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Geological, Mineralogical and Geochemical Features of the Kiziltepe (Aladag) Skarn Deposit (Ezine/Canakkale-North West Turkey)

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Abstract

Kiziltepe Skarn Mineralization located 35 km south of the Canakkale and 8 km southwest of Ezine County near the Kestanbol Pluton. Cambrian to Holocene aged magmatic, metamorphic and sedimentary rocks crop out in the study area. The basement of the study area is formed by Pre(?) - Lower Cambrian metasandstone, metaconglomerate, phyllite and chalc schist of low-grade metamorphic Geyikli formation. Recrystallized limestones of the Middle-Late Permian Bozalan Formation cover the Geyikli Formation. Cretaceous Denizgoren Ophiolites thrust over the older units. Upper Oligocene-Lower Miocene Hallaclar Volcanics composed of altered andesite and rhyolite. Kestanbol Pluton represented by quartz-monzonite and monzonite besides monzodiorite syenite and quartz-syenite porphyry are cut the older units. Lower- Middle Miocene Ezine Volcanics composed of pyroxene-andesite and trachyte.

Kiziltepe skarn deposit was developed close to Kestanbol Pluton contacts with the carbonaceous rocks of the Bozalan Formation and Denizgoren Ophiolites. Therefore Ca-silicates and some metallic enrichment such as iron, copper, zinc and lead were developed in this altered zone. Mainly garnet (grossular), tremolite/actinolite, epidote and zoisite/clinozoisite paragenesis was observed while minor amount of talc, wollastonite, augite, diopside were determined in the skarn zone. Main ore minerals are magnetite, hematite, chalcocopyrite, sphalerite, galenite, cerussite, covellite, digenite, malachite and pyrite.

Chemical data obtained from samples reveal that Cu-Pb-Zn > 1% ppm and Au, Ag, Cd, Mo, and Fe₂O₃ contents reach up to 67.30 ppb, 72.20 ppm, 710 ppm, 936 ppm and 87.95%. Many ancient mining exploitation cavities were coincided located near the Kiziltepe area. 1110 ppb and 724.90 ppb Au values were detected from two samples taken from skarn mineralization.

Keywords: *Skarn-type mineralization, geology, geochemistry, ore deposits, Aladag, Kiziltepe, Ezine*

1. INTRODUCTION

Kiziltepe located 35 km south of the Canakkale city center and 8 km southwest of Ezine County (Canakkale-Turkey) and western edge of the Biga Peninsula (NW Turkey). Ezine county and Aladag, Kemalli, Uskufcu, Kocali and Gokcebayir Villages were known settlements in the study area (Fig. 1).

In this study, it is aimed that geochemical features of contact metamorphic and metasomatic zone mineralization among the granitoidic rocks of Kestanbol Pluton and carbonate rocks of Bozalan Formation together with the altered serpentinites of the Denizgoren Ophiolites. In addition, primary geochemical characteristics of different rock types of Kestanbol Pluton, Denizgoren Ophiolites, Hallaclar Volcanites and dykes.

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Figure 1. Location map of the study area

2. MATERIAL AND METHODS

Field and laboratory studies were carried out to understand the geological, mineralogical, petrographical and geochemical characteristics of the exposed units in the study area. During the field studies formation boundaries were updated and hand specimens collected from different rock units and skarn zone. 27 of these samples were chemically analyzed in the General Directorate of Mineral Research & Exploration of Turkey (MTA). In order to investigation of mineralogical and petrographical features 37 thin section samples investigated under polarizan microscope at the MTA, Geological Engineering Departments of Ankara University and Selcuk University. The rest 27 sample collected from skarn zone were polished and investigated under ore microscopy at the Ore Deposit-Geochemistry Division of the Geological Engineering Department of the Ankara University and MTA Laboratories.

In order to determine the geochemical characteristics of the rock units 62 samples were chemically analyzed of their major (SiO_2 , Al_2O_3 , Fe_2O_3 , MgO , CaO , Na_2O , K_2O , TiO_2 , P_2O_5 , MnO , Cr_2O_3), some minor and trace (Cu, Pb, Zn, Ni, Ga, Nb, Th, V, Zr, Y, Sc) element compositions at the ACME Analytical Laboratories Ltd., Vancouver (Canada). Samples were jaw crushed to 70% passing 10 mesh (2 mm), a 250 g aliquot was riffle split and pulverized to 95% passing 150 mesh (100 μm) in a mild-steel ring-and-puck mill. Samples after thawing process calibration standards, verification standards and reagent blanks were included in the sample sequence. Sample solutions were aspirated into an ICP emission spectrograph (ICP-ES) (Spectro Ciros Vision) for the determination of the major oxides. The detection limit for the major oxides is 0.01 wt %, excepting for SiO_2 , Al_2O_3 , Fe_2O_3 , Cr_2O_3 and LOI, of which detection limits are 0.04, 0.03, 0.04, 0.001 and 0.1 wt. %, respectively. Sample solutions were aspirated into an ICP-MS (Perkin-Elmer Elan 6000 or 9000) for the determination of the trace including REEs. The limits of detection are 0.05 ppm, excepting Pr, Nd, Sm, Tb and Lu, of which detection limits are 0.02, 0.4, 0.1, 0.01 and 0.01 ppm, respectively. Some sulphide samples exceeded the upper limits of this method and these samples were re-analyzed. In the re-analyzing process 1.0 g sample digested in 100 ml aqua regia ($\text{HCl-HNO}_3\text{-H}_2\text{O}$) and sample solutions analyzed into ICP-AES.

