11.5	4.9	0.26	2.12	0.33	1.93	0.67	3.45	0.55	3.34	0.99	3.71	18.9	4.74
Lis2			12.0	3.3	0.2			0.09		0.08		0.14	0.02	0.06		0.11		0.10
Kar1			1592.1	3.7	0.3	0.2	0.05	0.31	0.07	0.37	0.11	0.39	0.04	0.34	0.06	0.22	1.0	0.22
Kar2	3.7	0.6		8.8	10.9	3.3	0.27	1.68	0.28	1.83	0.61	3.02	0.49	2.92	0.98	4.01	19.9	5.53
Kar3			8412.0	149.7	1.7	0.4						0.13	0.04	0.32	0.06	0.33	1.6	0.48
BayG-4		0.6		14.0		2.2		1.77									20.2	
Kusvl3																		
Kusvl4																		
Kusvl5																		
Kusvl6		0.5		22.0		4.9		3.05									34.4	
Kıs21																		
Kıs22																		
Kıs23																		
Kıs24		0.8		44.0		5.2		1.63									49.8	
BayG-5		1.9						0.88									30.2	
BayG-6		1.0						2.88									40.3	
BayG-7		0.9						1.87									29.3	
BayG-8																		
BayG-9																		
Kıs2	1.5	0.7	1690.5	6.5	12.2	2.7	0.17	1.02	0.16	0.93	0.29	1.36	0.26	1.30	0.38	1.61	8.3	2.53
Kıs3	1.7	0.5	1188.1	15.3	8.6	1.8	0.13	0.87	0.14	0.81	0.26	1.32	0.23	1.13	0.36	1.61	9.3	2.46
Kıs5	0.8	0.2	189.9	6.2	2.8	1.4	0.05	0.37		0.41	0.13	0.61	0.10	0.54	0.20	0.82	4.4	1.06
Kıs6	4.9	0.9	68.7	34.6	19.2	4.5	0.39	2.22	0.40	2.54	0.81	3.94	0.66	4.18	1.16	5.30	30.7	8.29
Kıs7			140.9	1.9		0.1						0.08	0.01	0.09				0.05
Kıs8			207.1	1.3		0.1				0.03				0.06				0.04
Kıs9	4.9	0.6	15.9	23.2	17.8	3.5	0.26	1.67	0.25	1.54	0.53	2.49	0.47	3.19	1.05	4.29	27.1	8.22
Kıs10	7.7	1.4	20.4	60.4	43.3	6.4	0.36	2.31	0.34	2.05	0.75	3.70	0.66	4.82	1.40	6.01	36.5	10.31
Kıs11	10.4	1.2	7.6	47.9	37.9	10.1	0.50	3.30	0.54	3.71	1.31	7.49	1.56	12.31	3.44	18.22	102.3	26.62
Kıs12	3.3	1.0	5.5	13.9	26.6	4.4	0.33	1.88	0.26	1.49	0.43	1.80	0.25	1.39	0.21	1.38	9.6	3.08
Kıs13	5.2	1.3	0.7	11.0	29.7	8.1	0.47	2.83	0.41	2.60	0.83	3.67	0.63	4.10	1.09	4.75	27.8	8.24
Kıs14	4.5	0.7	42.5	33.3	16.8	3.8	0.40	2.56	0.37	2.57	0.86	4.00	0.70	4.11	1.04	4.87	26.9	7.29
Kıs15	3.3	0.9	9.0	10.5	27.2	5.4	0.29	1.69	0.25	1.40	0.44	1.83	0.31	1.98	0.42	2.04	13.0	4.33
Kıs16	2.5	0.6	154.8	9.0	5.9	0.8	0.37	2.53	0.38	2.40	0.87	3.86	0.63	3.93	1.07	3.80	20.2	5.56
Kıs17	0.9	0.1	376.5	6.4	2.7	1.5	0.06	0.34	0.05	0.34	0.11	0.56	0.10	0.64	0.16	0.73	4.2	1.07
Kıs19	2.6	0.9	4.6	6.0	24.3	3.2	0.25	1.52	0.21	1.15	0.35	1.46	0.23	1.44	0.26	1.65	12.2	4.11
Lis3		1.5	0.7		0.2		0.08		0.04		0.05		0.06				0.1	61.10
Lis4		0.9	0.4				0.06		0.06		0.12		0.14	0.05	0.13	0.70	0.2	25.20
Lis5		2.0	0.5		0.1		0.05						0.05		0.11	0.30	0.1	11.01

Metal and metal oxides results measured by ICP-MS and ICP-AES at ACME Analytical Laboratory are given in Table 1 and Table 2. For geological considerations, the results for K, Ti, P and Cr metals are given by converting them into their oxides. Some cells in the tables are blank because the relevant metal contents of some samples were either not measured, or their values were below the LOD (Limit of detection).

