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ORIGINAL RESEARCH ARTICLE

An evaluation of elemental enrichment in rocks: In the case of Kısacık and its neighborhood (Ayvacık, Çanakkale/Türkiye)

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ABSTRACT

In this study, the enrichment of the major oxide, trace element/heavy metal and rare earth element contents of the rocks outcropping in Kısacık and its vicinity (Ayvacık-Çanakkale/Türkiye) were investigated. The rocks in the field were handled in 5 groups, and whole rock analyses were carried out for 22 samples collected representing these rock groups and Element Enrichment Factor (EEF) of the major oxide, trace element/heavy metal and rare earth element contents of the rocks were calculated. As a result, it was determined that the Kısacık volcanics were enriched in SiO_2, Fe_2O_3, K_2O, Be, Co, Cs, Th, U, W, La, Eu, Tm, Yb, Lu, Mo, As, Cd, Sb, Bi and Hg elements at a rate of >1 to >150 according to the upper crust values, and the Fe_2O_3, MgO, CaO, TiO_2, P_2O_5, MnO, Cr, Sc, Co, Nb, Sr, Mo, Cu, Ni, Cad, Sb, Bi, V, Cu and Cd concentrations of the Ophiolitic Mélange were enriched in ratios ranging from >1 to >36 according to the upper crust values. It has been also observed that the listvenitic rocks in the Ophiolitic Mélange are enriched in Cr, Co, Ni, As and Hg elements compared to the upper crust. As to Kazdağ Group, MgO, CaO, K_2O, MnO, Cr, Co, Ta, U, W, Mo, Cu, Ni, As and Cd were enriched. Listvenite were enriched in SiO_2, Fe_2O_3, MgO, Mn, Cr, Co, Ni, As, Sb and Hg at a rate of >1 to >32 according to the upper crust values. When the rocks in the area were evaluated together, some oxides (e.g., CaO, MgO, Fe_2O_3, TiO_2) and elements (e.g., Cr, Ni, Co) were enriched due to parental rock, while some oxides (e.g., SiO_2, K_2O and MnO) and elements (As, Sb, Hg) were enriched due to epigenic processes such as hydrothermal alteration and weathering.

Keywords: Background Values; Upper Crust; Trace Element; Heavy Metal; Element Enrichment Factor (EEF); Çanakkale; Türkiye

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1. Introduction

Rocks differ in mineral content and element concentrations, depending on their origin and formation processes[1–7]. In addition to the genetic variation (e.g., plate setting, parental magmas) in the element concentrations of the rocks, processes such as metamorphism, metasomatism, hydrothermal alteration, and weathering also cause differentiation, enrichment or depletion in some elements. While the rock-forming geological processes do not cause such a difference in the element content of rocks in the anomaly level, factors other than the rock-forming processes can be the source of the aforementioned enrichment or depletion. While enrichment and depletion in rocks are important in terms of medical geology, elemental enrichment, especially in the context of environmental issues, gained great importance after the second half of the 20th century due to its effects on the environment in which the rocks are located[2,8–15]. When element transitions from rocks to soil and aquatic system exceed tolerable limits, it also negatively affects the quality of soil and water. Therefore, it negatively affects plants, animals and even human life indirectly and/

or directly[10,16]. There are many studies examining the effects of element and element toxicity on environments, living things (plants and animals) and humans. Especially after the second half of the 20th century, when the importance of the relationship between geological environment and health was understood, the tendency to this issue increased[17,18]. In studies on tissues of penguin and seals from Antarctica, copper and cadmium concentrations were found to be higher than in uncontaminated regions. These high concentrations in tissues have been associated with the geology of Antarctica. About 22 elements are known to be essential for living things (especially humans and animals). 16 of them are indispensable for nutrition. However, there must be a balance between the essentiality and toxicity of the elements. Otherwise, negative side effects will be seen on the organisms[19]. Zinc, for example, plays an essential role in zinc-dependent enzymes, activating growth (height, weight, and bone development), and cobalt plays an essential role in vitamin B_{12} regulation. But zinc toxicity has is in both acute and chronic forms[20]. Lung diseases such as asthma have been detected in people exposed to 0.005 mg Co/cm^3 while working with alloys containing Co in the industrial sector.

Rocks are transformed into soil by the geological and geochemical processes they are exposed to, in relation to the physicochemical properties of the minerals they contain (hence the elements they contain). They leave the elements they contain to the environment they are in (terrestrial and aquatic systems). In this process, the mineral/element content of the rocks is one of the most important elements. While studies on heavy metal/trace element contents of soils and their environmental effects are dominant, studies on the evaluation of the element contents of rocks in the context of environmental effects are much more limited[4,7,27,9,14,21–26]. Various parameters such as geoaccumulation index (Igeo), enrichment factor (EF), pollution index (PI) and combined pollution index (CPI) are used in the assessment of heavy metal/trace element pollution/contamination in soils. With these parameters, the degree of soil pollution/contamination is determined[28–31]. In the assessment of element enrichment/contamination in rocks, these parameters are used by adapting them to the rocks, and it can be said that there is no other commonly accepted parameter used[5]. In this study, the pollution index was used by adapting it to the rocks.

West Anatolia, especially Biga peninsula is one of Türkiye's most important metallogenic belts and has been one of the important mining areas since ancient times[32–36]. There are many active mining operations in the peninsula today. There are also many hydrothermal alteration areas pointing to mineralization in the region. Although hydrothermal alteration areas are guide areas for mineralization, such areas are also element enrichment/contamination areas. The Kısacık area (Ayvacık, Çanakkale/Türkiye) is an area where volcanic rocks are exposed to intense hydrothermal alteration, and buried gold mineralization was detected by the General Directorate of Mineral Research and Exploration in the region. In this study, the major oxides, heavy metal/trace element and rare earth element (REE) contents of the rocks outcropping in Kısacık and its vicinity in the south of Biga peninsula (Çanakkale-Türkiye) were compared with the upper crust average values and investigated within the framework of element enrichment/contamination in the scope of environmental geochemistry.

1.1 Geology of the area

The subject of the study, Kısacık and its surroundings (Ayvacık, Çanakkale-Türkiye) are in Western Anatolia, on the Biga peninsula. The basement rocks of the area are Pre-Triassic Kazdağ Group Metamorphics and Permo-Triassic Ayvacık-Karabiga Zone rocks[33,37,46,38–45]. Kazdağ Group Metamorphics mainly consist of gneiss, amphibolite, and marbles. The Ayvacık-Karabiga Zone, on the other hand, has an Ophiolitic Mélange character. In the field, mylonitic gneisses and metaserpentinites (Alakeçi Mylonitic Zone) developed due to thrusting between the Ophiolitic melange and Kazdağ Group metamorphics in the northwest of the field (**Figure 1**). All these units are covered by Tertiary volcanic rocks and sedimentary rocks that are in lateral and vertical transition with these rocks[44]. In addition, listvenites are cropped out in the Alakeçi Mylonitic zone, which is found in the northwest of the area, in the tectonic lines of ophiolitic/ultrabasic rocks and as a product of hydrothermal alteration due to Tertiary magmatics[33,37,48–50,38–40,42–45,47]. The youngest units in the field are travertine formations and alluviums observed in

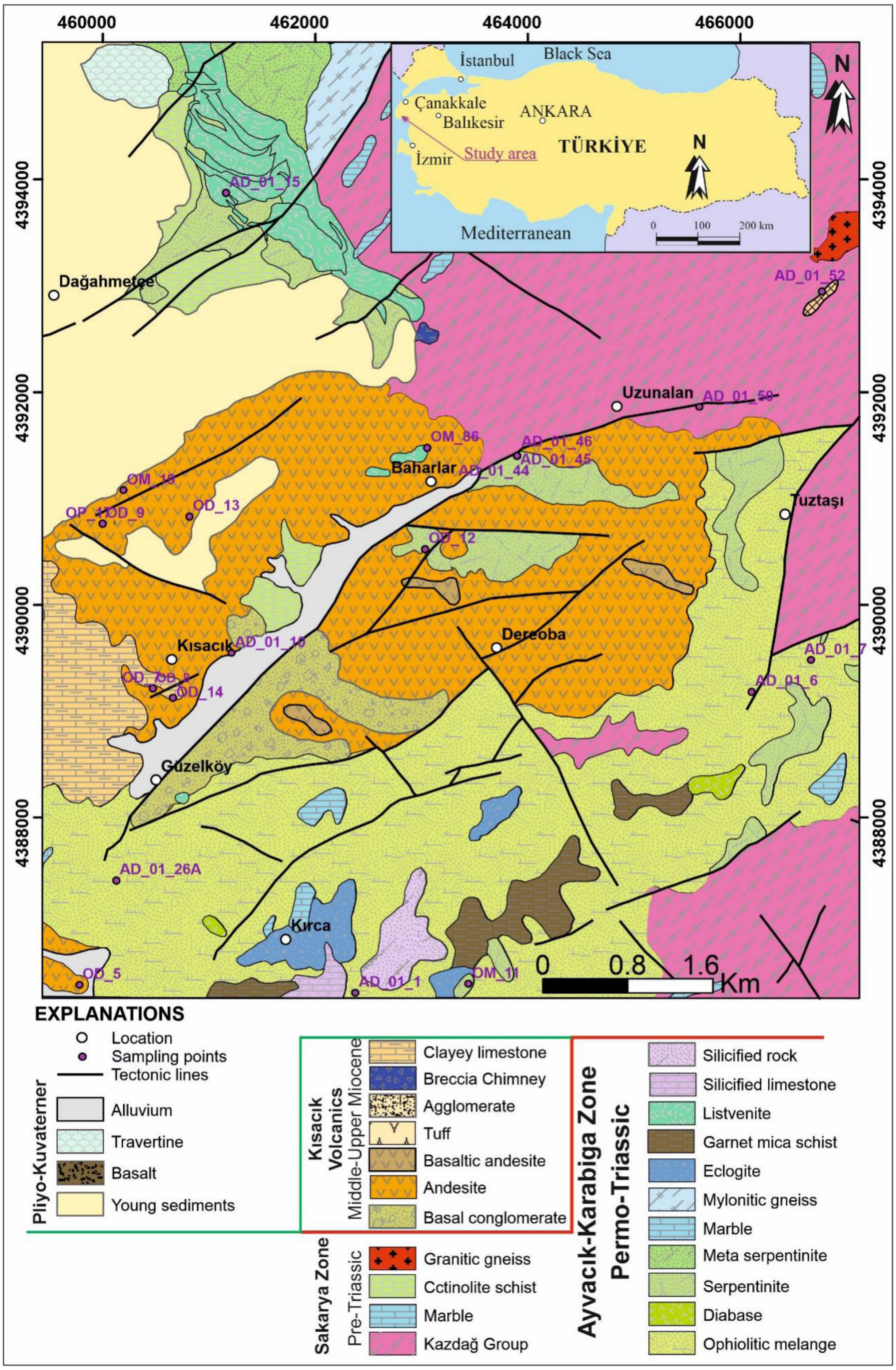

Figure 1. Geological and sampling map of the study area[33,37,39].

different parts (**Figure 1**).

