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Research Article

Geochemical Assessment of the Genetic Association of the Alakeçi Gold-Bearing Listvenitization Zone (Bayramiç, Çanakkale/Türkiye) Utilizing Trace and Rare Earth Elements

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ABSTRACT

The Alakeçi Listvenit gold enrichments are located in the Biga Peninsula, Northwest Turkey. This study aims to investigate the genetic relationship within the Alakeçi listvenitic gold enrichments using trace element (TE) and rare earth element (REE) geochemistry. To achieve this, 29 samples associated with listvenitization in the area underwent analysis for major oxides, trace elements, and rare earth elements, employing inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS).

The geochemical analysis of the Alakeçi gold-bearing listvenitization zone indicates that gold enrichments within the listvenitization zone result from leaching caused by hydrothermal processes affecting the ultrabasic rocks in which listvenitization occurs. It is suggested that the hydrothermal processes, also active in the Kısacık gold deposit in the region, contribute to this gold enrichment, as indicated by the TE and REE patterns. Thus, in addition to the listvenitization of ultrabasic rocks, the field observations suggest that processes forming epithermal gold mineralization also play a role in the gold enrichments within the listvenitizations.

Introduction

Listvenitization is a fascinating geological process that transforms ultramafic rocks (like peridotite) into silica-carbonate rock called listwaenite. This alteration isn't just visually striking with its swirling patterns of white, green, and black minerals, but it's also geologically significant because it can host valuable gold deposits [1]–[4]. Fluids rich in silica and carbonate minerals infiltrate ultramafic rocks, replacing the original minerals with a mix of magnesite, dolomite, quartz, and mica. This process can be triggered by various geological events like subduction zones or hydrothermal activity. Listvenites act as natural treasure chests, often harboring gold, silver, mercury, arsenic, and other valuable minerals [5], [6]. This connection makes them a prime target for exploration and mining. The gold in these rocks can occur in various forms, like tiny grains within the quartz veins or disseminated throughout the listwaenite itself. Research on gold-bearing listvenites is ongoing, with scientists continuously unraveling the secrets of their formation and mineralization. Understanding the specific conditions that favor gold deposition: This involves analyzing the chemistry and textures of listvenites to identify key factors influencing gold enrichment. Known occurrences of listvenites include the Araç Massif in Türkiye [3]–[9], the Eastern Desert of Egypt, and the Mother Lode gold belt in California, USA. As noted in the literature, hydrothermal processes/fluids are the active processes in the formation of listvenites. Hydrothermal fluids are heated by a variety of geological processes, which allows them to move through the rock via fractures and cracks. In this process, they dissolve minerals and elements from the areas they pass through and carry them along their path [10]. As a result of this process, hydrothermal fluids become enriched in some TE and REE elements. In a suitable environment, these elements can also be enriched in the environment by the precipitation of the fluid. These elements that participate in the mineralization process can provide clues about the formation processes and genetic characteristics of the mineralizations [11]. The geochemical behavior of TEs and REEs is an important in in listwaenite proses. As ultramafic rocks are subjected to hydrothermal alteration, they become listvenites. In this process, hydrothermal fluids release the elements they carry within them into new mineral formations within the listwaenitic zone, due to a decrease in temperature, pressure, pH, and Eh. As a result, the newly formed minerals are enriched in these elements (TE, REEs). TEs and REEs are also found in a wide variety of rocks [11]–[14]. 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 adularia-sericite alteration as well as listwaenite. This information can be used to better understand the formation of epithermal process and to identify potential exploration targets for epitermal systems. Thus, geologists can use TE/REEs as valuable tools for exploring and evaluating epithermal gold deposits.

Anatolia's strategic location and rich natural resources were key factors in its emergence as a cradle of civilizations in antiquity [15]. 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 [15], [16]. The rich mineral potential of the region has triggered numerous studies in the fields of general geology and mining geology [9], [17]–[38]. The region is characterized by a diverse array of mineral deposits, evidenced by numerous abandoned mine workings and ongoing mining operations [17], [18], [26], [37], [39]–[43]. 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. Listvenites, which are not very common in Türkiye, attracted the attention of the General Directorate of Mineral Research and Exploration (MTA) in the 1990s. Studies have been carried out on the potential of the listvenites in the area to host ore [4]–[6], [9], [44]. Although the studies have concluded that the gold enrichment in the area does not reach economic levels, it is not too far-fetched to think that a buried ore body could be discovered if the area is studied in detail [38], [45]. The aim of this study is to understand the genetic characteristics of gold enrichments in the listvenites of the Alakeçi area in terms of TE and REEs, and to contribute to detailed mineral exploration studies.