The precision of the method was evaluated by calculating the relative standard deviation (RSD). The LOD values for metals metal oxides given in percentage units in Table 1 and Table 2, vary between 0.01–0.04%, while those given in ppm vary between 0.002–0.1 ppm. In addition, the relative standard deviations (RSD) for all metals and metal oxides ranged from 0.38–5.52% (Table 1 and Table 2). The accuracy of the method was verified by analyzing standard reference materials.

2.3. Evaluation of the data

The genetic characteristics of the gold mineralization in the Kısacık area were investigated using trace and rare earth elements (REE) in this study. The results of the previous genetic studies, which were conducted by the corresponding author as part of his doctoral dissertation, will be presented in a separate study. This study aims to verify the results of the previous studies and contribute to the understanding of the genesis of the gold mineralization in the area.

The rocks in the area, especially those that are thought to be associated with magmatism, were identified through field observations and mine geology studies. In this context, analyses of major oxides, TEs, REE, and metals were performed on samples from boreholes drilled by the MTA in the area, from sections with high gold anomalies, and from magmatic and other relevant rocks. Spider diagrams proposed by different researchers [33–36] were used to determine the genetic relationship between the mineralization and the host rocks [33–36].

The trace and REE contents of rock and ore samples were normalized to geological environment values, such as chondrite, normal mid-ocean ridge basalt (NMORB), upper crust, and lower crust.

3. Results and discussion

The TE and REE contents of rocks potentially associated with gold mineralization in the Kısacık area were assessed using spider diagrams normalized to various geological environments and materials (chondrites, NMORB, lower continental crust, bulk continental crust, upper continental crust), as proposed by different authors. Fig. 2 illustrates that the gold enrichments observed in the Kısacık field exhibit similar patterns in the spider diagram proposed by Sun and McDonough [33] and normalized to NMORB. Notably, two samples (Kıs7 and Kıs 8) from the ore-bearing silicifications near Baharlar Village, located south of the Kısacık field, displays a distinct pattern compared to the other samples (Fig. 2). Furthermore, the REE contents of the ore samples exhibit significant enrichment, reaching up to 10000 times NMORB for light REEs and up to 1/10 times NMORB for some heavy REEs (Fig. 2). Pb values were also enriched by 10 to 100 times compared to NMORB.

To investigate the relationship between the behavior patterns of the Kısacık gold deposit and other mineralizations in the region (mineralizations associated with listvenitization, gold mineralizations in the Kuşçayır area, gold mineralizations in ultramafic rocks), the TE and REE contents of the Kısacık gold deposit and other mineralizations were analyzed using spider diagrams normalized to NMORB values proposed by Sun and McDonough [33]. The NMORB spider diagram proposed by Sun and McDonough [33] is based on the

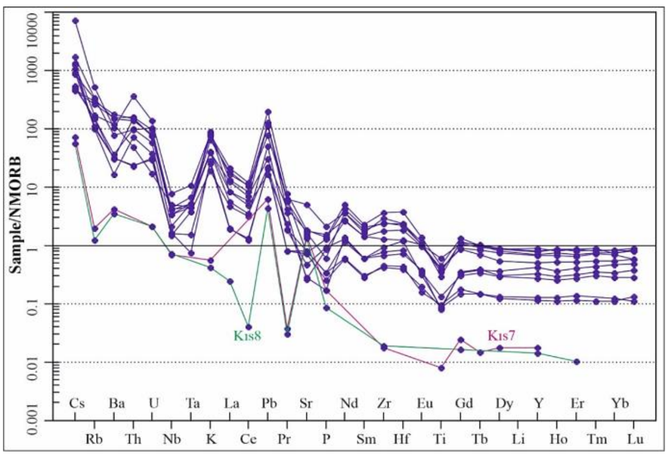

Figure 2. Spider diagram of rare earth element (REE) contents of ore samples from the Kısacık epithermal gold mineralizations, normalized to NMORB