Hydrothermal alteration development in the field is common especially in volcanic rocks. Hydrothermal alteration in volcanic rocks is mostly in sericitic alteration character accompanied by hematitization and limonitization. Listvenite developed in the Alakeçi Mylonitic zone is also a product of hydrothermal alteration and widely contains Fe-Mg carbonate, quartz and fuchsite (mica mineral).

2. Material and method

2.1 Sampling and analytical procedure

The rocks outcropping in the field are classified under 5 groups. Representing these rock groups, 22 rock samples were collected from the field. After the samples were ground in Gümüşhane

University Central Laboratory, they were sent to the ACME laboratory (Canada) and whole rock major element, trace element (including heavy metal) and rare earth element (REE) analyses were carried out. Major oxide and trace element (including heavy metals) analyses were performed by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Rare earth element analyses were performed by inductively coupled plasma-mass spectrometry (ICP-MS) at ACME Analytical Laboratories (Canada). The laboratory is an accredited laboratory and analyses were carried out in accordance with international standards. So, the accuracy and sensitivity tests of the analyses were carried out in accordance with routine procedures, and the t-test was carried out to ensure that the certified values used during the analysis and the values obtained were the same, and values were obtained within acceptable limits[51]. The precision of the method was determined by calculating the relative standard deviation (RSD). For major and trace element/heavy metal analysis, 0.2 g powder sample was mixed with 1.5 g $LiBO_2$ and analyzed after dissolving it in a liquid containing 5% HNO_3, while 0.250 g powder sample was dissolved in four different acids for rare earth element analysis and analyzed.

2.2 Evaluation of data

Statistical studies of the data of the rocks in the field were carried out with IBM SPSS 21 and Excel, which is the module of Microsoft Office Package Program. The reference values used in the study are the upper crust values recommended by Rudnick and Gao[52]. In the study, besides determining the descriptive statistical parameters of the element contents of the rocks in the area, the element concentrations of the rocks were compared with the upper crust averages to compare the element enrichments in the rocks (**Appendixes 1–4**). While making this comparison, first, it was decided which statistical parameter would be used as the average concentration of the element in the rocks. In this context, in deciding whether the concentrations of the investigated element in the rocks show a distribution close to the normal distribution, first, it was checked whether the mean and median values were close to each other, and then whether the skewness coefficient, which is one of the descriptive statistics parameters, was close to ±1 and the kurtosis parameter was close to 0. Based on these data, when it was decided that the data showed a normal distribution, the average concentration was directly taken as the mean value for the element, otherwise either the median or the geometric mean was accepted as the mean for the element in question. This value, which was accepted as the average for the element, was compared with the upper crust average.

The enrichment ratio of elements in rocks (Element Enrichment Factor, EEF) was calculated with the following formula, inspired by the pollution index parameter used in the determination of heavy metal pollution in soils:

$$EEF = Xri/Xbi \quad (1)$$

where,

Xri = the concentration of element i in the rock,

Xbi = corresponds to the reference value for element i in question. Reference values for elements are taken from Rudnick and Gao[52].

EEF < 1 corresponds to no element enrichment, 1 < EEF < 3 corresponds to medium element enrichment and 3 > EEF to high element enrichment.

3. Results

3.1 Statistical evaluation

Considering their age and lithological differences, the rocks in the study area have been grouped under 5 headings: Kısacık Volcanics (11 samples), Ophiolitic Melange (5 samples), Listvenite-like rock in Ophiolitic Melange (3 samples), Kazdağ Group rocks (2 samples) and Listvenite (only one sample). Descriptive statistics of major oxide, trace element (including heavy metals) and rare earth element concentrations of the rock samples belonging to each group were calculated with IBM SPSS 21 and presented in Appendixes with the upper crust averages of these elements (**Appendixes 1–4**).

When the averages of individual element concentrations of each of the rock groups are compared with the upper crust averages; it has been determined that the average element concentrations of the Kısacık volcanics exceed the upper crust values for SiO_2, Be, Co, Cs, Th, U, W, La, Nd, Sm, Eu, Tm, Yb, Lu, Mo, As, Cd, Sb, Bi and Hg at remarkable rates (**Appendixes 1–4** and **5a**).

When the element averages of the Ophiolitic Mélange group rocks are considered, it is observed that Fe_2O_3, MgO, CaO, TiO_2, P_2O_5, Mn, Cr, Sc, Co, V, Cu and Cd elements are enriched according to the upper crust values (**Appendixes 1–4** and **5b**). It is understood that the major oxides and the elements exceeding the upper crust averages in the rocks of the Ophiolitic Mélange group show high values originating from their parental rocks, especially Fe_2O_3, CaO, Cr, and Co.

It is seen that the averages of Fe_2O_3, MgO, Cr, Co, Ni, As and Hg of the listvenitic rocks in the Ophiolitic Mélange (Baharlar listvenitic rocks) are enriched compared to the upper crust averages (**Appendixes 1–4** and **5c**). The low SiO_2 concentrations in these rocks indicate the ultrabasic origin of the rocks. It is understood that the enrichment of As and Hg elements in the rocks is associated with hydrothermal alteration, while the other elements, which are high, are high in connection with the origin of the rocks.

It was determined that the averages of MgO, CaO, K_2O, MnO, Cr, Co, Ta, U, W, Mo, Cu, Ni, As and Cd of 2 samples belonging to Kazdağ Group rocks were enriched according to the upper crust values (**Appendixes 1–4** and **5d**). It has been evaluated that the high K_2O, U and As values in the rocks are related to the hydrothermal alteration to which the rocks are exposed, while the other high-concentration elements were enriched depending on the origin rocks. Considering the SiO_2 concentrations of the Kazdağ Group Rocks, it is seen that the sample AD-01-52 is not fresh/parent rock, unlike the other sample, and has a relationship with the hydrothermal alteration processes, so the high K_2O, U and As concentration in this sample are also remarkable (**Appendix 5d**). Sample AD-01-50, which is high in Cr, MgO, CaO elements, originally indicates the origin of the upper mantle. Likewise, the high Cr concentration in sample AD-01-52 indicates the closeness of both samples in origin (**Appendix 5d**).

Considering the element concentrations of listvenite, it was determined that SiO_2, Fe_2O_3, MgO, MnO, Cr, Co, Mo, Ni, As, Sb and Hg elements enriched at different rates according to the upper crust values (**Appendixes 1–4** and **Figure 2**). In particular, there is a remarkable high enrichment of SiO_2, Fe_2O_3, Cr, Co, Ni, As, Sb and Hg elements (**Appendixes 1–4** and **5e**). High concentrations of Fe_2O_3, MgO, Cr, Co, Ni, and possibly Mo in listvenite are compatible with the parental rock properties of the rocks, while high SiO_2, As, Sb, Hg and possibly MnO concentrations are associated with the geolog-

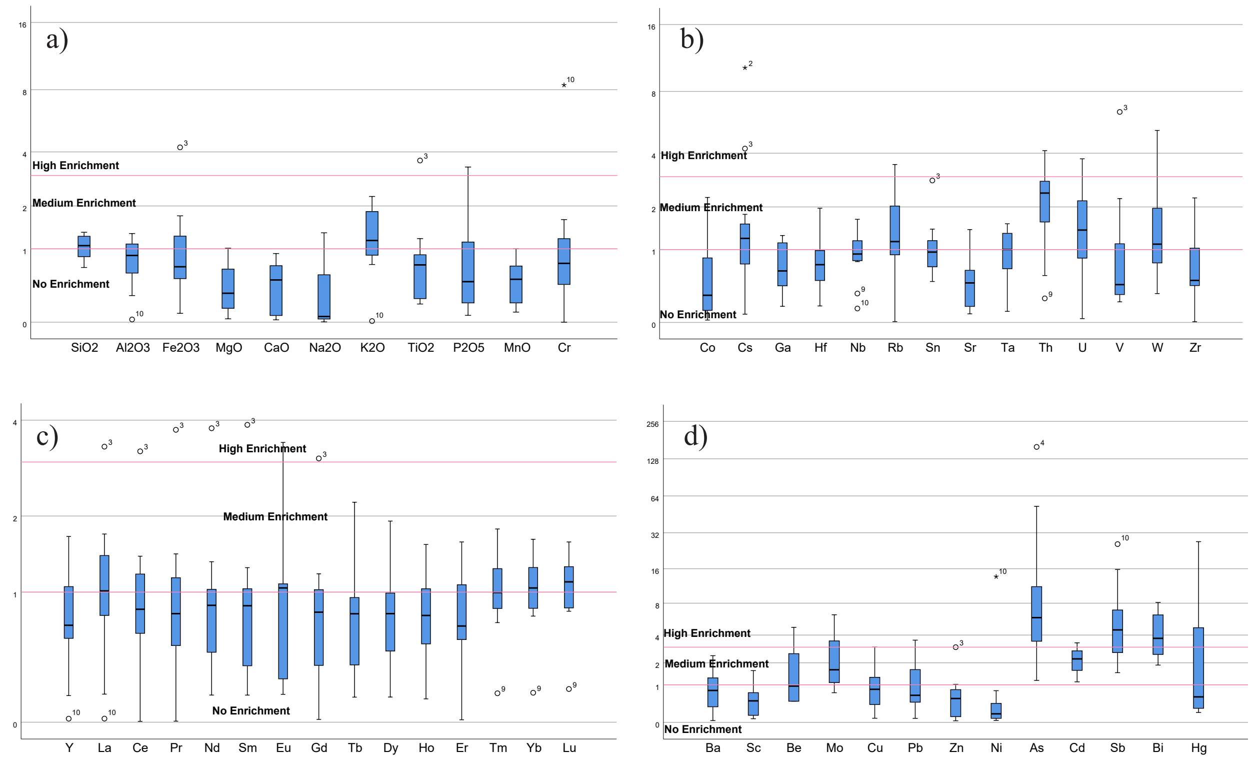

Figure 2. a) Box diagram of EEFs for major oxide + Cr of Kısacık Volcanics; b) EEF box diagrams of Co, Cs, Ga, Hf, Nb, Rb, Sn, Sr, Ta, Th, U, V, W, and Zr in the Kısacık Volcanics; c) Box diagram of the EEFs of REEs in the Kısacık Volcanics; d) Box diagram of the EEF of heavy metal and related elements in the Kısacık Volcanics (oxides in % and others in ppm).

ical processes to which the parental rocks are exposed such as, hydrothermal alteration, weathering, and cataclastic deformation/metamorphism.