All geochemical data were evaluated with basic and multivariate statistical methods using student t test, correlation coefficient, simple regression and scatter diagrams, cluster analyses and factor analyses.

3. RESULT AND DISCUSSION

3.1. Geological Settings

Cambrian to Holocene aged 8 different magmatic, metamorphic and sedimentary geological units cropped out in the study area. Pre-Lower Cambrian aged Geyikli Formation forms the basement of the study area and represented by the alternation of low-grade metamorphic featured rocks such as calcschists, metasandstones and phyllites (e.g. [1]-[6]). Middle-Late Permian Bozalan Formation consists of low metamorphic detritic rocks such as gravelly sandstone, quartzite and phyllites from bottom and carbonaceous rocks and marbles to the top recrystallized limestones and extends over the Geyikli Formation by unconformity (e.g. [2]-[4], [7]-[8]). Cretaceous aged Denizgoren Ophiolites usually consists of serpentized peridotites and emplaced on the other

units by tectonic boundary (e.g. [4], [8]-[10]). Upper Oligocene-Lower Miocene Hallaçlar Volcanics consists of yellow, pink and beige-colored andesite, basalt, spherulitic rhyolite, and pyroclastic rocks with same composition (e.g. [8], [11], [12]). In addition, Upper Oligocene-Lower Miocene aged Kestanbol pluton cuts the older units and mainly represented by intense fractured dirty yellow and pink quartz-monzonites together with basic enclaves such as monzonite, monzodiorite porphyry, monzonite porphyry, syenite porphyry and quartz syenite porphyry (e.g. [11]-[16]). Lower-Middle Miocene aged Ezine Volcanics consist of gray, dark gray, black and greenish-black color, coarse crystalline K-feldspar andesite, trachyandesite, dacite, rhyodacite and andesitic, rhyolitic pyroclastics (e.g. [5]-[6], [8], [12]). Plio-Quaternary aged Bayramic Formation represented by conglomerate, sandstone and mudstone (e.g. [6], [17]). All of the older units overlain unconformably by alluvium consist of slightly consolidated and unconsolidated terrestrial clastics (Figure 2).

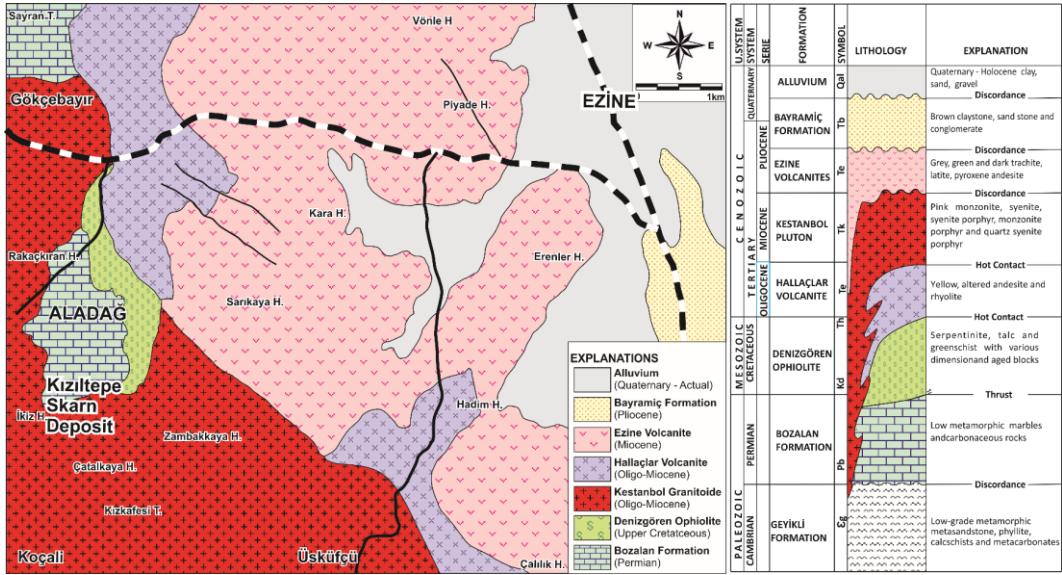


Figure 2. Geological map and tectono-stratigraphical section of the study area (After [6])

3.2. Kıziltepe Skarn Mineralization

A contact metamorphic and Cu, Pb, Zn and Fe skarn zone formed developed by the intrusion of the magmatic rocks belonging to Kestanbol Pluton in carbonate rocks of Bozalan Formation and some talc and asbestos formation developed in the altered peridotites of the Denizgoren Ophiolites at the Aladag (Figure 3).