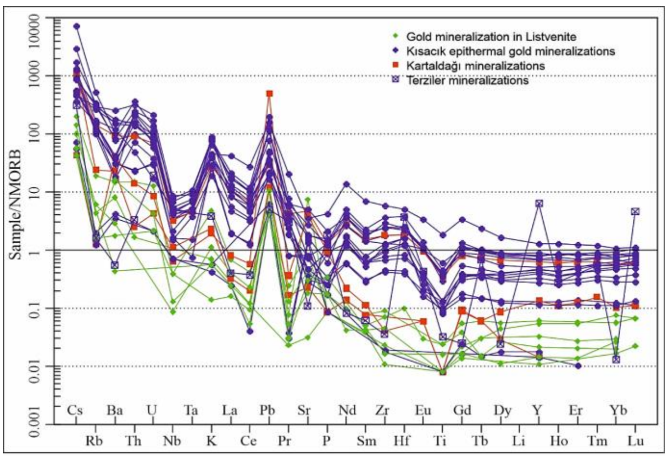

Figure 3. Spider diagram of TE and REE contents of Kısacık gold deposit and other mineralization in the close vicinity, normalized to NMORB.

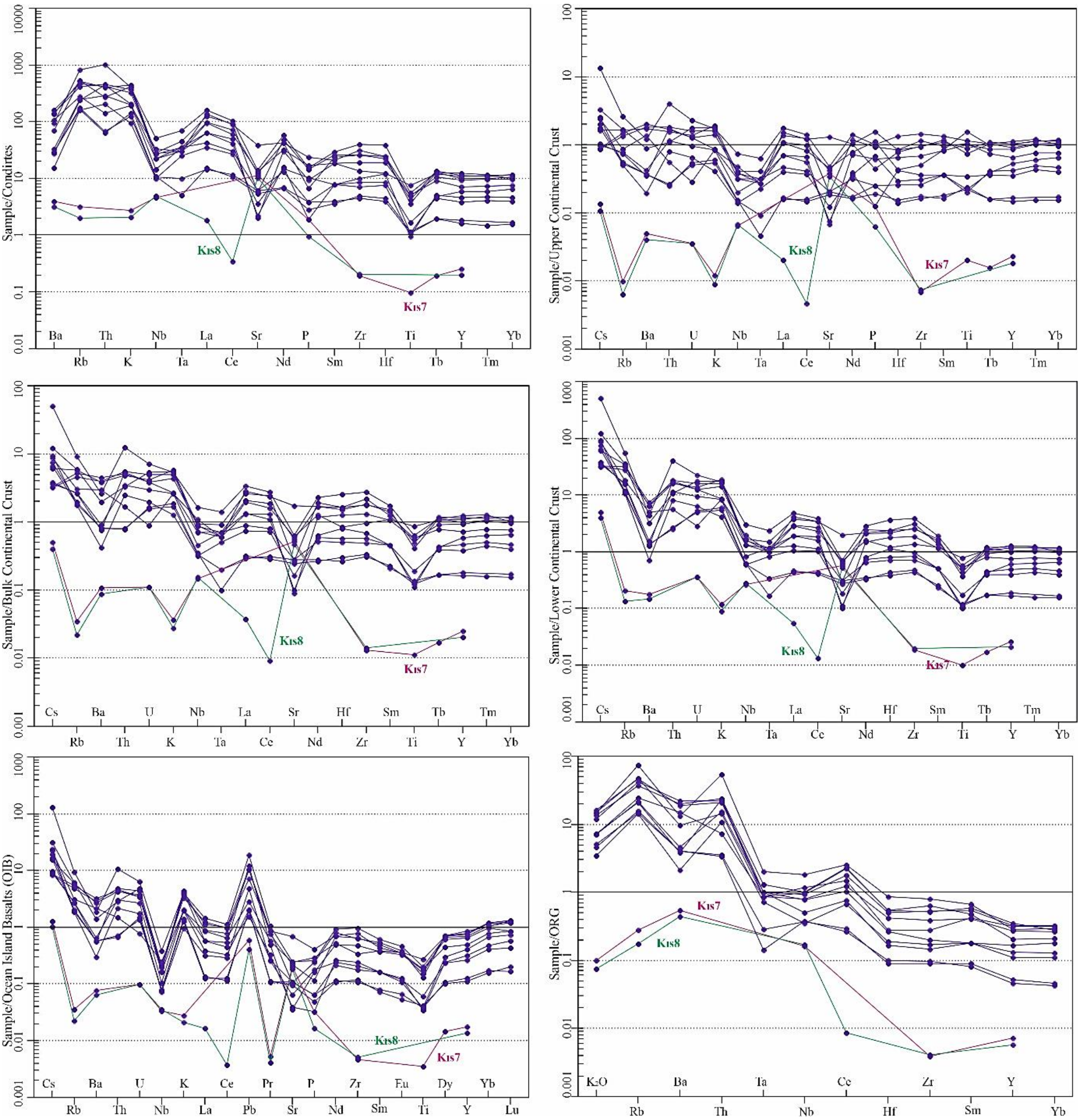

Figure 4. The spider diagrams of gold enrichments in volcanic rocks of the Kısacık area, normalized to condrites and different geological settings.

compositions of 30 elements, including trace elements, REEs, and metals. This allows for the evaluation of a large number of elements simultaneously. The trace and REE patterns of the Kısacık deposit were found to be generally consistent with the patterns of gold enrichments in the listvenitizations in the northern part of the deposit, and to be relatively similar to the patterns of gold enrichments in quartz veins developed in schists in the Kuşçayır-Kartaldağı area, much further north of the Kısacık deposit. The mineralizations in the Terziler region were found to have a different pattern from the other mineralizations (Fig. 3). The coherence within each ore deposit group is also noteworthy.

The TE and REE contents of the Kısacık village gold enrichment samples are normalized to the condrites proposed by Thompson [35] (Fig. 4). It is determined that they show a compatible pattern with each other, except for the samples Kıs7 and Kıs8. The Kısacık village gold enrichments are enriched in incompatible elements up to 1000 times compared to the condrites, and light REEs are enriched by 10 to 100 times. For heavy REEs and some trace elements, enrichments exceeding 10 times have been observed (Fig. 4).

The trace and REE contents of Kısacık gold mineralization samples were also normalized to different geological settings proposed by various