3.2 Elemental enrichment in rock groups

Element enrichment factors of the rock groups in the study area were calculated separately for each group. Box and line chart diagrams of Element Enrichment Factors in the Rock belonging to the element contents of the Kısacık Volcanic rocks were plotted (**Figure 2a–d**). Since the number of samples representing other rock groups was not sufficient to form a box diagram, only line chart diagram was plotted for other rock groups (**Figures 3–7**).

Considering the EEF box diagrams of the Kısacık Volcanics, SiO_2 and K_2O oxides fall in the Medium Enrichment Class in more than half of the samples, while Fe_2O_3, Al_2O_3 and P_2O_5 oxides fall in the Medium Enrichment Class in more than 25% of the samples. These data obtained are compatible with the source rock of the Kısacık Volcanics. In more than half of the samples, it was determined that Cs, Rb, Sn, Ta, Th, U, W, La, Eu, Tm, Yb, Lu and Be elements were in the Medium Enrichment Class. It was determined that while Cd was in the Medium Enrichment Class in more than 75% of the samples, As was in the High Enrichment class in more than 75% of the samples. Al_2O_3, Fe_2O_3 oxides and Cr, Ga, Hf, Nb, V, Zr, Ba, Be, Cu, Pb, Hg and almost all rare earth elements fall into the No Enrichment Class in more than half of the samples. Sr, Sc, Zn, Ni and Co fall into the No Enrichment Class in almost all of the samples. Mo and Hg in more than 25% of the samples and Sb and Bi in more than half of the samples fall into the High Enrichment Class (**Figure 2a–d**).

When the line chart diagrams (EEF = Xri/Xbi) of the rock groups are examined, the oxides and elements of the Kısacık Volcanics show general compatibility in all samples (**Figure 2a–d**). Only one example, in this context, does not show element enrichment, but presents an anomaly (OM_86). Sample OM_18 shows enrichment in Cr (8 times), Co (more than 2 times), Mo (more than 2 times), Ni (more than 16 times), As (almost 64 times), Sb (more than 16 times) and Hg (close to 4 times) (**Figure 3a–d**). Considering the parental rock of the Kısacık Volcanics, the Ni enrichment in the sample is remarkable. Therefore, it is thought that it would be useful to conduct a detailed study on Ni enrichment. The enrichment of other elements in the Kısacık Volcanics is mostly related to hydrothermal alteration (mainly sericitization, pyritization, hematitization and argillization due to hydrothermal alteration associated with ore-bearing fluids). The OD_8 sample of the Kısacık Volcanics shows an enrichment of Fe_2O_3, TiO_2, and P_2O_5 over 4 times. The effect of hydrothermal processes in these enrichments is clearly observed. When the Kısacık Volcanics' samples are evaluated together, there are remarkable enrichments in Be, Cs, Hf, Sn, Ta, Th, U,

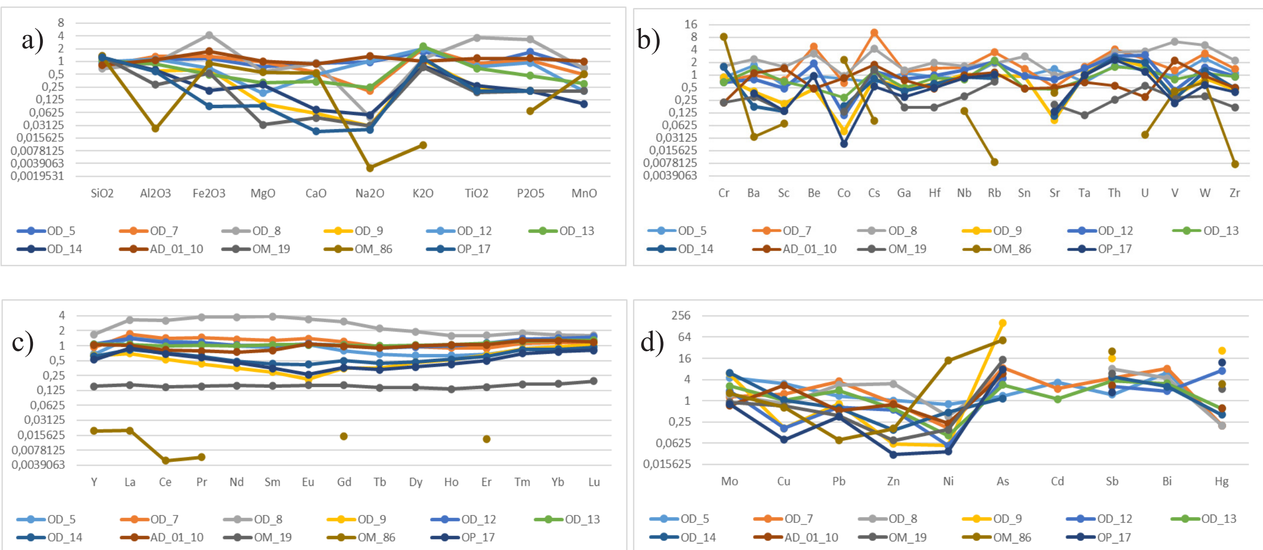

Figure 3. a) The major oxide line chart diagram (EEF values) of the Kısacık Volcanics according to the upper crust averages; b) EEF line chart diagram for Co, Cs, Ga, Hf, Nb, Rb, Sn, Sr, Ta, Th, U, V, W, and Zr in Kısacık Volcanics; c) EEF line chart diagram for REEs in Kısacık Volcanics; d) EEF line chart diagram for heavy metal and associated elements in Kısacık volcanics (oxides in %, others in ppm).

V, W, Zr. Rare earth elements show 2 to 4 times enrichment in sample OD_8, and some of them are in the High Enrichment Class (EEF > 3) (**Figure 3c**). In the Kısacık volcanics, remarkable enrichment has been detected (**Figure 3b–d**), especially with heavy metals and related elements, and these enrichments are mostly associated with hydrothermal alterations.

MgO, MnO, Cr, Co, Nb, Sr, V, Cu, Ni, Cd and Bi were enriched at varying rates (between 2 and 32 times) in the ophiolitic rock group samples (**Figure 4a–d**). In 3 samples of the ophiolitic group rocks, REE is compatible with each other and indicates the same origin (**Figure 4c**). In these samples, positive Eu anomaly is also observed with respect to the upper crust (**Figure 4c**). The enrichment in Cu, Ni, Bi, Cr, Co indicates the same parental origin[53–55].

Major oxide concentrations of the listvenitic rocks in the Ophiolitic Mélange show compatibility with each other (**Figure 5a**). Low values of SiO_2 and CaO in the rocks (EEF < 1) present an outlier compared to listvenite rocks. In the rocks, an enrichment of almost 32 times in Cr and 8 times in

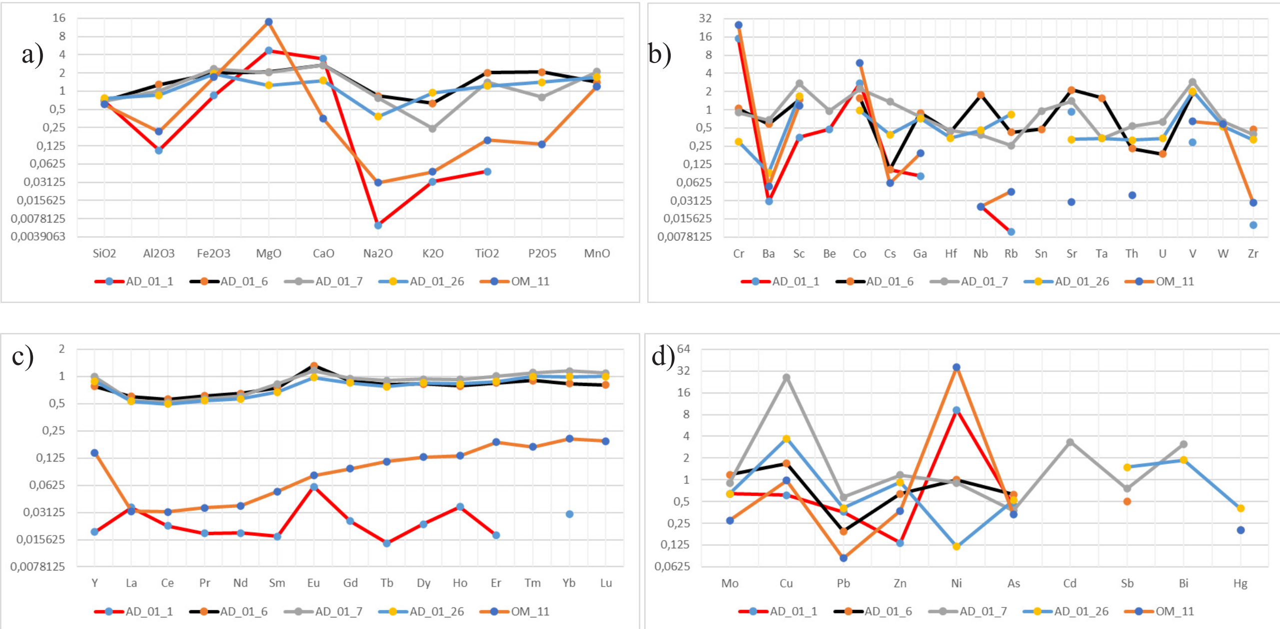

Figure 4. a) The major oxide line chart diagram (EEF values) of the Ophiolitic Mélange according to the upper crust averages; b) EEF line chart diagram for Co, Cs, Ga, Hf, Nb, Rb, Sn, Sr, Ta, Th, U, V, W, and Zr in Ophiolitic Mélange; c) EEF line chart diagram for REEs in Ophiolitic Mélange; d) EEF line chart diagram for heavy metal and associated elements in Ophiolitic Mélange.

Co, and an enrichment in Ni more than 32 times is observed, which indicates an originally similar parental rock. Remarkably high enrichment of Cr, Co, Ni elements was thought to be because of weathering and lateritic processes. In the rocks, while there is no enrichment in REE, an enrichment of more than 8 times in Sb and Hg has been detected (**Figure 5c–d**). The enrichment in Sb and Hg was associated with the hydrothermal alteration to which the rocks were exposed.

Element enrichment patterns of the 2 samples taken representing the Kazdağ Group show a clear difference (**Figure 6a, b** and **d**). Considering the SiO_2, K_2O, MnO values of the sample (**Figure 6a, b** and **d**), it does not overlap with the general characteristics of the Kazdağ Group rocks. Therefore, the sample AD_01_52 is a silicified vein rock formed due to metamorphism in Kazdağ Group rocks. The difference in heavy metal enrichment pattern also supports this separation (**Figure 6d**). When REE patterns are considered (**Figure 6c**), it is seen that there is a genetic bond between the two rocks.