Material and Methods

Geological characteristics of the area

The Biga Peninsula in Northwest Anatolia, Türkiye, displays a diverse range of geological formations, encompassing rocks from the pre-Tertiary, Tertiary, and post-Tertiary periods [9], [45]. According to the findings of Okay et al. [46], the pre-Tertiary units are divided into three distinct tectonic zones: the Sakarya Tectonic Zone, Ayvacık-Karabiga Zone, and Ezine Zone, arranged from northwest to southeast.

The Sakarya Tectonic Zone is primarily composed of metamorphic rocks from the Kazdağ Group and the Karakaya Complex [47] (Fig. 1). These rocks overlay both the metamorphic rocks and post-Triassic sediments. In the Ayvacık-Karabiga Zone, a notable ophiolitic mélanges, known as the Çetmi Ophiolitic Mélanges, is prevalent. This mélanges features eclogite blocks and Upper Triassic limestone blocks.

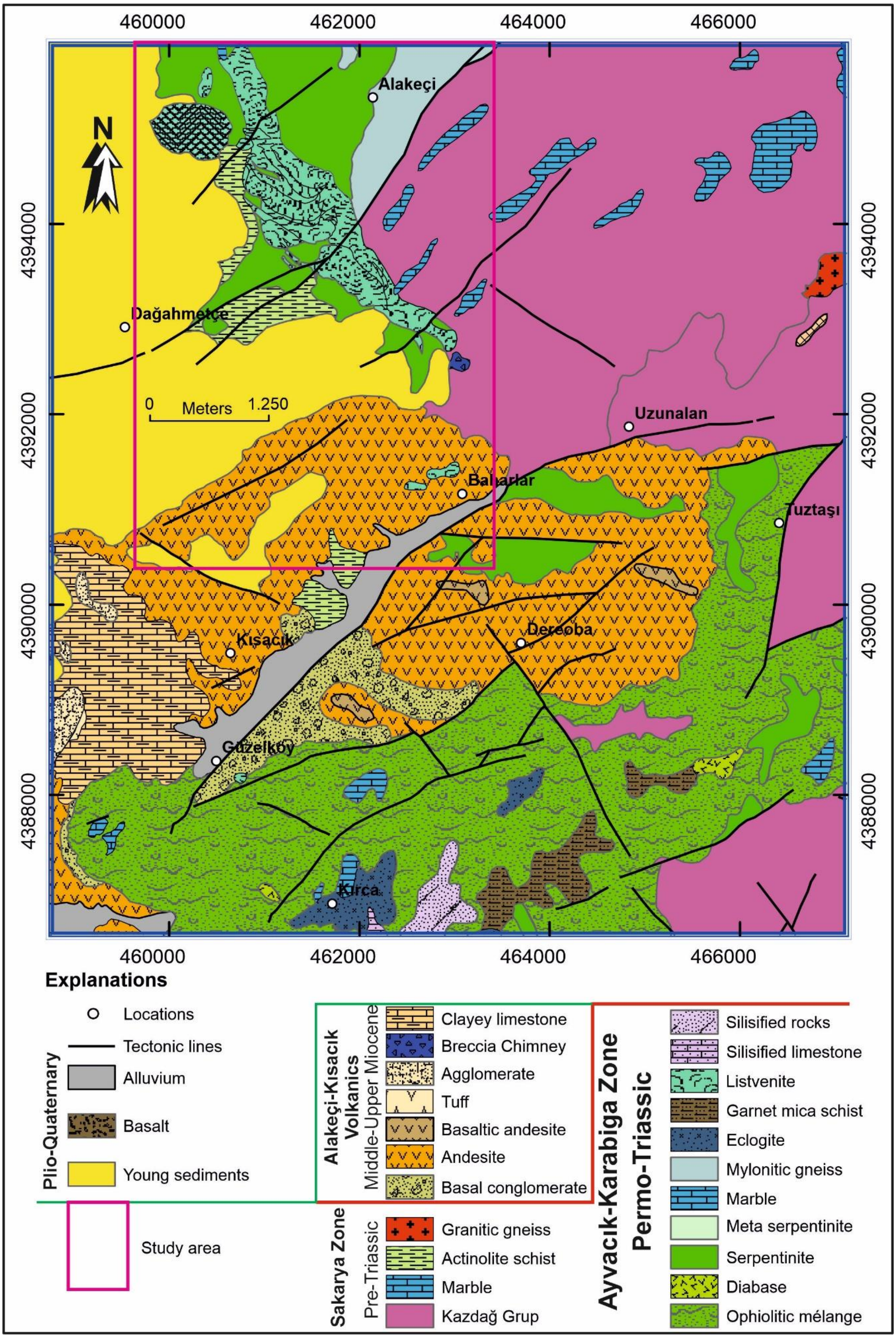
The Ezine Zone comprises continental-derived rocks, including the Permo-Carboniferous sedimentary sequence known as the Karadag Unit. This unit has undergone metamorphism under greenschist facies conditions and is accompanied by an overlying ophiolite, the Denizgören Ophiolite, which was emplaced during the Permo-Triassic period in the western part of the zone. Additionally, the Ezine Zone houses high-grade metamorphic rocks of sedimentary origin, specifically the Çamlıca Mica Schist [17], [45], [46] (Fig. 1).