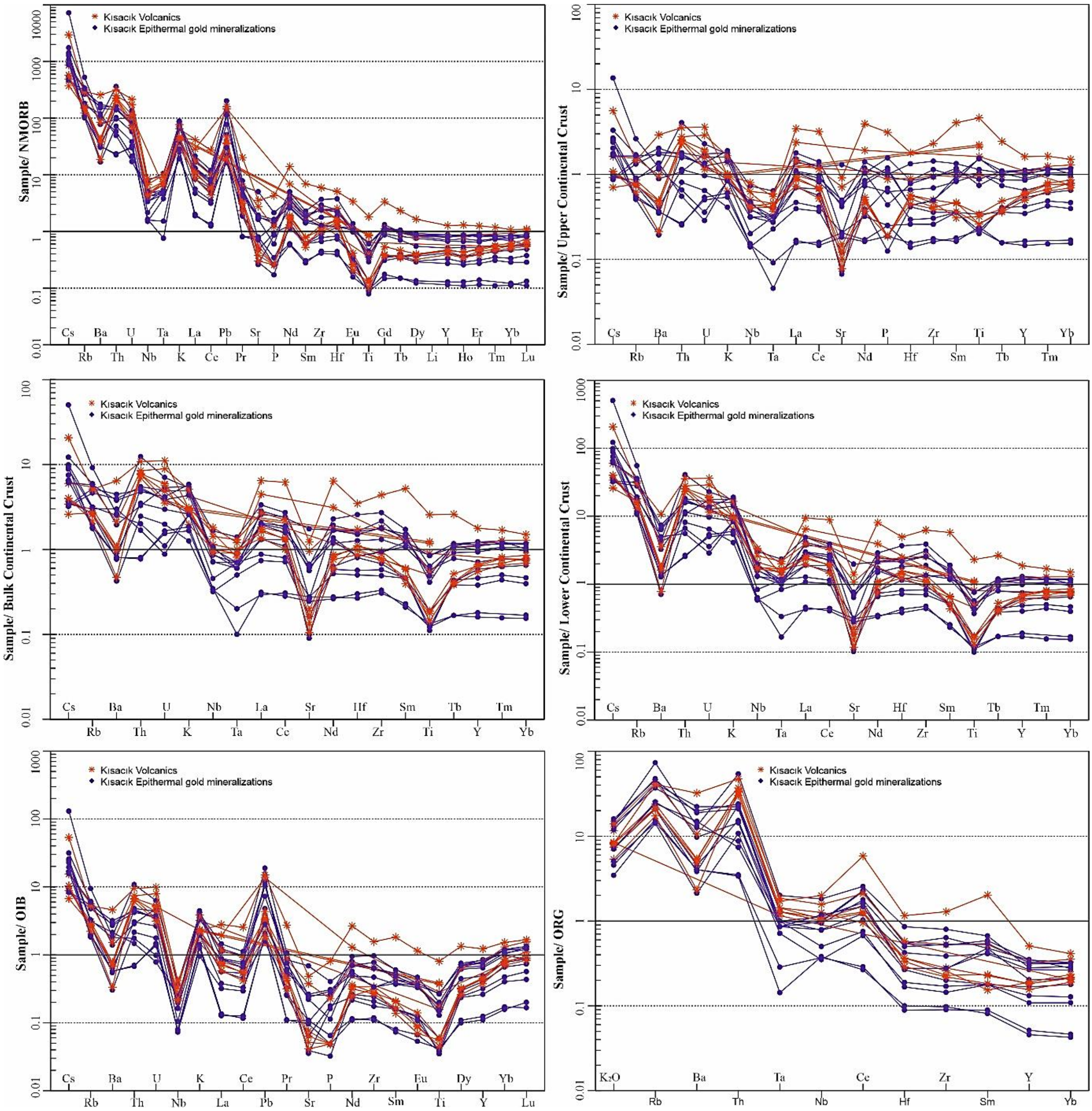

Figure 5. Spider diagrams of Kısacık volcanics and Kısacık epithermal gold mineralizations/enrichments normalized to NMORB, upper continental crust, bulk continental crust, lower continental crust, OIB, ORG.

authors, including chondrite, upper continental crust, Bulk continental crust, lower continental crust, Ocean Island Basalts (OIB) and Ocean Ridge Granites (ORG) (Fig. 4).

It is clear that samples Kıs7 and Kıs 8 have a different pattern than other Kısacık mineralization samples for all geological settings. Sample Kıs7 and Kıs8 are compatible with chondrites, while it shows depletion of up to 1/100 times, and sometimes 1/1000 times compared to upper continental crust and bulk continental crust values (Fig. 4). Kısacık ore samples are relatively compatible with upper continental crust normalized values and have a relatively good agreement with bulk continental crust values. There are enrichments in incompatible elements according to lower continental crust values, while REE elements are relatively compatible (Fig. 4, Fig 5). Based on the data in Fig. 4, it can be said that the upper crustal effect is relatively high in Kısacık gold mineralization, and the genetic effect belonging to the lower crust is also relatively effective.

Trace and REE contents of gold enrichments in the Kısacık area and some gold enrichments in the vicinity of the study area were compared to the TE-REE contents of associated magmatic rocks in the region, normalized