When the line chart diagram of the listvenite was examined, it was determined that SiO_2, Fe_2O_3, MnO, Cr, Co, Mo, Ni, As were enriched at varying rates (**Figure 7a, b** and **d**). No enrichment with rare earth elements was observed in the rock. In the rock, the enrichment in SiO_2, Fe_2O_3 and MnO oxides and the enrichment in As, Mo, Sb, Hg have developed due to hydrothermal alteration. Conversely, enrichment of Cr, Co, Ni is related to ultrabasic origin of the listvenite rock and is associated with exfoliation and laterization.

4. Discussion

Rock types have elemental contents at certain intervals depending on their formation and original

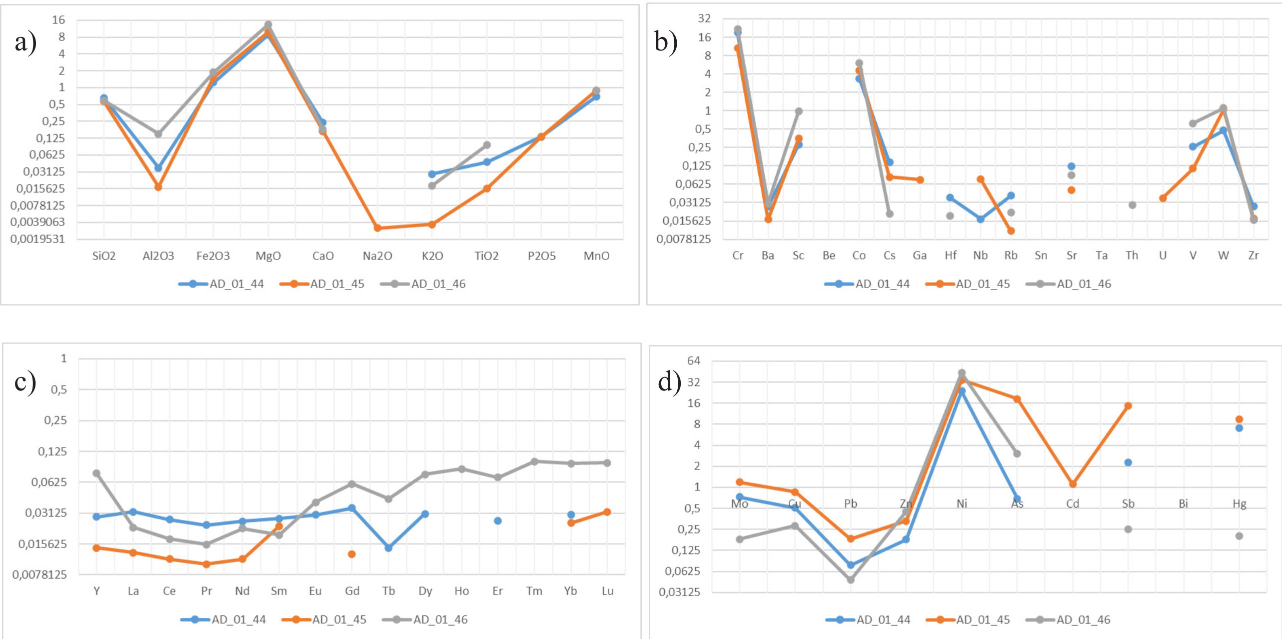

Figure 5. a) The major oxide line chart diagram (EEF values) of the Baharlar Listvenitic Rocks according to the upper crust averages; b) EEF line chart diagram for Co, Cs, Ga, Hf, Nb, Rb, Sn, Sr, Ta, Th, U, V, W, and Zr in Baharlar listvenitic rocks; c) EEF line chart diagram for REEs in Baharlar listvenitic rocks; d) EEF line chart diagram for heavy metal and associated elements in Baharlar listvenitic rocks (oxides in %, others in ppm).

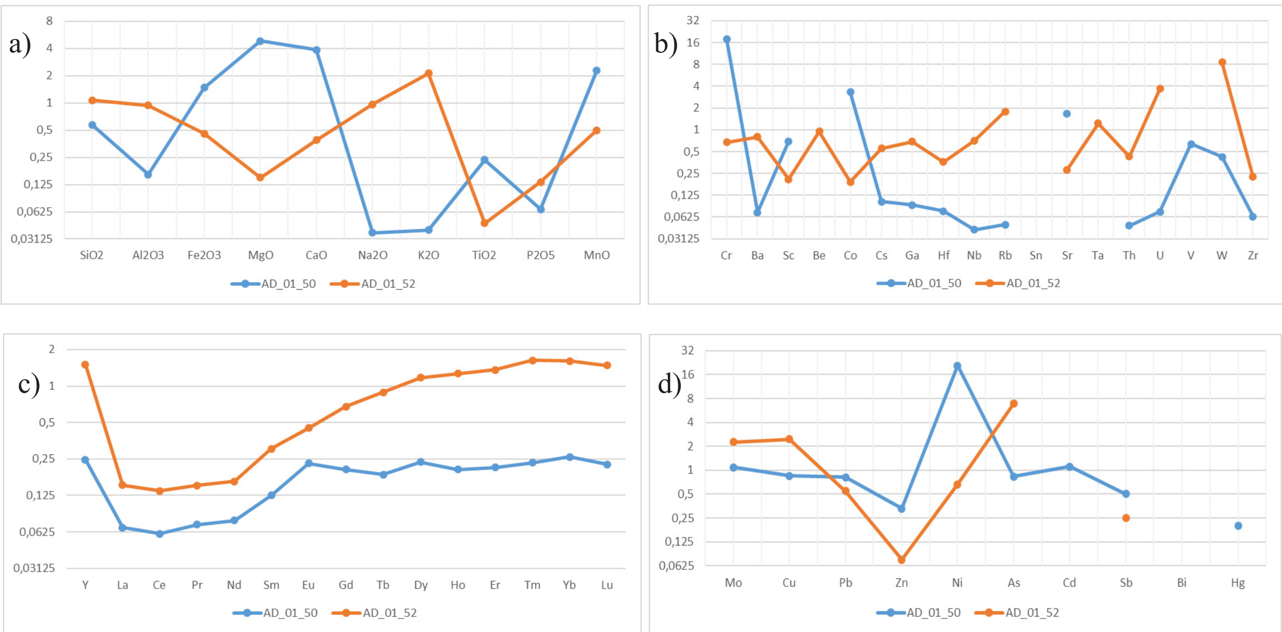

Figure 6. a) The major oxide line chart diagram (EEF values) of the Kazdağ Group Rocks according to the upper crust averages; b) EEF line chart diagram for Co, Cs, Ga, Hf, Nb, Rb, Sn, Sr, Ta, Th, U, V, W, and Zr in Kazdağ Group Racks; c) EEF line chart diagram for REEs in Kazdağ Group Rocks; d) EEF line chart diagram for heavy metal and associated elements in Kazdağ Group Rocks (oxides in %, others in ppm).

characteristics. Concentrations outside these range are accepted as anomaly (positive/negative) for the rocks in question. While a positive anomaly is seen as enrichment in a sense, when it reaches toxic limits, it is considered as a contamination phenomenon. Rocks that have reached the level of pollution by any element cause negative effects in terrestrial-aquatic environments with which they interact.

Considering the petrological features of the Kısacık volcanics, it is seen that the Fe_2O_3, TiO_2 and P_2O_5 contents have higher enrichment than the felsic and intermediate rocks. In the rock, while the maximum Fe_2O_3 is 21.26%, TiO_2 2.31% and P_2O_5 0.50%, in felsic and intermediate rocks, the Fe_2O_3 contents are 3.81% and 4.28%, P_2O_5 contents are 742 and 0.12 ppm, and TiO_2 contents are 0.56% and 0.43%

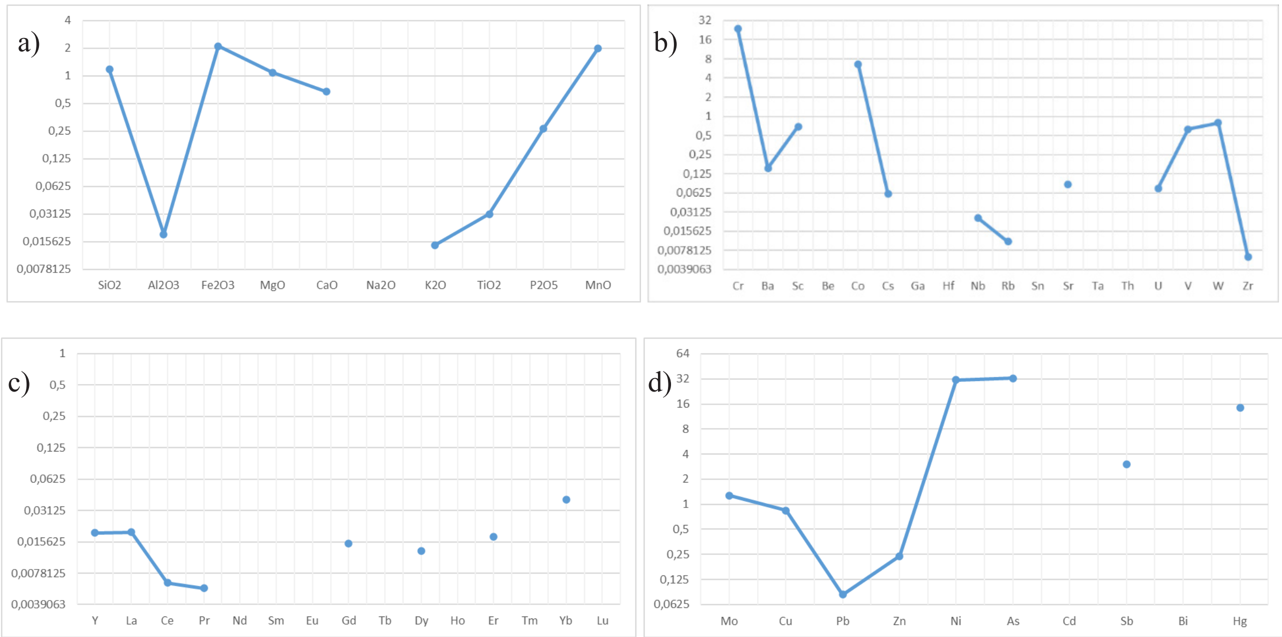

Figure 7. a) The major oxide line chart diagram (EEF values) of the Listvenite according to the upper crust averages; b) EEF line chart diagram for Co, Cs, Ga, Hf, Nb, Rb, Sn, Sr, Ta, Th, U, V, W, and Zr in Listvenite; c) EEF line chart for REEs in Listvenite according to upper crust averages; d) EEF line chart diagram for heavy metal and associated elements in Listvenite (oxides in %, others in ppm).