In the Tertiary and Post-Tertiary periods of the region, a sequence of magmatic and sedimentary rocks is evident. Commencing with middle Eocene neritic limestone, the succession comprises Upper Eocene turbidites, interbedded andesite, and andesitic tuff, overlying the neritic limestone concordantly. Volcanic rocks near the study area are classified into Kuşçayır and Kısacık volcanics based on their age. Kuşçayır volcanics, situated in the north, are older, while Kısacık volcanics in the south are younger. Eocene (?)/Oligo-Miocene calc-alkaline magmatism initiated in the region, marked by a disconformity plane [48]–[52]. This magmatic activity persisted from the Eocene (?)/Oligocene to the Upper Pliocene Quaternary (?) period, involving both plutonic and volcanic rocks and associated pyroclastics [29], [45]. Notably, dacite, andesite, rhyolite, and acidic tuffs are exposed [49], [52], often interbedded with sedimentary rocks containing coal in specific areas.

Sedimentary rocks, primarily lacustrine and terrestrial clastics, are identified in Upper Miocene-Pliocene age terrains, while Quaternary alluvium is also present. Granitic rocks are located in the northern part outside the study area [45]. The most recent manifestation of magmatism in the region, basalt, is found in the western vicinity of the Alakeçi lisvenites (Figure 1). Young travertines with geotourism potential [53], [54]are occasionally observed in the region, often occurring in association with alluvium [45].

The examined listvenites are located within the Alakeçi mylonitic zone, which is associated with mylonitic gneisses. This zone, trending ENE and aligned with the primary foliation of the Kazdağ Group, is composed of mylonitic gneiss situated between an ophiolitic melange and the Kazdağ Group. Along this zone, listvenite is exposed as an elongated body, spanning several hundred meters in length and approximately 100-150 meters in width. It follows an ~NW-SE trend and intersects the NE-SW trending dextral structure (Figure 1).

The listvenite is composed of Fe-Mg carbonate, quartz, and Cr-bearing white mica, with disseminated chromite and accessory pyrite. Its distinctive features include a yellowish-green to reddish-brown surface appearance, attributed to the oxidation of Fe-bearing carbonate to iron oxides.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Explanations
Locations
Tectonic lines
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Basalt
Young sediments
Plio-Quaternary
Study area
Alakeçi-Kısacık Volkanics
Middle-Upper Miocene
Clayey limestone
Breccia Chimney
Agglomerate
Tuff
Basaltic andesite
Andesite
Basal conglomerate
Sakarya Zone
Pre-Triassic
Granitic gneiss
Actinolite schist
Marble
Kazdağ Grup
Ayvacık-Karabiga Zone
Permo-Triassic
Silisified rocks
Silisified limestone
Listvenite
Garnet mica schist
Eclogite
Mylonitic gneiss
Marble
Meta serpentinite
Serpentinite
Diabase
Ophiolitic mélange

Figure 1. Geology of the study area (from [5], [17], [45], [55])

Sampling and analytical procedure

To explore the genetic relationship between gold enrichments in listwaenite and adjacent rocks, 29 samples were gathered from listwaenite as well as the host, wall, and associated rocks in the vicinity. Ground samples underwent preparation at the Gümüşhane University Central Laboratory and the MTA Laboratory before being sent to the ACME Analytical laboratory in Vancouver, Canada. ACME Analytical laboratory conducted analyses for whole-rock major oxide, trace elements (including heavy metals), and rare earth elements (REE) on the provided samples.