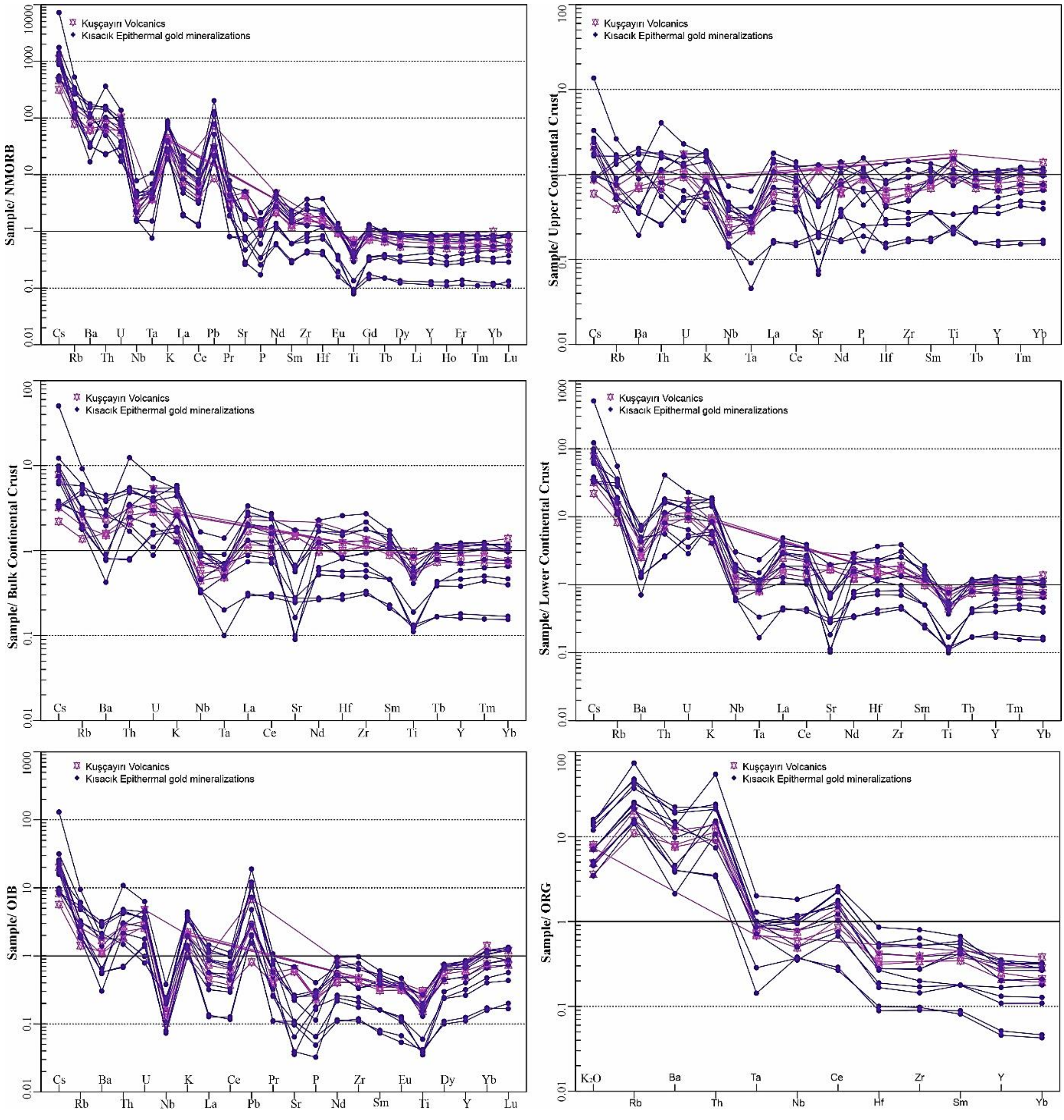

Figure 6. Normalized spider diagrams of the Kuşçayırı volcanics and Kısacık epithermal gold enrichments relative to NMORB, upper continental crust, bulk continental crust, lower continental crust, OIB and ORG tectonic settings.

to different geological settings. This was done to investigate the relationship between the Kısacık gold mineralization and the nearby gold enrichments and magmatism (Fig. 5, Fig. 6, Fig. 7). The contribution of ultramafic rocks to meteoric/hydrothermal leaching that affects mineralization was also investigated using trace-REE element spider diagrams of different geological settings for the relevant rock (Fig. 5, Fig. 6, Fig. 7).

When the spider diagrams of the Kısacık area gold enrichments and the Kısacık Volcanics are compared to each other, it is seen that the gold mineralizations in the Kısacık area have a compatible pattern with the Kısacık volcanics. The gold enrichments in the Kuşçayırı-Kartaldağı area also have a close similarity to the Upper volcanic rocks (Fig. 5, Fig. 6, Fig. 7). It can be said that an important factor in the compatibility found in the spider diagrams is the leaching of elements from ultramafic rocks by meteoric effects in hydrothermal alteration processes and their contribution to the mineralization process.

When gold mineralization/enrichments are evaluated in the context of geological setting, it is seen that the patterns of both gold enrichment samples and the element patterns of the Kısacık Volcanics are compatible, especially with the lower continental crust. The NTE patterns of the enrichments seen in the volcanic rocks of