(**Appendix 1**)[56]. It was observed that the Cr, Cs, Rb, Th, U, V and W concentrations in the Kısacık volcanics exceeded the concentrations in intermediate and felsic rocks (**Appendixes 1** and **2**). It is understood that hydrothermal alteration processes are effective in the enrichment of the Kısacık volcanic rocks for the mentioned elements rather than parental rock.

It is noteworthy that the maximum MgO content of the ophiolitic rocks is enriched according to the averages of upper crust, felsic and intermediate rocks (approximately 16 times compared to the upper crust). However, considering the parental rocks of ophiolitic rocks, it will be seen that the MgO content is below the average of the relevant rock (MgO content of ultramafic rocks is 38.47%). Therefore, there is no real enrichment in the rock. Although the MgO concentrations are high (max. value 33.31%) in Baharlar listvenitic rocks within the ophiolitic rocks, an enrichment with these values cannot be mentioned when the parental rocks are considered (**Appendix 1**). While the Cr and Co compositions of the Baharlar listvenitic rocks were enriched with respect to intermediate and felsic rocks (**Appendix 2**), it was observed that the Cr concentrations were higher when compared to the ultramafic rocks[56], but the Co concentrations were normal. It is thought that the parental rock is important in the high Cr contents in the rocks, but the hydrothermal alteration and weathering processes also increase the enrichment in Cr.

The MgO and CaO contents of the Kazdağ group rocks exceed the upper crust averages (12.06% and 13.88%, respectively) (**Appendix 1**). Considering that the Kazdağ group rocks are close to the diorite/granodiorite type rocks in general, these values will be seen to be high. It can be said that the high values found in the Kazdağ group rocks are related to the metamorphic and hydrothermal processes that the rocks are exposed to.

When listvenite is considered, although there is not a very high enrichment in SiO_2 compared to the upper crust, it is understood that listvenite has a significant SiO_2 enrichment when the source rock of listvenite (ultramafic rock) is considered. This enrichment is directly related to the hydrothermal alteration forming the litvenitization. Listvenite shows an enrichment in terms of Cr and Co compared to the upper crust. However, when compared to the source rock, there is an enrichment in terms of Cr, but a serious enrichment in terms of Co cannot be mentioned (**Appendix 2**). It is understood that the main rock of the rock is effective in the enrichment of listvenite in terms of Cr, but the alteration and weathering (lateritization) that the rock is exposed to contribute to the enrichment.

When the field rocks are considered in terms of rare earth elements, it is seen that the rare earth concentrations between La-Gd of the Kısacık Volcanics are enriched compared to the intermediate and felsic rocks (**Appendix 3**). It can be said that hydrothermal alteration and weathering processes are effective[57–61] in this enrichment in the Kısacık Volcanics. There is no enrichment by REEs in ophiolitic rocks, Baharlar listvenitic rocks in ophiolitic rocks, Kazdağ Group rocks and listvenite when compared with their parental rocks.

Considering the heavy metal and related element contents (max. content) of the Kısacık Volcanics, a remarkable enrichment is observed according to the intermediate and felsic rocks, as well as the ultramafic and mafic rocks (**Appendix 4**). Considering that the parental rocks of the Kısacık Volcanic rocks are closer to intermediate and felsic characters, the mentioned enrichment is remarkable. This enrichment was associated with the hydrothermal and weathering processes to which the rocks were exposed. In ophiolitic rocks, on the other hand, heavy metal and related elements Cu, Cd, Bi contents show an enrichment according to ultramafic rock types[56]. When heavy metal and related elements are taken into account in Baharlar listvenitic rocks, Ni, As, Sb, Hg contents (max. contents of them) showed an enrichment compared to the source rock[56] (**Appendix 4**). It is thought that the enrichment in As, Sb, Hg contents of the rock is related to hydrothermal alteration, and hydrothermal alteration and weathering are effective in the enrichment of Ni.

It is observed that Ni and As contents of heavy metal and related elements in Kazdağ Group Rocks are enriched compared to the source rock[56]. Hydrothermal alteration was effective in these enrichments. However, Ni enrichment is also affected by the mafic minerals in the rock (**Appendix 4**).

Listvenite showed a remarkable enrichment of Ni, As, Sb and Hg elements compared to the source rock[56]. While the Ni enrichment in listvenite is primarily related to the source rock, the enrichment by As, Sb and Hg elements is associated with the hydrothermal alteration process that formed the listvenite and the subsequent weathering.

5. Conclusions

In this study, the major oxide and trace element/heavy metal and REE contents of the rocks outcropping in Kısacık (Ayvacık/Çanakkale-Western Türkiye) and its vicinity were examined, and it was investigated whether they showed an enrichment according to the upper crust average values. The rocks in the area are discussed under 5 groups as Kısacık volcanics, Ophiolitic Melange, listvenitic rocks (Baharlar Listvenitic Rocks) in Ophiolitic Mélange, Kazdağ Group Rocks and Lisvenite. Considering the main oxide and element contents of the Kısacık Volcanics, it was observed that the averages of SiO_2, Fe_2O_3 and K_2O were above the upper crust. It was determined that more than half of the samples were in the Medium Enrichment Class in terms of SiO_2. When other elements are considered, it has been determined that the averages of Cr, Cs, Th, U, W, La, Nd, Sm, Eu, Tm, Yb, Lu, Be, Mo, As, Cd, Sb, Bi and Hg elements exceed the upper crust values. It is seen that more than half of the samples exceed the upper crust values and fall into the Medium Enrichment Class, especially by the elements Cs, Rb, Ta, Th, U, W, La, Eu, Tm, Yb, Lu, Mo, and Cd.

Considering the oxide and elemental contents of the Ophiolitic Mélange, Fe_2O_3, MgO, CaO, TiO_2, P_2O_5 and MnO oxide averages are observed to exceed the upper crust values. When the rocks are evaluated in terms of trace element/heavy metal and rare earth elements, although there is an enrichment in Cr, Sc, Co, Nb, Sr, Mo, Cu, Ni, Cd, Sb and Bi elements, according to EEF, only Cr, Sc, Co, V, Cu and Ni elements fall into the High Enrichment Class.

Considering the listvenitic rocks in the Ophiolitic Melange, it was determined that the averages of Fe_2O_3, MgO oxides and Cr, Co, Ni, As and Hg exceeded the upper crust averages. It was determined that the Cr, Co, Ni, Sb, As and Hg enrichments were more than 3 times in some samples and fell into the High Enrichment Class. Of these, the enrichment by Cr, Co, Ni elements was associated with the original rock, while the enrichment by Sb, As, and Hg elements was due to hydrothermal alteration.

When the oxide and element concentrations of the Kazdağ Group were compared with the upper crust averages, it was determined that MgO, CaO, K_2O, and MnO exceeded the upper crust values. High MgO and CaO values are associated with the parental rock, while high K_2O and MnO values are associated with hydrothermal alteration and weathering. It was also observed that the averages of Cr, Co, Ta, U, W, Mo, Cu, Ni, As and Cd exceeded the upper crust values. The enrichment by Cr, Co, U, W, Ni and As were in the High Enrichment Class according to EEF.

As to Listvenit, SiO_2, Fe_2O_3, MgO and MnO concentrations exceed the upper crust values, and fall into the Medium Enrichment Class. The high values of these values present a significant relationship in the listvenitization process. Because listvenites are a process of silicification and carbonation of ultrabasic rocks and a relative enrichment with Fe_2O_3 and MgO. Concentrations of elements Cr, Co, Ni, As, Sb and Hg of listvenites fall into the High Enrichment Class according to EEF. Among these elements, the enrichment in Cr, Co, Ni elements is related to the parental rock, while the enrichment in As, Sb and Hg elements is due to hydrothermal alteration.

When the element contents of the rocks are evaluated together, it has been determined that the enrichment in some elements originates from the parental rock and that secondary, epigenic processes increase these enrichments to remarkable levels, while the enrichment of some elements developed through secondary, epigenetic processes such as hydrothermal alteration.

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Conflict of interest

The author declares that he has no conflict of interest.

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Appendixes

Appendix 1

Table 1. Descriptive statistics for the major oxides + Cr element of the rock groups of the study area and their averages of upper crust, ultramafic, mafic, intermediate, and felsic rocks (oxides in %, Cr in ppm)