Evaluation of the data

This study delves into the genetic characteristics of gold enrichment in the Alakeçi listwaenite zone, with a specific focus on TE (trace elements) and REE (rare earth elements). The objective is to corroborate previous findings [4], [5], [24], [38], [45], [56], [57] and advance our comprehension of the genesis of gold enrichment in the zone. Rocks in the area, particularly those linked with magmatism and ultramafic rocks, were identified through field observations and mine geology studies.

Major oxides, TE, REE, and metals were analyzed in samples from various rocks such as magmatic and ultramafic rocks, as well as the listvenitic zone. Genetic relationships between enrichment and host rocks were determined using spider diagrams proposed by different researchers [58]–[61]. TE and REE contents of rock and listvenite samples were normalized to values from geological-setting environments, including chondrite, normal mid-ocean ridge basalt (NMORB), upper crust, and lower crust etc.

TE and REE contents of rock and listvenite samples were normalized to values from geological-setting environments, including chondrite, normal mid-ocean ridge basalt (NMORB), upper crust, and lower crust.

Results and Discussion

The TE and REE contents of rocks potentially associated with listvenitization in the Alakeçi (Bayramiç, Türkiye) area were evaluated using spider diagrams normalized to various geological environments and materials (chondrites, NMORB, lower continental crust, bulk continental crust, upper continental crust, ocean island basalts (OIB), ocean ridge granitoids (ORG)), following the methodologies proposed by different authors [58]–[60].

Figure 2 illustrates that the gold enrichments observed in the Alakeçi listvenitization zone generally exhibit similar patterns in the spider diagram proposed by Sun and McDonough [58] and normalized to NMORB. Comparable patterns are also noted in two samples of silicified rocks located south of the Alakeçi listvenitization zone, the origin of which is uncertain (Baharlar Village) (Figure 2).

When compared to NMORB, all ore-bearing rock samples show significant enrichments of Cs, Rb, Ba, Th, Pb, and Pr. In particular, Cs and Rb values reach up to 10,000-fold enrichments in some samples. Sr values in the samples are highly variable, ranging from 10 to 1/1000. On the other hand, heavy REEs and Ti elements generally exhibit depletion in a relatively narrow range of 1/10 to 1/100 (Figure 2).

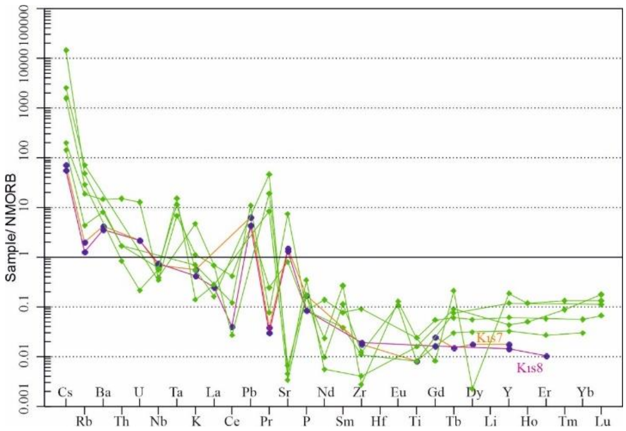

Figure 2. Spider diagram of TE and REE contents of gold bearing samples from the Alakeçi listvenitization zone, normalized to NMORB (NMORB values from [58])

To explore the relationship between the behavioral patterns of the Alakeçi listvenitization zone and the Kısacık gold deposit located to the south in the region, the TE (trace elements) and REE (rare earth elements) contents of both the gold-bearing Alakeçi listvenitization zone and the Kısacık gold deposit were subjected to analysis using spider diagrams normalized to NMORB values, as proposed by Sun and McDonough [58]. The NMORB spider diagram by Sun and McDonough [58] is constructed based on the compositions of 30 elements, encompassing trace elements, REEs, and metals, enabling the simultaneous evaluation of a diverse set of elements.