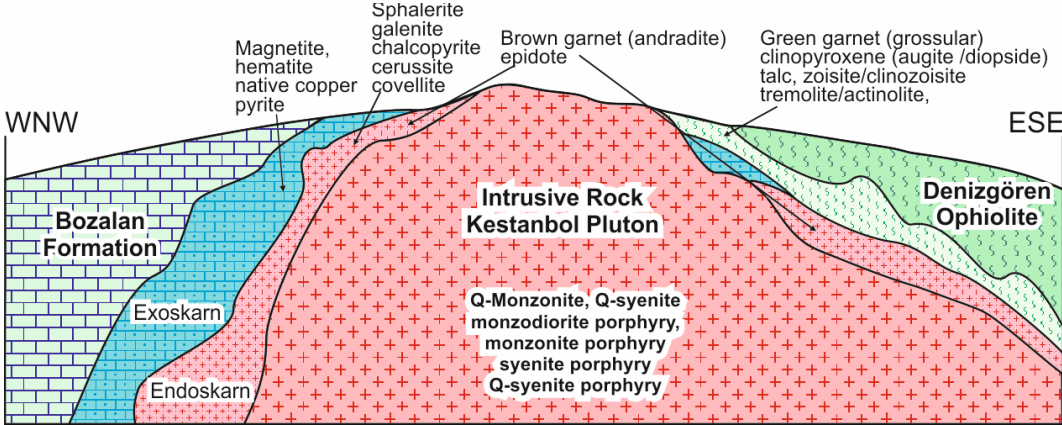


Figure 3. Schematic Cross Section model of Kıziltepe (Aladag) Skarn Zone (Modified from [18]).

Intrusive rock represented by mainly monzonite, Q-monzonite and syenites of the Kestanbol Pluton (e.g. [5]-[6], [9], [18]). Monzonites composed of mainly plagioclase, alkali feldspar, quartz, biotite, hornblende and

minor amount sphene while syenites composed of mainly alkali feldspar, plagioclase, quartz, biotite, hornblende and minor amount sphene. There are some coarse-grained K-feldspar, biotite, quartz, pyroxenes (diopside, augite) in the endoskarn zone. Ore mineral paragenesis are consist of magnetite, hematite, galena, sphalerite, chalcopyrite, cerussite, covellite, malachite, azurite, pyrite, limonite (goethite and lepidocrocite) in skarn zone (Figure 4 c, d, e, f, g).

Magnetite and hematites observed near the pluton contact (Figure 4 d). Hematites were formed by the alteration of magnetites. There are epidote, grossular, tremolite/actinolite, augite, diopside and talc formations near the wall rocks (Figure 4 b and h). Galena, cerussite, sphalerite, chalcopyrite pyrite and covellite were observed in the outer zone of skarn mineralization (Figure 4 c, f, g). Chalcopyrite, pyrite and covellite near the magnetite mineralization. Galena and sphalerite mineralization are near the carbonate rocks. Some galena and sphalerite veins are in the marbles and recrystallized limestones. There are minor amount pyrite and chalcopyrite in the rocks. Some of the pyrites were oxidized from the edges. In addition, cavity filling and / or veins in the form of limonite (lepidocrocites and goethite) are observed in some place. Goethite and lepidocrocites were observed side by side and enlarged intertwined.

Talc and asbestos formation contact between the pluton and ophiolites (Figure 5 b, h). There are malachite, azurite and native copper formations around the Kiziltepe Skarn Zone in and near environs. Some Ca-silicate mineral formed in the contact zone such as tremolite, actinolite, augite, epidote etc. (Figure 4 b, c, h).



Figure 4. Some views of the contact metamorphic zone a) Skarn zone between the Kestanol Pluton and Bozalan Formation, b) Talc and tremolite formations in the contact metamorphic zone between the Kestanol Pluton and Denizgoren ophiolites, c) Copper enrichments in the skarn zone, d) Magnetite vein in the Bozalan Formation, e) Magnetite (mag) and hematite (hem) (+N, X10), f) Magnetite (mag) and sphalerite (Sph), (+N, X10), g) Galena (gn) (+N, X63), h) Epidote and tremolite (N, X3.2), e, f and g polished sections, h thin section

3.3. Geochemical Characteristics of Kestanbol Pluton and Skarn Zone

The major oxides and some trace element analyzes of the samples taken from the Kestanbol Pluton (Table 1) and endoskarn and exoskarn zones (Table 3 and Table 5) were made.

Kestanbol Pluton:

The granitoidic rocks of the Kestanbol pluton contain 63.3% SiO₂, 16% Al₂O₃, 4% Fe₂O₃, 1.8% MgO and 3.2% CaO on average (Table 1). In the genetic and petrological investigations carried out in these rocks, it has been determined that the rocks belonging to Kestanbol pluton fall down to the area of volcanic arc granitoids with subalkaline and calcalkaline properties.