Group		SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Cr
Kisacık Volcanics	Mean	70.15	11.99	5.50	1.10	1.56	1.18	3.55	0.57	0.13	0.05	146.42
	Median	70.73	13.53	3.47	0.78	1.76	0.18	3.26	0.46	0.07	0.05	75.26
	Geo. Mean	68.43	8.89	3.55	0.71	0.86	0.33	2.34	0.37	0.07	0.04	81.11
	Minimum	45.10	0.40	0.44	0.08	0.08	0.01	0.03	0.12	0.01	0.01	20.53
	Maximum	89.23	20.20	21.26	2.51	3.28	4.34	6.39	2.31	0.50	0.10	773.13
	Std. Dev.	15.80	6.05	5.78	0.88	1.28	1.62	1.91	0.65	0.15	0.03	224.41
	Kurtosis	−1.53	−0.32	6.22	−1.11	−1.59	−0.22	−0.40	7.01	3.76	−0.52	8.99
	Skewness	−0.25	−0.60	2.32	0.54	0.18	1.23	−0.11	2.51	1.83	0.53	2.95
Ophiolitic Mélange	Mean	45.78	10.67	8.85	11.93	7.66	1.32	1.06	0.62	0.17	0.15	789.56
	Median	46.11	13.28	9.82	5.16	9.68	1.25	0.68	0.78	0.17	0.14	95.79
	Geo. Mean	45.66	7.38	8.39	8.02	6.00	0.44	0.52	0.31	0.11	0.15	234.13
	Minimum	40.14	1.63	4.27	3.12	1.26	0.02	0.09	0.03	0.02	0.12	27.37
	Maximum	50.80	19.76	11.69	34.61	12.29	2.73	2.63	1.30	0.31	0.21	2,353.61
	Std. Dev.	3.78	7.86	2.79	13.08	4.36	1.29	1.11	0.54	0.12	0.04	1,045.02
	Kurtosis	2.05	−2.45	2.43	3.73	−0.38	−2.93	−1.40	−2.09	−0.90	−0.17	−0.73
	Skewness	−0.41	−0.23	−1.36	1.93	−0.80	0.09	0.75	−0.03	0.00	0.99	1.06
Listvenitic Rocks	Mean	40.48	1.04	7.85	26.51	0.70	0.01	0.05	0.03	0.02	0.08	1,578.20
	Median	39.13	0.57	7.69	24.47	0.65	0.01	0.05	0.03	0.02	0.09	1,737.84
	Geo. Mean	40.40	0.70	7.73	26.07	0.69	0.01	0.03	0.03	0.02	0.08	1,506.54
	Minimum	38.19	0.26	6.28	21.74	0.60	0.01	0.01	0.01	0.02	0.07	971.55
	Maximum	44.12	2.30	9.57	33.31	0.85	0.01	0.08	0.06	0.02	0.09	2,025.20
	Std. Dev.	3.19	1.10	1.65	6.05	0.13		0.04	0.03	0.00	0.01	544.67
	Skewness	1.56	1.58	0.42	1.34	1.46		−0.42	0.59		−1.73	−1.21
Kazdag Group	Mean	54.80	8.48	4.88	6.22	7.64	1.64	3.03	0.09	0.02	0.14	858.66
	Median	54.80	8.48	4.88	6.22	7.64	1.64	3.03	0.09	0.02	0.14	858.66
	Geo. Mean	52.26	5.99	4.15	2.11	4.39	0.61	0.81	0.07	0.01	0.11	319.30
	Minimum	38.30	2.48	2.31	0.37	1.39	0.12	0.11	0.03	0.01	0.05	61.58
	Maximum	71.30	14.48	7.45	12.06	13.88	3.15	5.94	0.15	0.02	0.23	1,655.74
	Std. Dev.	23.33	8.49	3.63	8.27	8.83	2.14	4.12	0.08	0.01	0.13	1,127.24
Listvenite	Concentration	78.12	0.29	10.61	2.70	2.42		0.04	0.02	0.04	0.20	2,189.41
Total	Mean	59.53	9.35	6.76	7.56	3.42	1.20	2.30	0.43	0.11	0.10	669.20
	Median	53.18	9.49	6.52	2.48	1.82	0.18	2.09	0.16	0.04	0.08	95.79
	Geo. Mean	57.03	4.98	5.12	2.37	1.58	0.32	0.70	0.18	0.06	0.07	211.25
	Minimum	38.19	0.26	0.44	0.08	0.08	0.01	0.01	0.01	0.01	0.01	20.53
	Maximum	89.23	20.20	21.26	34.61	13.88	4.34	6.39	2.31	0.50	0.23	2,353.61
	Std. Dev.	17.97	7.12	4.62	10.90	4.12	1.48	2.23	0.56	0.13	0.07	847.13
	Kurtosis	−1.41	−1.62	3.39	1.57	1.34	−0.75	−1.02	5.66	3.29	−0.43	−0.76
	Skewness	0.41	0.00	1.35	1.66	1.57	0.92	0.56	2.18	1.76	0.72	0.96
R and G*		66.62	15.40	5.04	2.48	3.59	3.27	2.80	0.64	0.15	0.1	92
Ultramafic**		42.35	2.27	12.40	38.47	2.24	0.66	0.02	0.05	0.0446	0.20	1,800
Mafic**		50.27	15.64	11.06	7.54	10.07	2.52	1.00	0.50	0.259	0.23	185
Intermediate**		65.26	15.7	4.28	2.02	3.85	4.08	2.55	0.56	0.17	0.08	38.3
Felsic**		69.45	14.73	3.81	1.83	3.34	3.56	2.99	0.43		0.07	56.2

R and G*: Rudnick and Gao[52]
**[56]

Appendix 2

Table 2. Descriptive statistics for the Co, Cs, Ga, Hf, Nb, Rb, Sn, Sr, Ta, Th, U, V, W and Zr elements of the study area rock groups and their averages of upper crust, and ultramafic, mafic, intermediate and felsic rocks (in ppm)

Group		Co	Cs	Ga	Hf	Nb	Rb	Sn	Sr	Ta	Th	U	V	W	Zr
Kisacık Volcanics	Mean	10.02	10.25	12.42	4.53	11.28	125.05	2.43	161.55	0.87	23.22	4.30	120.00	3.15	151.95
	Median	5.10	6.00	11.15	3.90	11.00	97.20	2.00	146.00	0.90	25.45	3.80	42.00	2.10	94.90
	Geo. Mean	4.85	5.42	10.45	3.77	9.49	76.16	2.03	113.64	0.73	18.24	2.73	65.38	2.32	87.36
	Minimum	0.40	0.40	2.90	0.90	1.70	0.70	1.00	27.20	0.10	2.70	0.10	21.00	0.60	1.40
	Maximum	39.50	50.30	22.50	10.40	20.00	293.30	6.00	453.80	1.40	43.30	10.10	621.00	9.90	437.80
	Std. Dev.	11.54	14.31	6.94	2.77	5.48	80.31	1.72	133.27	0.39	12.83	3.06	176.31	2.78	124.54
	Kurtosis	3.96	7.23	−1.39	1.20	−0.10	0.68	3.77	0.97	0.32	−0.46	−0.22	7.88	2.75	1.69
	Skewness	1.83	2.63	0.28	1.09	−0.17	0.63	1.82	1.15	−0.55	−0.17	0.51	2.73	1.71	1.21
Ophiolitic Mélange	Mean	46.44	1.96	9.16	2.17	6.34	26.36	1.50	306.60	0.67	2.93	1.03	150.40	1.10	47.10
	Median	38.20	0.50	12.50	2.30	4.60	21.50	1.50	293.20	0.30	2.85	0.90	184.00	1.10	61.60
	Geo. Mean	38.52	0.99	6.52	2.15	2.17	10.97	1.41	154.53	0.50	2.05	0.91	112.07	1.10	22.41
	Minimum	16.80	0.30	1.40	1.80	0.30	0.80	1.00	9.60	0.30	0.40	0.50	28.00	1.00	2.40
	Maximum	102.50	6.60	15.40	2.40	21.00	70.40	2.00	681.60	1.40	5.60	1.70	281.00	1.20	90.40
	Std. Dev.	33.41	2.67	6.34	0.32	8.54	28.34	0.71	269.13	0.64	2.16	0.61	103.87	0.10	40.66
	Kurtosis	2.83	3.78	−2.82		3.49	0.65		−0.94		0.68		−1.74		−2.89
	Skewness	1.59	1.95	−0.53	−1.55	1.81	1.06		0.44	1.73	0.20	0.94	−0.06	0.00	−0.33
Listvenitic Rocks	Mean	80.30	0.40	1.30	0.15	0.55	2.03		27.87		0.30	0.10	32.00	1.67	3.87
	Median	78.20	0.40	1.30	0.15	0.55	1.80		27.90		0.30	0.10	25.00	2.00	3.30
	Geo. Mean	77.94	0.30	1.30	0.14	0.42	1.77		26.14		0.30	0.10	25.46	1.56	3.76
	Minimum	57.60	0.10	1.30	0.10	0.20	0.90		16.20		0.30	0.10	11.00	0.90	3.10
	Maximum	105.10	0.70	1.30	0.20	0.90	3.40		39.50		0.30	0.10	60.00	2.10	5.20
	Std. Dev.	23.82	0.30		0.07	0.49	1.27		11.65				25.24	0.67	1.16
	Skewness	0.39	0.00				0.80		−0.01				1.15	−1.69	1.67
Kazdag Group	Mean	30.25	1.60	6.80	1.15	4.50	76.90		310.05	1.10	2.50	5.05	62.00	8.50	27.80
	Median	30.25	1.60	6.80	1.15	4.50	76.90		310.05	1.10	2.50	5.05	62.00	8.50	27.80
	Geo. Mean	13.74	1.16	4.38	0.87	2.06	24.77		218.02	1.10	1.50	1.41	62.00	3.60	23.08
	Minimum	3.30	0.50	1.60	0.40	0.50	4.10		89.60	1.10	0.50	0.20	62.00	0.80	12.30
	Maximum	57.20	2.70	12.00	1.90	8.50	149.70		530.50	1.10	4.50	9.90	62.00	16.20	43.30
	Std. Dev.	38.11	1.56	7.35	1.06	5.66	102.95		311.76		2.83	6.86		10.89	21.92
Listvenite	Concentration	112.70	0.30			0.30	0.90		26.90			0.20	61.00	1.50	1.20
Total	Mean	34.39	5.78	10.27	3.20	7.91	75.82	2.22	183.67	0.84	14.66	3.38	109.10	3.07	89.79
	Median	16.65	2.65	10.45	2.50	8.50	63.85	2.00	111.90	0.90	5.90	2.45	61.00	1.70	68.10
	Geo. Mean	14.39	1.89	7.41	1.95	3.64	21.66	1.88	99.11	0.70	6.39	1.52	64.58	2.00	30.45
	Minimum	0.40	0.10	1.30	0.10	0.20	0.70	1.00	9.60	0.10	0.30	0.10	11.00	0.60	1.20
	Maximum	112.70	50.30	22.50	10.40	21.00	293.30	6.00	681.60	1.40	43.30	10.10	621.00	16.20	437.80
	Std. Dev.	36.60	10.96	6.88	2.72	6.90	81.40	1.56	192.11	0.42	14.34	3.37	139.19	3.81	109.44
	Kurtosis	−0.07	14.04	−0.97	1.99	−0.90	0.67	4.88	0.78	−1.02	−0.90	−0.35	9.13	7.48	3.85
	Skewness	1.06	3.58	0.27	1.34	0.49	1.06	2.05	1.28	−0.30	0.67	0.90	2.79	2.68	1.85
R and G*		17.3	4.9	17.5	5.3	12	84	2.1	320	0.9	10.5	2.7	97	1.9	193
Ultramafic**		175	0.1	1.8	0.4	9	1.1	0.5	5.5	0.5	0.0045	0.002	40	0.5	38
Mafic**		47	1.1	18	1.5	20	38	1.5	452	0.8	3.5	0.75	225	0.9	120
Intermediate**		13.5	2.3	19.9	4.8	11.3	72.4	1.2	490	0.81	8.8	1.9	67	0.4	177
Felsic**		17.3	3	20.2	4.7	10.3	109.2	3	296.4	0.9	11.4	2.48	66.1	2	163.6

R and G*: Rudnick and Gao[52]
**[56]

Appendix 3

Table 3. Descriptive statistics of rare earth element concentrations and their averages of upper crust, and ultramafic, mafic, intermediate and felsic rocks (in ppm)