Figure 3 illustrates that the TE and REE patterns of the Alakeçi listvenitization zone and the Kısacık mineralizations display a certain degree of internal consistency while also exhibiting some differences between the two groups. Despite these differences, the overall similarity observed between the groups is noteworthy. This similarity is interpreted as evidence for the influence of common processes in the mineralization of the region.

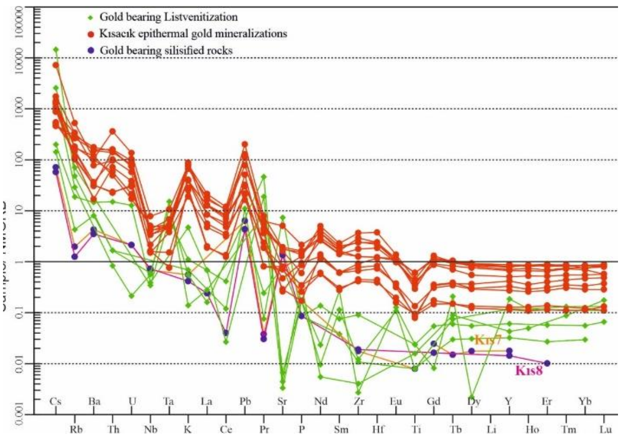

Figure 3. Spider diagram of TE and REE contents of Alakeçi listvenitization zone and Kısacık gold enrichment area, normalized to NMORB (NMORB values from [58]).

Spider diagrams were generated for the TE and REE contents of samples from the gold-bearing Alakeçi listvenitization zone, normalized to different geological settings proposed by various authors, including chondrite, upper continental crust, bulk continental crust, lower continental crust, ocean island basalts (OIB), and ocean ridge granitoids (ORG) (Figure 4).

Upon examining the TE and REE spider diagrams of the samples from the Alakeçi listvenitization zone, normalized to chondrite values as suggested by Thompson [60] (Figure 4), a consistent trend is observed, except for the Sr contents, which exhibit a wide range of variation. In terms of REE patterns, the values closely resemble chondrite values. Depletion of up to 1/10 is observed for the Zr and Ti elements, while a striking enrichment of up to 10 times is evident in the Y contents. Among the incompatible elements, Th and K show enrichments ranging from >10 to 100< (Figure 4).

In comparison to the upper continental crust, bulk continental crust, lower continental crust, OIB, and ORG diagrams, it is observed that some samples from the Alakeçi listvenitization zone, excluding values of Cs, Rb, Ta, and Sr, generally exhibit a consumption character between 1/10 and 1/100 (Figure 4).

When evaluating the TE and REE patterns of the listvenitization zone samples from all tectonic settings together, it can be noted that the values normalized to OIB are more in line with the listvenitization zone. Considering the parent rock of the listvenitizations, the observed results align with expectations. The deviations observed in the spider diagrams are considered to be influenced by geological processes active in the Kısacık gold deposit, a gold mineralization in the region.

To explore the relationship between gold mineralizations in the listvenitization zone and the rocks of the region, the TE (trace elements) and REEs of the Alakeçi listvenitization zone were compared with the TE and REE contents of samples from the Kısacık volcanics and the fresh rock of the listvenitization (Figure 5), using spider diagrams normalized to chondrite and different geological settings.

Upon examination of the spider diagrams, it was observed that the TE and REE patterns of the ultrabasic rocks in the region exhibited a pattern compatible with the gold enrichments in the Alakeçi listvenitization zone. In contrast, the volcanic rocks of the area, while consistent within themselves, formed a distinct group (Figure 5). Additionally, the TE and REE patterns of the silicified rocks (Kıs7 and Kıs8), which present gold enrichments, were found to occupy the same area as both the ultrabasic rock and the listvenitization zone, suggesting a relationship between these rocks and gold enrichments.

It can be concluded that a significant factor contributing to the compatibility observed in the spider diagrams is the leaching of elements from ultramafic rocks through meteoric effects in hydrothermal alteration processes, thereby contributing to the mineralization process.

Conclusions

The geochemistry of the Alakeçi gold-bearing listvenitization zone has shown that the gold enrichments within the listvenitization zone are the product of leaching caused by hydrothermal processes that affect the ultrabasic rocks where the listvenitization occurs. In this process, it has been accepted that the hydrothermal processes that are also active in the Kısacık gold deposit in the region are also effective in this gold enrichment, in the light of the TE and REE patterns. Therefore, in the field, in addition to the effect of the listvenitization of ultrabasic rocks, the processes that form epithermal gold mineralization also have an effect on the gold enrichments within the listvenitizations.