Table 1. Major oxides (%) and some trace element (ppm, Au: ppb) analysis and statistical summaries of the granitoidic rocks (S.D.: Standard deviation, S.E.: Standard error, t_h: Calculated t value: L.L.: The lower limit, U.L.: Upper limit, Sample number: 7, tt: Table t value: 1.94).

NO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	MnO	Cr ₂ O ₃	Ba	Co	Sr	W	Mo	Cu	Pb	Zn	Ni	As	Ag	Au	Sum
S 33	62.0	16.2	4.6	2.3	4.4	3.8	4.9	0.6	0.1	30.0	1231.0	27.5	852.0	128.8	0.6	48.7	19.2	28.0	13.2	1.4	0.1	2.0	99.57
S 34	61.0	15.7	4.4	2.6	3.9	2.5	5.4	0.6	0.1	40.0	1334.0	21.4	795.8	66.4	0.3	38.4	39.5	63.0	21.9	1.4	0.1	10.5	99.58
S 55	64.7	15.2	3.8	1.9	2.9	3.5	5.2	0.5	0.1	40.0	1160.0	28.6	664.8	173.4	4.9	80.1	30.2	28.0	15.0	3.2	0.1	1.2	99.61
S 56	67.3	15.1	2.4	1.0	1.8	2.8	4.7	0.3	0.1	20.0	1171.0	13.7	413.4	58.3	0.2	15.1	30.0	29.0	13.2	0.5	1.0	5.9	99.72
S 57	61.7	15.7	4.8	2.3	3.9	3.7	5.0	0.6	0.1	20.0	1354.0	26.4	815.1	114.1	0.5	20.8	18.6	25.0	14.5	1.8	0.1	5.9	99.57
S 58	65.3	15.5	3.7	1.7	3.2	3.6	4.9	0.5	0.1	30.0	1159.0	22.8	679.7	132.5	1.2	6.4	12.9	15.0	15.1	1.3	0.1	5.9	99.65
S 65	61.5	16.8	5.0	1.0	2.6	3.5	5.6	0.6	0.1	20.0	1474.0	35.1	972.0	72.7	1.7	86.1	7.0	46.0	14.5	7.5	0.1	5.9	99.54
Mean	63.3	15.7	4.1	1.8	3.2	3.3	5.1	0.5	0.1	28.6	1269.0	25.1	741.8	106.6	1.3	42.2	22.5	33.4	15.3	2.4	0.1	10.8	
S.D.	2.4	0.6	0.9	0.6	0.9	0.5	0.3	0.1	0.0	9.0	121.5	6.7	178.4	42.4	1.7	31.3	11.3	15.9	3.0	2.4	0.0	0.6	
S.E.	0.9	0.2	0.3	0.2	0.3	0.2	0.1	0.0	0.0	3.4	45.9	2.5	67.4	16.0	0.6	11.8	4.3	6.0	1.1	0.9	0.0	0.2	
t _h	70.1	69.8	12.3	7.7	9.5	18.2	42.5	10.8	10.2	8.4	27.6	9.9	11.0	6.7	2.1	3.6	5.3	5.6	13.5	2.7	0.3	3.7	
L.L.	61.1	15.2	3.3	1.2	2.4	2.9	4.8	0.4	0.1	20.3	1156.7	18.9	576.8	67.4		13.2	12.1	18.7	12.5	0.2	1.0	3.3	
U.L.	65.5	16.3	4.9	2.4	4.1	3.8	5.4	0.6	0.1	36.9	1381.3	31.3	906.9	145.8	2.9	71.2	32.9	48.2	18.1	4.6	0.1	11.4	

Endoskarn Zone

The average Cu, Pb and Zn contents of the samples collected from endoskarn zone were 2.7%, 2.5% and 2.7%, respectively. Cu reaching 14.6%, Pb reaching 17.2% and Zn reaching 16.5% are important. Cr is high in some specimens, whereas Mo and W increase in the outer sections of the endoskarn zone (Table 2).

Table 2. Major oxides (%) and some trace element (ppm, Au: ppb) analysis and statistical summaries of the granitoidic rocks (M: Mean, S.S.: Standard deviation, S.E.: Standard error, t_c: Calculated t value: L.L.: The lower limit, U.L.: Upper limit, Sample number: 16, tt: Table t value: 1.75).