Group		Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Kısacık Volcanics	Mean	16.11	35.52	62.70	7.17	27.95	4.77	1.01	3.45	0.55	3.09	0.65	1.75	0.31	2.06	0.33
	Median	14.20	31.40	52.00	5.56	23.45	4.05	1.05	3.19	0.55	3.08	0.64	1.54	0.30	2.10	0.35
	Geo. Mean	10.93	21.77	33.55	3.70	19.88	3.27	0.68	1.99	0.43	2.52	0.55	1.15	0.27	1.81	0.29
	Minimum	0.40	0.60	0.30	0.04	4.20	0.73	0.16	0.06	0.10	0.56	0.11	0.03	0.05	0.34	0.06
	Maximum	35.50	103.6	203.8	26.62	102.3	18.22	3.44	12.31	1.56	7.49	1.31	3.71	0.54	3.30	0.50
	Std. Dev.	9.85	27.64	54.23	7.18	27.97	5.04	0.96	3.34	0.41	1.95	0.34	1.06	0.13	0.83	0.13
	Kurtosis	0.42	3.38	4.76	6.03	6.76	6.90	4.82	5.29	3.94	2.18	0.29	−0.03	0.92	1.00	1.45
	Skewness	0.24	1.43	1.84	2.21	2.44	2.47	1.95	2.03	1.70	1.17	0.39	0.07	−0.20	−0.68	−0.85
Ophiolitic Mélange	Mean	11.86	10.78	20.52	2.51	10.14	2.18	0.72	2.26	0.37	2.15	0.45	1.36	0.24	1.29	0.24
	Median	16.40	16.50	31.30	3.84	15.20	3.15	0.98	3.41	0.54	3.23	0.65	1.96	0.29	1.67	0.28
	Geo. Mean	5.98	5.63	10.02	1.17	4.66	0.97	0.37	1.12	0.17	1.12	0.26	0.69	0.19	0.72	0.20
	Minimum	0.40	1.00	1.40	0.13	0.50	0.08	0.06	0.10	0.01	0.09	0.03	0.04	0.05	0.06	0.06
	Maximum	20.80	18.60	35.20	4.32	17.60	3.90	1.32	3.82	0.63	3.63	0.77	2.33	0.33	2.31	0.34
	Std. Dev.	9.45	8.92	17.24	2.12	8.62	1.86	0.61	1.85	0.30	1.71	0.35	1.04	0.13	1.00	0.13
	Kurtosis	−2.92	−3.27	−3.28	−3.28	−3.26	−3.17	−3.08	−3.22	−3.06	−3.09	−3.05	−2.75	3.28	−2.62	2.17
	Skewness	−0.53	−0.57	−0.58	−0.58	−0.57	−0.52	−0.43	−0.59	−0.58	−0.61	−0.57	−0.60	−1.78	−0.45	−1.51
Listvenitic Rocks	Mean	0.83	0.70	1.17	0.12	0.53	0.11	0.04	0.14	0.02	0.21	0.07	0.11	0.03	0.10	0.02
	Median	0.60	0.70	1.10	0.11	0.60	0.11	0.04	0.14	0.02	0.21	0.07	0.11	0.03	0.06	0.02
	Geo. Mean	0.66	0.65	1.09	0.11	0.50	0.11	0.03	0.12	0.02	0.19	0.07	0.10	0.03	0.08	0.02
	Minimum	0.30	0.40	0.70	0.07	0.30	0.09	0.03	0.05	0.01	0.12	0.07	0.06	0.03	0.05	0.01
	Maximum	1.60	1.00	1.70	0.17	0.70	0.13	0.04	0.24	0.03	0.29	0.07	0.16	0.03	0.19	0.03
	Std. Dev.	0.68	0.30	0.50	0.05	0.21	0.02	0.01	0.10	0.01	0.12		0.07		0.08	0.01
	Skewness	1.36	0.00	0.59	0.59	−1.29	0.00		0.16						1.70	
Kazdag Group	Mean	18.40	3.40	6.20	0.79	3.25	1.01	0.34	1.77	0.38	2.75	0.61	1.81	0.28	1.87	0.27
	Median	18.40	3.40	6.20	0.79	3.25	1.01	0.34	1.77	0.38	2.75	0.61	1.81	0.28	1.87	0.27
	Geo.Mean	12.82	3.14	5.72	0.74	3.04	0.92	0.32	1.49	0.28	2.05	0.42	1.24	0.19	1.29	0.18
	Minimum	5.20	2.10	3.80	0.51	2.10	0.59	0.23	0.82	0.13	0.92	0.17	0.49	0.07	0.52	0.07
	Maximum	31.60	4.70	8.60	1.07	4.40	1.43	0.45	2.71	0.62	4.58	1.05	3.13	0.49	3.21	0.46
	Std. Dev.	18.67	1.84	3.39	0.40	1.63	0.59	0.16	1.34	0.35	2.59	0.62	1.87	0.30	1.90	0.28
Listvenite	Concentration	0.40	0.60	0.40	0.04				0.06		0.05		0.04		0.08	
Total	Mean	12.55	20.64	36.75	4.24	16.92	3.05	0.76	2.42	0.43	2.38	0.56	1.43	0.27	1.48	0.27
	Median	13.05	16.60	32.00	3.46	12.60	1.85	0.45	1.71	0.47	2.16	0.59	1.49	0.27	1.67	0.30
	Geo. Mean	5.67	7.07	11.13	1.24	6.60	1.28	0.39	0.99	0.23	1.28	0.38	0.69	0.21	0.78	0.19
	Minimum	0.30	0.40	0.30	0.04	0.30	0.08	0.03	0.05	0.01	0.05	0.03	0.03	0.03	0.05	0.01
	Maximum	35.50	103.6	203.8	26.62	102.3	18.22	3.44	12.31	1.56	7.49	1.31	3.71	0.54	3.30	0.50
	Std. Dev.	10.80	24.95	46.97	5.92	22.90	4.04	0.81	2.77	0.37	1.96	0.37	1.14	0.15	1.13	0.16
	Kurtosis	−0.74	4.79	7.01	9.71	10.59	10.93	5.88	7.16	3.49	0.67	−0.71	−1.05	−0.62	−1.43	−1.06
	Skewness	0.45	1.91	2.30	2.77	2.94	2.98	2.04	2.24	1.40	0.76	0.18	0.24	−0.16	0.00	−0.39
R and G*		21	31	63	7.1	27	4.7	1.0	4.0	0.7	3.9	0.83	2.3	0.3	2.0	0.31
Ultramafic**			1.3	3.5	0.49	1.9	0.42	0.14	0.54	0.12	0.77	0.12	0.3	0.041	0.38	0.036
Mafic**		21	6.1	16	2.7	14	4.3	1.5	6.2	1.1	5.9	1.4	3.6	0.6	3.2	0.55
Intermediate**		16.3	32.5	64.6	4.1	24.4	4.23	1.2	3.3	0.56	1.2	1.35	0.6	0.5	1.4	0.23
Felsic**		25	35.96	67.9	5.1	30	5.7	1.1	4.7	0.56	3.4	1.3	2.1	0.45	2.25	0.35

R and G*: Rudnick and Gao[52]
**[56]

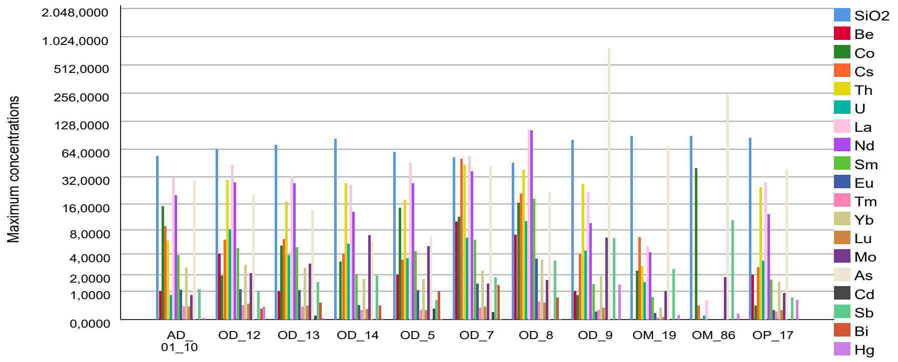
Appendix 4

Table 4. Descriptive swtatistics and upper crust averages of Ba, Sc, Be, Mo, Cu, Pb, Zn, Ni, As, Cd, Sb, Bi, and Hg elements of the rock groups of the study area and their averages of upper crust, and ultramafic, mafic, intermediate and felsic rocks (in ppm)