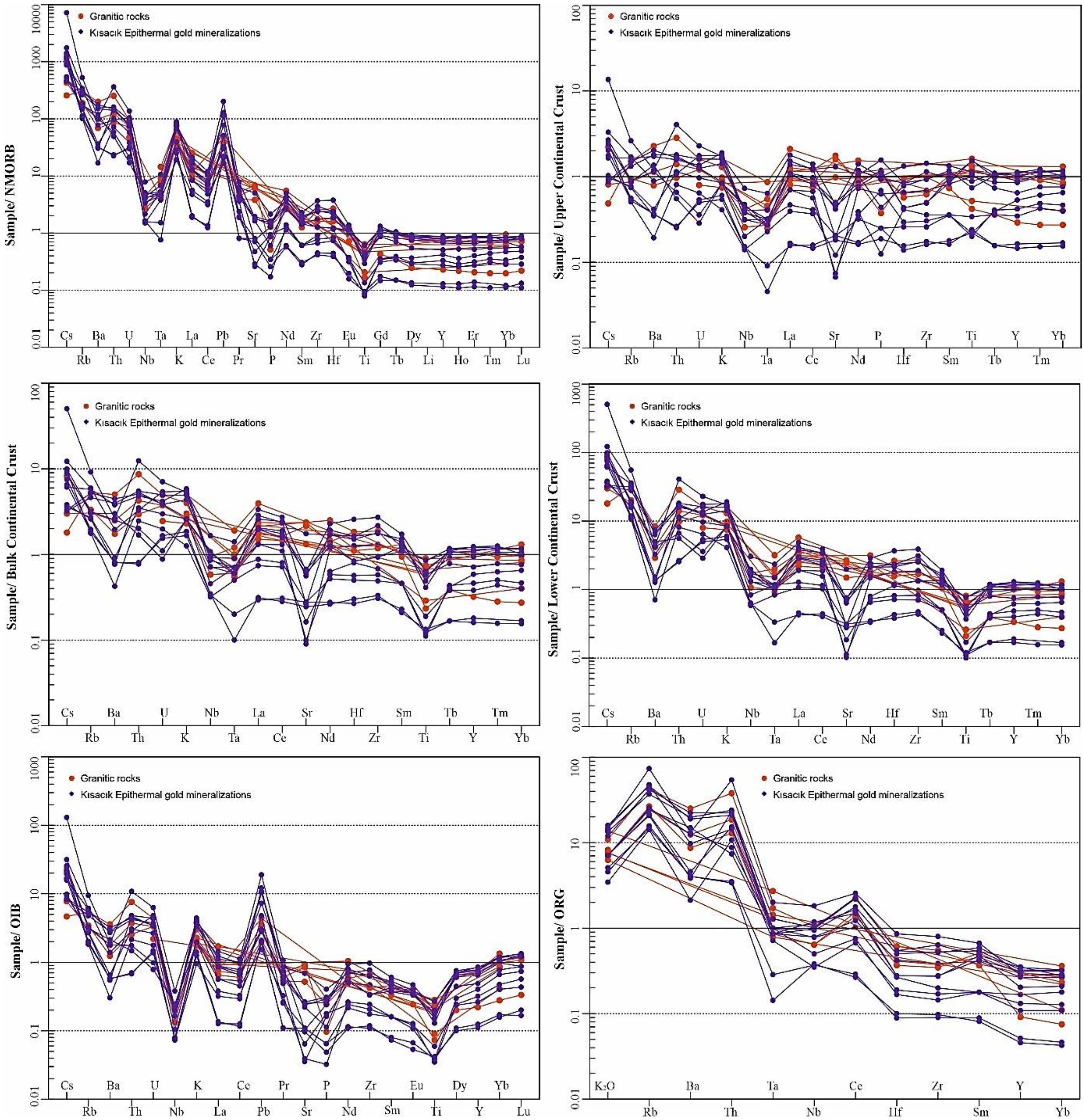

Figure 7. Spider diagrams of granitic rocks and Kısacık gold enrichments normalized to NMORB, upper continental crust, bulk continental crust, lower continental crust, OIB and ORG tectonic settings.

the Kısacık-Kırantepe area are compatible with the Lower volcanic rocks, while the patterns of the gold enrichments in the Kuşçayırı-Kartaldağı area and in the listvenites are not very compatible, with only one example being compatible. This indicates that there is at least a two-phase effect in the enrichments in the Kuşçayırı-Kartaldağı area, one of which is one of the phases that caused the gold mineralization in the volcanic rocks of the Kısacık area.

When the spider diagrams of the gold enrichments in the silicifications near the village of Baharlar and the gold enrichments in the listvenites are examined, it is seen that they do not show compatibility with the enrichments in the volcanic rocks of the Kısacık area and the patterns of the gold enrichments in the Kuşçayırı-Kartaldağı area. While they have a discordant pattern with the other two gold enrichments, it has been determined that there is a compatibility within themselves (Fig. 5, Fig. 6, Fig. 7).