NO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	MnO	Cr ₂ O ₃	Ba	Co	Sr	W	Mo	Cu	Pb	Zn	Ni	As	Ag	Au
S 11	16.2	1.1	6.2	1.1	7.8	0.01	0.02	0.04	0.32	190	2	117	43	49	936	146060	172700	82600	128	56	70	62
S 13	30.1	1.3	36.8	0.1	25.3	0.01	0.01	0.01	0.81	20	3	123	4	141	38	14350	4200	6000	84	68	67	11
S 14	84.1	0.6	0.7	0.6	0.1	0.01	0.01	0.02	0.13	50	2	68	5	269	301	1250	36900	53400	57	2	15	7
S 15	35.1	18.1	14.8	1.3	17.5	0.01	0.09	1.26	0.69	4170	9	28	1897	37	372	12680	9000	18800	384	10	0	1
S 16	44.8	0.9	5.4	0.6	3.0	0.01	0.01	0.02	0.95	40	2	146	54	92	498	6490	78900	165100	67	20	18	15
S 18	33.4	14.3	21.2	0.6	16.5	0.01	0.05	0.89	0.66	3440	8	167	941	43	300	22690	11300	10600	308	43	4	8
S 19	34.1	0.5	27.6	0.1	18.5	0.01	0.01	0.01	0.55	40	1	42	6	178	58	83760	15700	11000	49	229	72	67
S 20	22.7	1.4	29.9	0.2	19.1	0.01	0.01	0.03	0.99	100	5	25	35	221	264	28710	26900	27800	137	28	38	21
S 21	75.3	0.3	0.7	0.2	4.1	0.01	0.01	0.01	0.46	30	3	66	20	210	260	1780	49100	59100	32	8	25	9
S 27	65.2	15.1	2.4	3.5	3.1	1.69	5.20	0.40	0.02	30	1331	14	528	75	3	1169	57	60	14	4	0	6
S 28	52.6	10.1	18.1	3.3	0.4	3.88	0.54	0.30	0.05	20	51	45	67	102	3	40350	200	200	20	3	12	42
S 30	56.0	8.3	5.5	5.9	2.4	1.43	4.12	0.22	0.07	20	1079	21	189	46	3	71710	100	100	14	8	14	34
S 31	58.0	13.0	8.9	3.0	3.1	6.08	3.19	0.43	0.10	130	822	25	286	28	1	9568	95	83	28	2	1	25
S 32	65.0	15.6	3.7	1.8	3.6	3.72	4.86	0.54	0.07	30	938	32	775	193	1	120	23	24	13	1	0	2
S 61	66.1	17.5	4.9	0.8	0.1	0.24	5.19	0.57	0.01	20	1191	14	96	88	9	568	592	109	13	42	3	15
S 62	61.5	16.9	8.7	0.8	0.1	0.14	5.09	0.51	0.01	20	738	18	119	74	23	626	908	204	16	35	1	15
M.	50.0	8.4	12.2	1.5	7.8	1.08	1.78	0.33	0.37	522	387	59	317	115	192	27618	25417	27199	85	35	21	21
S.D.	19.7	7.3	11.3	1.6	8.5	1.87	2.32	0.37	0.36	1289	521	51	511	76	258	40630	45228	44710	110	56	26	20
S.E.	4.9	1.8	2.8	0.4	2.1	0.47	0.58	0.09	0.09	322	130	13	128	19	64	10158	11307	11177	28	14	7	5
t _c	10.2	4.6	4.3	3.7	3.7	2.31	3.07	3.59	4.10	1.62	2.97	4.69	2.48	6.04	2.98	2.72	2.25	2.43	3.10	2.49	3.24	4.09

LL	39.5	4.5	6.2	0.6	3.3	0.09	0.54	0.13	0.18	-165	109	32	44	75	54	5967	1317	3375	27	5	7	10
UL	60.5	12.3	18.2	2.4	12.3	2.07	3.01	0.52	0.56	1209	664	86	589	156	329	49268	49518	51023	144	65	35	32

In the correlation analyzes conducted to determine the direction and strength of the relationships between the components Fe₂O₃; has strong positive correlation with CaO and Mn and strong negative correlation with SiO₂. Cu shows strong positive correlation with Au, Pb and Ag besides strong negative correlation with SiO₂. Pb and Zn show strong positive correlation with each other and Mo. According the correlation and cluster analysis trace elements such as Cu, Mo, Pb, Zn, Au, Ag, As and W Show similar behaviors in the geochemical environments different from major components (Table 3).

Table 3. Correlation coefficients between the components of the endoskarn samples