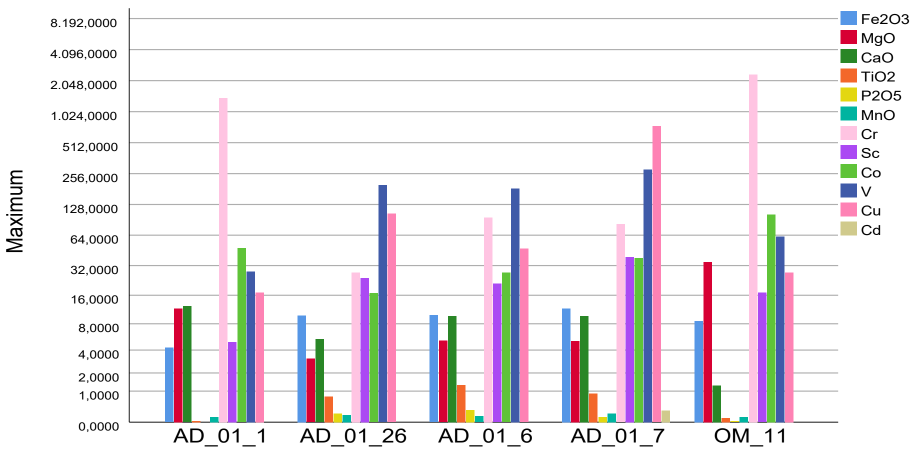
Group		Ba	Sc	Be	Mo	Cu	Pb	Zn	Ni	As	Cd	Sb	Bi	Hg
Kisacık Volcanics	Mean	586.55	8.18	3.50	2.80	30.63	20.26	44.55	68.85	114.89	0.20	2.80	0.70	0.24
	Median	532.00	7.00	2.00	1.80	23.50	11.00	37.00	8.00	28.30	0.20	1.80	0.60	0.03
	Geo.ean	363.84	5.18	2.41	2.12	18.75	12.88	20.58	11.00	36.03	0.18	1.90	0.62	0.07
	Minimum	22.00	1.00	1.00	0.80	2.20	1.30	2.00	1.70	5.60	0.10	0.60	0.30	0.01
	Maximum	1,607.00	23.00	10.0	6.90	84.20	60.40	201.00	643.20	765.80	0.30	10.30	1.30	1.35
	Std. Dev.	488.98	7.68	3.34	2.24	27.71	19.12	57.17	190.79	226.96	0.10	2.96	0.38	0.41
	Kurtosis	0.25	0.21	0.80	−0.40	0.34	0.56	6.31	10.91	8.31		3.89	−0.72	5.48
	Skewness	0.88	1.13	1.35	1.08	1.12	1.26	2.33	3.30	2.84	0.00	2.02	0.76	2.31
Ophiolitic Mélange	Mean	188.40	21.20	1.50	0.80	186.60	5.50	43.40	450.56	2.20	0.30	0.37	0.40	0.01
	Median	60.00	21.00	1.50	0.70	47.00	6.10	43.00	47.00	2.10	0.30	0.30	0.40	0.01
	Geo.Mean	93.96	17.56	1.41	0.72	70.00	4.53	34.20	96.53	2.14	0.30	0.33	0.39	0.01
	Minimum	20.00	5.00	1.00	0.30	17.10	1.40	9.00	5.60	1.60	0.30	0.20	0.30	0.01
	Maximum	445.00	39.00	2.00	1.30	737.80	9.80	78.00	1,721.50	3.00	0.30	0.60	0.50	0.02
	Std. Dev.	206.77	12.30	0.71	0.37	309.95	3.26	27.68	731.94	0.56		0.21	0.14	0.01
	Kurtosis	−2.99	1.28		0.09	4.76	−0.77	−1.47	3.77	−0.78				
	Skewness	0.64	0.30		0.05	2.17	0.03	0.02	1.95	0.61		1.29		1.73
Listvenitic Rocks	Mean	16.33	7.67		0.77	15.40	1.73	21.33	1,599.83	35.47	0.10	2.30		0.28
	Median	18.00	5.00		0.80	14.30	1.30	22.00	1,628.20	14.50	0.10	0.90		0.35
	Geo.Mean	15.82	6.54		0.59	13.94	1.48	19.93	1,552.23	16.18	0.10	0.81		0.12
	Minimum	11.00	4.00		0.20	7.90	0.80	12.00	1,119.50	3.30	0.10	0.10		0.01
	Maximum	20.00	14.00		1.30	24.00	3.10	30.00	2,051.80	88.60	0.10	5.90		0.47
	Std. Dev.	4.73	5.51		0.55	8.11	1.21	9.02	466.80	46.35		3.14		0.24
	Skewness	−1.39	1.67		−0.27	0.60	1.41	−0.33	−0.27	1.62		1.61		−1.25
Kazdag Group	Mean	290.00	6.50	2.00	1.85	46.30	11.60	13.50	503.55	18.50	0.10	0.15		0.01
	Median	290.00	6.50	2.00	1.85	46.30	11.60	13.50	503.55	18.50	0.10	0.15		0.01
	Geo.Mean	159.80	5.48	2.00	1.73	40.41	11.37	10.49	174.49	11.49	0.10	0.14		0.01
	Minimum	48.00	3.00	2.00	1.20	23.70	9.30	5.00	31.20	4.00	0.10	0.10		0.01
	Maximum	532.00	10.00	2.00	2.50	68.90	13.90	22.00	975.90	33.00	0.10	0.20		0.01
	Std. Dev.	342.24	4.95		0.92	31.96	3.25	12.02	668.00	20.51		0.07		
Listvenite	Concentration	102.00	10.00		1.40	23.60	1.40	16.00	1,454.80	156.30		1.20		0.72
Total	Mean	369.32	11.00	3.00	1.92	65.10	12.74	37.00	466.89	71.57	0.18	2.02	0.63	0.23
	Median	221.50	9.00	2.00	1.30	23.85	7.95	23.50	34.25	17.40	0.15	1.05	0.50	0.03
	Geo.Mean	152.76	7.31	2.15	1.34	26.32	6.76	21.38	56.82	16.39	0.16	0.97	0.55	0.06
	Minimum	11.00	1.00	1.00	0.20	2.20	0.80	2.00	1.70	1.60	0.10	0.10	0.30	0.01
	Maximum	1,607.00	39.00	10.0	6.90	737.80	60.40	201.00	2,051.80	765.80	0.30	10.30	1.30	1.35
	Std. Dev.	426.49	9.67	2.93	1.84	152.73	15.57	43.19	688.77	166.37	0.10	2.62	0.36	0.35
	Kurtosis	2.10	1.81	2.59	2.75	20.40	4.06	9.91	0.01	15.86	−2.39	4.67	0.40	4.86
	Skewness	1.50	1.34	1.80	1.88	4.45	2.10	2.80	1.22	3.84	0.46	2.16	1.15	2.12
R and G*		664	14.4	2.1	1.1	28	17	67	47	4.8	0.09	0.4	0.16	0.05
Ultramafic**		0.7	10	0.2	0.3	15	0.5	40	2,000	0.8	0.05	0.1		0.01
Mafic**		315	27	0.7	1.5	94	7	118	145	2.2	0.21	0.6	0.16	0.09
Intermediate**		837	10.4	1.6	0.82	22.7	18.2	70.7	19.4	1.3	71	0.21		8.7
Felsic**		614	12.3	2.5	1.2	18.1	23.9	63.6	22.8	1.7	0.13	0.2		0.08

R and G*: Rudnick and Gao[52]
**[56]

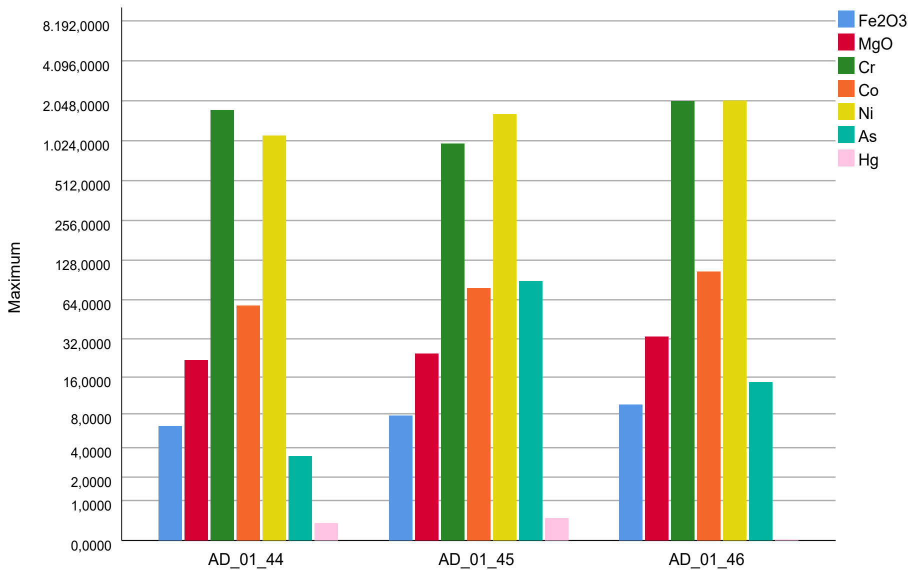
Appendix 5



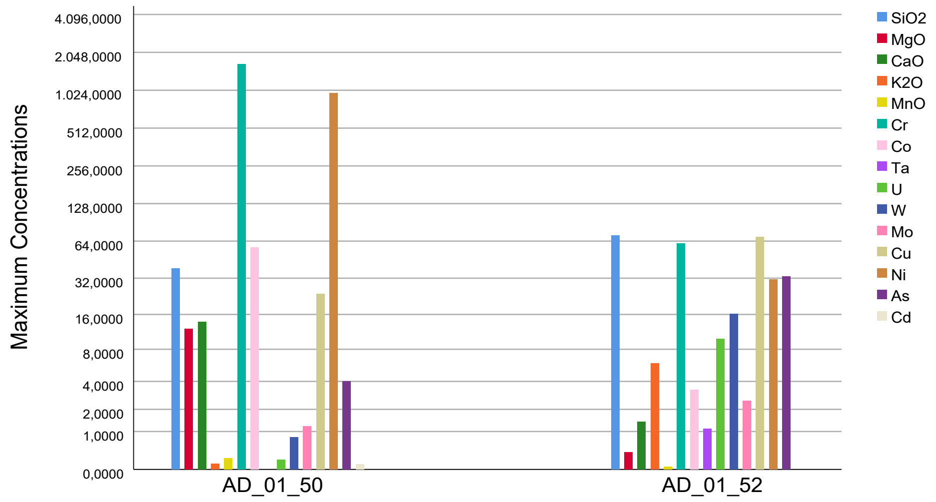
a) Bar diagram of the maximum element concentrations of the Kısacık volcanics (SiO_2 in %, others in ppm).



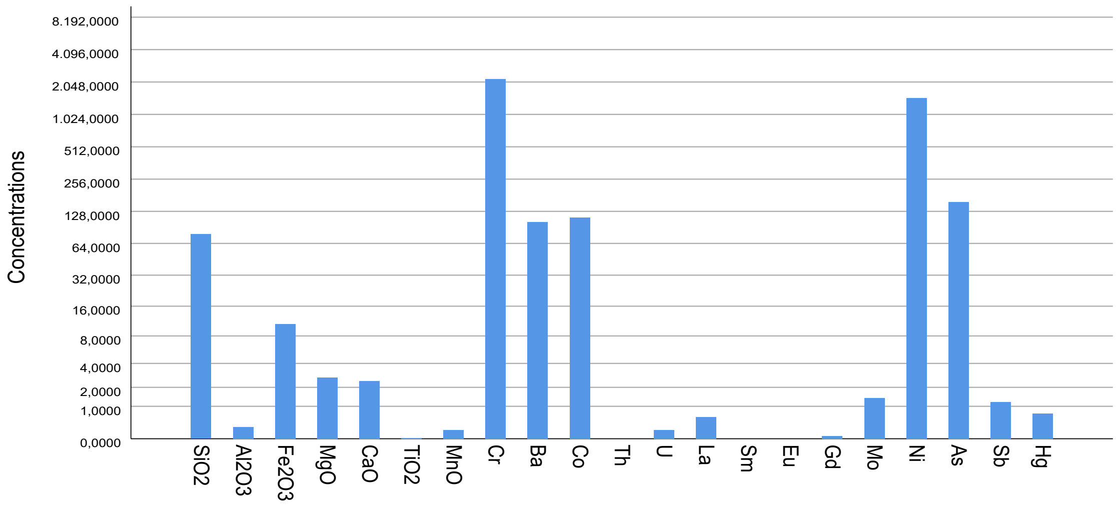
b) Bar diagram of maximum concentrations of enriched elements in ophiolitic mélange group rocks (oxides in %, others in ppm).



c) Bar diagram of maximum concentrations of enriched elements in listvenitic rocks in the Ophiolitic Melange (oxides in %, others in ppm).



d) Bar diagram of maximum concentrations of enriched elements in Kazdağ Group Rocks (oxides in %, others in ppm).



e) Concentrations of notable oxides and elements in listvenite (oxides in %, others in ppm).