To investigate the relationship between the Kuşçayırı volcanics and the mineralizations in the Kısacık area, spider diagrams were examined. It is seen that the Kuşçayırı volcanics have a close relationship with the gold enrichments seen in the volcanic rocks of the

Kısacık area (Fig. 6). This relationship can be partially observed, albeit weakly, in other enrichments in the area. Both in the sections where gold enrichments are present and in the Kuşçayırı volcanics, there is an enrichment relative to NMORB. When the spider diagrams of the gold enrichments and the Kuşçayırı volcanics are examined relative to upper continental crust, bulk continental crust, lower continental crust, OIB and ORG, it is seen that the patterns of the Kuşçayırı volcanics are also in a harmony with the gold enrichments developed in the volcanic rocks of the Kısacık area. There is a compatibility with the lower crust, both in the volcanic rocks and in the gold enrichments. It is seen that there is a decrease from heavy to light REEs, an increase in Pb value relative to the NMORB. While the gold enrichments in the Kısacık area and the Kuşçayırı volcanics show values close to the Upper Continental Crust, the gold enrichments in the Kuşçayır-Kartaldağı area and the gold enrichments in the listvenite show a depletion in REEs relative to the Upper Continental Crust (see also Fig. 3).

To investigate the relationship between granitic rocks and the gold mineralizations/enrichments in the area, spider diagrams of both were constructed (Fig. 7). When the spider diagram patterns were examined, it was seen that the patterns of the granitic rocks were also compatible with the patterns of the gold enrichments in the Kısacık epithermal gold mineralization area. When the spider diagram patterns of the gold enrichments in the northern and near southern parts of the study area were considered, no significant differences were observed between the patterns. However, the most striking pattern similarity overlaps with those of the gold mineralizations in the Kısacık area (Fig. 7).

Spider diagrams of the gold enrichments and granitic rocks were constructed relative to NMORB, upper continental crust, bulk continental crust, lower continental crust, OIB and ORG tectonic settings. When the obtained spider diagrams were examined, it was determined that the patterns of the granitic rocks were also in good agreement with the patterns of the gold enrichments developed within the volcanic rocks in the Kısacık area. There is a compatibility with the upper continental crust and also relatively bulk continental crust, both in the volcanic rocks and in the gold enrichments. Compared to the NMORM, it is seen that it is enriched in light REEs, However, the enrichment trend decreases as it moves towards heavy REEs and approaches the NMORB values. It is seen that the REE values of the granitic rocks and the gold enrichments in the Kısacık area are compatible with the upper continental crust values (Fig. 7).

4. CONCLUSIONS

The TE and REE geochemistry of gold mineralizations in the Kısacık area suggests that they are of epithermal origin and have a multi-sourced genetic relationship. The gold enrichments in the Kısacık area are consistent with the TE and REE patterns of the upper continental and bulk continental crust and weakly lower continental crust. This suggests that the gold mineralization is related to hydrothermal fluids that leached elements from these crustal sources. The gold enrichments in the listvenites and silisified rocks (near Baharlar village) in the area are also relatively consistent with the TE and REE patterns of each others. This suggests that these mineralizations may have also been affected same sources in the mineralization process.

The findings of this study support the conclusion that the Kısacık gold deposit is a multi-sourced epithermal deposit that formed as a result of the interaction of hydrothermal fluids genetically related to both the upper continental crust and the relatively lower continental crust. Considering the TE and REE patterns of spider diagrams of other mineralizations in the region, which were also created according to different plate setting environments, it is understood that meteoric fluids were also active in the mineralization process.

Implications for exploration:

- The trace and REE geochemistry of gold mineralizations can be used to identify areas that have potential to host epithermal gold deposits.
- The presence of trace and REE elements in gold mineralizations can be used to trace the movement of hydrothermal fluids and identify potential ore zones.
- The trace and REE geochemistry of gold mineralizations can be used to assess the potential richness of epithermal gold deposits.

Future research:

- Further research is needed to better understand the genetic relationships between the different types of gold enrichments in the Kısacık area.
- Additional studies are needed to investigate the role of hydrothermal alteration in the mineralization process.
- Research is needed to determine the timing and temperature of gold mineralization in the Kısacık area.

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