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	MnO	Cr ₂ O ₃	Ba	Co	Sr	W	Mo	Cu	Pb	Zn	Ni	As	Ag	Au
SiO ₂	1.00	0.24	-0.70	0.24	-0.75	0.28	0.50	0.00	-0.66	-0.33	0.49	-0.41	-0.13	0.28	-0.48	-0.60	-0.38	-0.14	-0.55	-0.43	-0.61	-0.47
Al ₂ O ₃	1.00	-0.23	0.35	-0.26	0.37	0.69	0.87	-0.49	0.41	0.63	-0.42	0.62	-0.55	-0.42	-0.39	-0.55	-0.58	0.17	-0.34	-0.76	-0.43	
Fe ₂ O ₃	1.00	-0.33	0.86	-0.18	-0.47	0.07	0.61	0.19	-0.47	0.22	-0.02	0.08	-0.13	0.16	-0.21	-0.26	0.34	0.53	0.54	0.24		
MgO	1.00	-0.44	0.59	0.50	0.13	-0.57	-0.13	0.60	-0.41	0.09	-0.46	-0.35	0.15	-0.28	-0.35	-0.29	-0.39	-0.39	0.09			
CaO	1.00	-0.38	-0.55	0.05	0.76	0.43	-0.53	0.33	0.25	0.08	0.14	0.19	-0.02	-0.11	0.60	0.51	0.58	0.10				
Na ₂ O	1.00	0.39	0.13	-0.51	-0.22	0.42	-0.36	0.05	-0.22	-0.45	-0.14	-0.34	-0.37	-0.36	-0.34	-0.40	-0.05					
K ₂ O	1.00	0.28	-0.73	-0.30	0.97	-0.62	0.03	-0.29	-0.58	-0.30	-0.45	-0.49	-0.50	-0.27	-0.56	-0.26						
TiO ₂	1.00	-0.14	0.80	0.24	-0.17	0.89	-0.54	-0.13	-0.30	-0.40	-0.41	0.62	-0.26	-0.64	-0.44							
MnO	1.00	0.34	-0.71	0.55	0.11	0.16	0.42	0.04	0.25	0.48	0.56	0.27	0.45	-0.02								
Cr ₂ O ₃	1.00	-0.29	0.25	0.87	-0.39	0.25	-0.08	-0.11	-0.09	0.94	-0.07	-0.27	-0.30									
Ba	1.00	-0.61	0.04	-0.32	-0.57	-0.25	-0.44	-0.48	-0.49	-0.28	-0.53	-0.24										
Co	1.00	-0.06	-0.07	0.57	0.18	0.50	0.58	0.37	0.11	0.35	0.04											
Sr	1.00	-0.38	0.05	-0.21	-0.25	-0.22	0.75	-0.23	-0.46	-0.44												
W	1.00	-0.08	-0.21	-0.10	0.12	-0.28	0.13	0.28	-0.08													
Mo	1.00	0.51	0.92	0.73	0.46	-0.01	0.38	0.26														
Cu	1.00	0.62	0.13	0.07	0.46	0.67	0.89															
Pb	1.00	0.74	0.11	0.07	0.51	0.44																
Zn	1.00	0.06	-0.06	0.23	0.08																	
Ni	1.00	0.01	-0.02	-0.18																		
As	1.00	0.69	0.65																			
Ag	1.00	0.68																				
Au	1.00																					

Exoskarn Zone

The Fe₂O₃ content of the exoskarn samples is 73.4% on average. Iron source is principally magnetite and hematite, and iron content in andradite, pyrite and chalcopyrite, which is observed in some samples, also affect this result. In the same samples, there are 899 ppm Cu, 76 ppm Pb and 156 ppm Zn on average (Table 4). A sample has 6753 ppm Cu and this value show importance of the exoskarn zone by means of copper. Outer zones of the main ore region heavily weathered at the surface. As a result of this process there are lots of small polluted areas by copper carbonate and oxides around the Kiziltepe deposits.

Table 4. Major oxides (%) and some trace element (ppm, Au: ppb) analysis and statistical summaries of the granitoidic rocks (M: Mean, S.S.: Standard deviation, S.E.: Standard error, tc: Calculated t value; L.L: The lower limit, U.L: Upper limit, Sample number:8, tt: Table t value1.83)

NO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	MnO	Cr ₂ O ₃	Ba	Co	Sr	W	Mo	Cu	Pb	Zn	Ni	As	Ag	Au	Sum
S 1	4.10	37.56	33.9	18.80	0.01	0.01	0.01	0.69	30.05	0.33	1.65	2.04	3.33	0	47.8	321.6	166.0	108.8	139.6	1.42	0.99	7.6	
S 3	8.80	30.83	34.7	1.80	0.01	0.01	0.02	0.57	70.01	0.38	0	5.4	18.00	6	6.0	48.7	164.0	107.7	24.50	1	4.8	99.78	
S 4	11.50	52.69	16.2	7.10	0.02	0.01	0.03	0.65	110.06	0.15	6.4	9.9	13.30	5	1.3	32.9	141.0	117.5	34.50	1	3.7	99.79	
S 6	20.90	18.64	52.4	8.30	0.01	0.01	0.02	0.55	20.01	0.22	2.9	4.25	7.70	6.67	53.0	10.3	121.0	76.1	30.00	9	8.2	98.76	
S 7	16.70	22.72	08.9	0.60	0.02	0.01	0.01	0.71	40.01	0.44	6	4.5	9.90	9	22.2	112.8	247.0	84.0	59.80	6	6.3	99.69	
S 8	10.10	07.84	75.0	0.10	0.01	0.01	0.01	0.53	20.01	0.31	2.8	1.8	14.50	8	10.2	45.4	187.0	18.4	23.00	1	2.7	99.77	
S 9	7.20	07.88	03.2	1.60	0.01	0.01	0.01	0.56	20.01	0.22	2.9	8.4	19.60	5	5.0	18.7	137.0	14.0	14.20	1	1.6	99.77	
S 10	17.90	11.69	24.5	7.30	0.02	0.01	0.01	0.46	20.02	0.20	1.0	6.1	32.60	4	345.8	18.3	88.0	97.3	28.10	1	4.4	99.77	
M.	12.20	23.73	44.8	5.70	0.01	0.01	0.02	0.59	41.32	0.28	1.1	11.5	26.10	9	898.9	76.1	156.4	77.9	44.20	4	6.5	99.64	
S.D.	5.80	16.11	02.0	6.20	0.01	0.00	0.01	0.09	32.72	1	98.8	16.5	16.90	9.2	368.3	104.3	47.6	40.4	40.80	5	5.8		
S.E.	2.10	06	3.90	2.20	0.00	0.00	0.00	0.03	11.60	0.7	34.9	5.9	6.00	3	837.3	36.9	16.8	14.3	14.40	2	2.1		