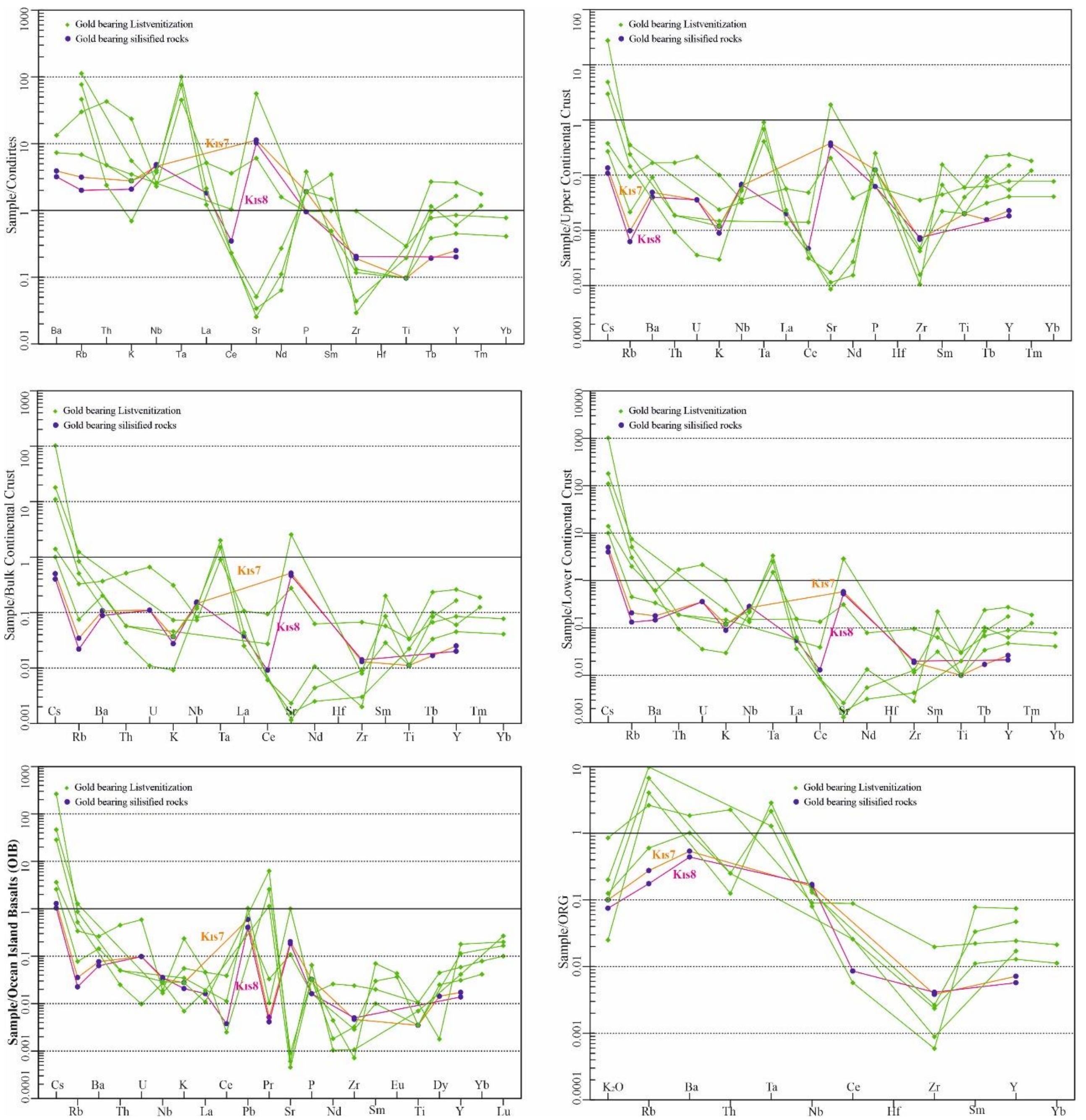

Figure 4. The spider diagrams of Alakeçi listvenitization zone, normalized to condrites, and different geological settings such as upper continental crust [59], bulk continental crust [59], lower continental crust [59], OIB [62], ORG [61].

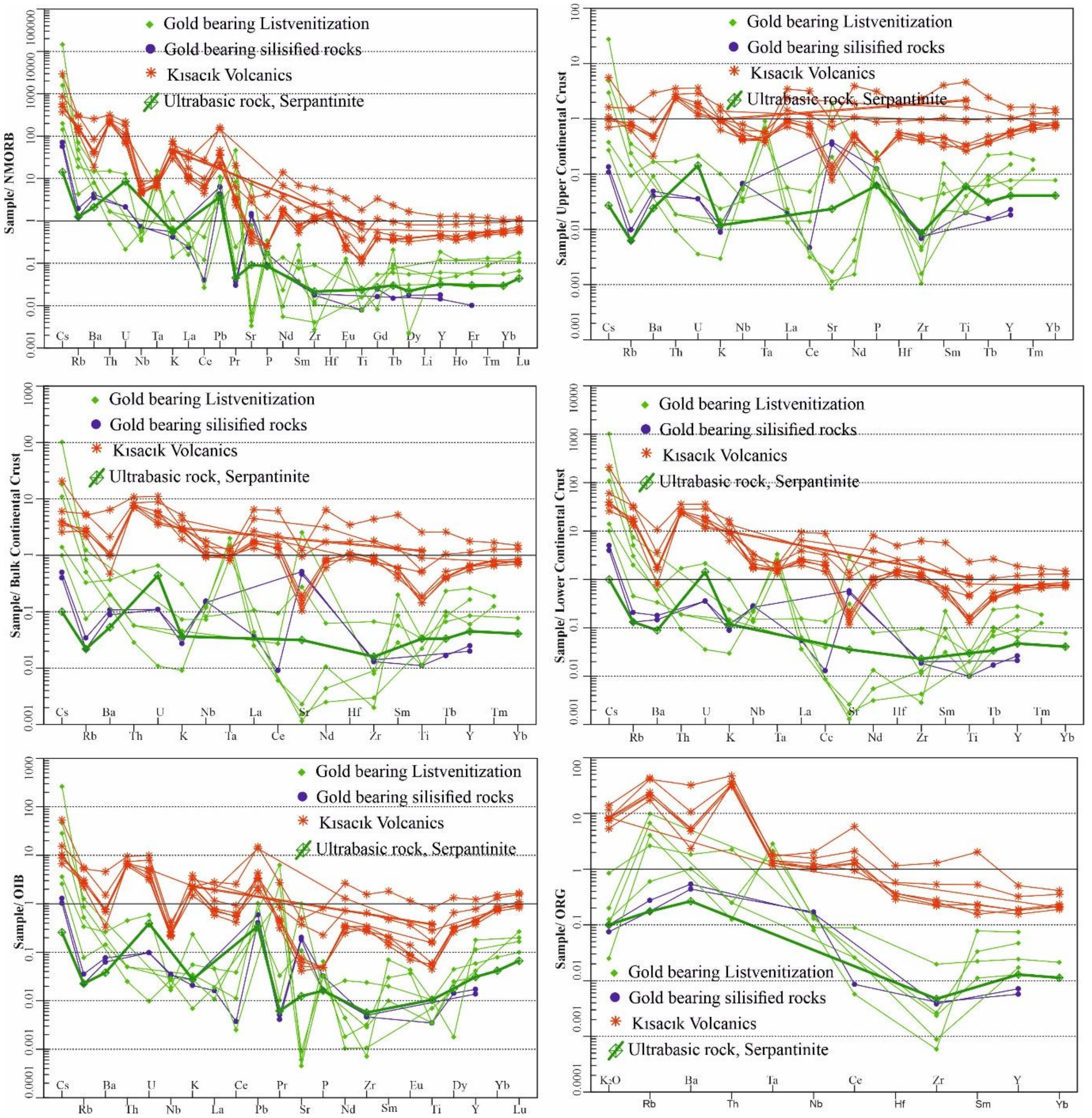

Figure 5. Spider diagrams of Alakeçi listvenitization zone and Kısacık volcanics normalized to NMORB, upper continental crust, bulk continental crust, lower continental crust, OIB, ORG.

Ethics committee approval and conflict of interest statement

There is no need to obtain permission from the ethics committee for the article prepared

There is no conflict of interest with any person / institution in the article prepared

Authors' Contributions

-Study conception and design: Vural

-Acquisition of data: Vural

-Analysis and interpretation of data: Vural

-Drafting of manuscript: Vural

-Critical revision: Vural

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