t _c	5.94	0.09	18.9	6.9	2.67	7.51	-5.61	19.5	3.63	3.1	8.2	2.0	4.43	0	1.1	2.1	9.3	5.5	3.12	4	3.1
L.L.	7.30	10.64	23.2	0.50	0.01	0.01	0.01	0.52	13.90	5.20	2.5	-2.3	12.00	2			-116.6	44.1	10.10	0	1.6
U.L.	17.00	36.82	66.5	10.90	0.02	0.01	0.02	0.66	68.64	0.36	7.25	4.40	31.62	87.8	163.3	196.1	111.8	78.30	8	11.4	

Fe₂O₃ has no positive correlation with any component in the correlation analyzes. SiO₂ shows strong positive correlation only with Cu. Trace elements have significant correlations each other's (Table 5). Iron enrichments are independent the other components.

CaO, Sr, Mo, As, Ag and Au have strong positive correlations within each other (Table 5). Accordingly, these components together form a cluster, and have settled down towards the end of the contact metamorphism process.

Table 5. Correlation coefficients between the components of the exoskarn samples

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	MnO	Cr ₂ O ₃	Ba	Co	Sr	W	Mo	Cu	Pb	Zn	Ni	As	Ag	Au
SiO ₂	1.00	-0.25	-0.22	0.14	-0.21	0.46	-0.05	0.13	-0.30	-0.17	-0.36	-0.17	-0.59	0.28	-0.54	0.63	-0.53	-0.18	0.11	-0.39	-0.06	-0.28
Al ₂ O ₃		1.00	-0.50	0.28	0.47	0.28	0.74	0.71	0.64	0.85	0.83	-0.07	0.43	-0.06	0.33	-0.14	0.38	0.09	0.79	0.44	0.25	0.39
Fe ₂ O ₃			1.00	0.03	-0.86	-0.25	-0.16	-0.13	-0.38	-0.03	0.59	0.12	0.63	0.64	-0.59	-0.34	-0.58	0.14	-0.67	-0.73	-0.78	-0.79
MgO				1.00	-0.37	0.70	0.28	0.02	0.54	0.41	0.09	0.50	-0.20	-0.71	-0.09	-0.50	0.08	0.72	0.25	0.08	-0.18	-0.17
CaO					1.00	-0.09	0.09	0.05	0.27	-0.03	0.68	-0.23	0.87	0.69	0.76	0.18	0.71	-0.33	0.53	0.79	0.76	0.87
Na ₂ O						1.00	0.49	0.18	0.16	0.39	0.30	-0.14	-0.24	-0.37	-0.30	-0.27	-0.17	0.04	0.44	-0.07	-0.26	-0.24
K ₂ O							1.00	0.80	0.28	0.85	0.74	-0.53	-0.04	0.31	-0.19	-0.15	-0.17	-0.13	0.40	-0.10	-0.26	-0.19
TiO ₂								1.00	0.13	0.84	0.46	-0.43	-0.19	-0.02	0.32	0.25	-0.33	-0.23	0.50	-0.25	-0.19	-0.18
MnO									1.00	0.40	0.46	0.47	0.49	-0.20	0.56	-0.22	0.65	0.69	0.36	0.66	0.53	0.51
Cr ₂ O ₃										1.00	0.59	-0.14	-0.05	-0.44	-0.16	-0.28	-0.09	0.08	0.59	-0.06	-0.28	-0.15
Ba											1.00	-0.38	0.62	0.05	0.47	-0.25	0.47	-0.16	0.59	0.54	0.27	0.46
Co												1.00	0.10	-0.29	0.34	-0.27	0.44	0.84	0.02	0.34	0.26	0.26
Sr													1.00	0.38	0.95	-0.18	0.93	0.02	0.35	0.93	0.75	0.91
W														1.00	0.34	0.77	0.22	-0.53	0.18	0.32	0.67	0.58
Mo															1.00	-0.15	0.98	0.26	0.26	0.96	0.82	0.94
Cu																1.00	-0.26	-0.33	-0.01	-0.14	0.38	0.12
Pb																	1.00	0.36	0.33	0.98	0.78	0.91
Zn																		1.00	-0.10	0.28	0.18	0.10
Ni																			1.00	0.43	0.29	0.45
As																				1.00	0.85	0.95
Ag																					1.00	0.93
Au																						1.00

4. CONCLUSIONS

Permian to Holocene magmatic, metamorphic and sedimentary rocks crop out in the study area. In the basement of the study area Middle-Late Permian Bozalan Formation consists of recrystallized limestone and marbles. Cretaceous aged Denizgoren Ophiolites thrust over Bozalan Formation and generally, observed as serpentinite. Oligo-Miocene Hallaclar Volcanics cuts the older units and composed of altered andesite and rhyolite. Oligo – Miocene Kestanbol Pluton represented by mainly porphyric monzonite and syenites. Miocene aged Ezine Volcanics composed of pyroxene-andesite and trachyte.

A contact metamorphic and skarn zone were developed by the intrusion of the Kestanbol Pluton into carbonaceous rocks of the Bozalan Formation and Denizgoren Ophiolites at the north of the Kiziltepe - Aladag. Ca-silicate and some metallic mineral enrichments such as iron, copper, zinc and lead were developed in the skarn zones. The skarn zone can be divided into endoskarn and exoskarn zones according to the determined mineral paragenesis.

In the endoskarn zone, there are large crystallized K-feldspar, biotite and quartz as well as red-brown garnet (andradite) and galena, sphalerite and chalcopyrite with epidote. It is important to note that, Ag is reached up to 70 ppm besides 2.7% Cu, 2.5% Pb and 2.7% Zn. In the exoskarn zone, there are magnetite, hematite, chalcopyrite and pyrite together with Ca-silicate minerals such as green garnet (grossular), pyroxene (augite, diopside), amphibole (actinolite-tremolite) epidote group (epidote, zoisite and clinozoisite). In this case, 73% of Fe₂O₃ is important. Secondary copper enrichments (covellite, digenite, cerussite and malachite) are formed near the skarn zone. In addition, talc and amphibole asbestos formed contact in the ophiolites and pluton.

According to the findings obtained from the field, laboratory and statistical studies performed in the Kiziltepe skarn zone, the Kestanbol pluton, which intruded into the carbonate and clastic rocks of the Bozalan formation and the serpentinized peridotites of the Denizgoren ophiolites, formed a contact metamorphic zone in this region. Kiziltepe Skarn Deposit and near environs should be detailed investigate for gold, copper, lead, zinc iron formations.

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REFERENCES

- [1]. Bingol, E., Akyurek, B., Korkmazer, B., 1973, Geology of Biga Peninsula and Karakaya formation characteristics. 50th Anniversary Geology Congress of Republic's, 1973, Ankara.
- [2]. Gozler, M.Z., Ergul, E., Akcaoren, F., Genc, S., Akat, U. and Acar, S., 1984. Geology and compilation the area among the East Canakkale Bay, South Marmara Sea- Bandirma-Balikesir-Edremit and Aegean Sea, Rep. Of Min. Res. Expl. Inst. of Turkey, Ankara,7430. 123p.
- [3]. Okay, A. I., Siyako, M., and Burkan K. A., 1990, Geology and tectonic evolution of Biga Peninsula, Bulletin of Turkey Petroleum Geologist Association, 2/1 83-121.
- [4]. Beccaletto, L. and Jenny, C., 2004. Geology and Correlation of the Ezine Zone: A Rhodope Fragment in NW Turkey? Journal of Earth Sciences (Turkish J. Earth Sci.), 13, 145-176.
- [5]. Aydin, U., 2010, Geological Features and Ore Deposits of Kiziltepe (Ezine/Canakkale), MSc Thesis, Selcuk University, Graduate Natural and Applied Sciences, Geological Engineering Main Science Branch 111 pp.
- [6]. Arik, F. and Aydin, U., 2010, Geological Features and Ore Deposits of Kiziltepe (Ezine/Canakkale) Area, Selcuk University Scientific Research Projects Coordinatories, Project number: 09201047, 97 p.
- [7]. Kalafatcioglu, A., 1963. Geology of Ezine vicinity and Bozcaada, age of limestone and serpentinite, Journal of Min. Res. Expl. Inst. of Turkey, Ankara, 60-70.
- [8]. Donmez, M., Akcay, A.E., Genc, S.C. and Acar, S., 2005, Middle-Upper Eocene volcanism and marine ignimbrites of Biga Peninsula, Journal of Min. Res. Expl. Inst. of Turkey, 131 49-61.
- [9]. Arik, F. And Aydin, U., 2011, Mineralogical and petrographical characteristics of the Aladag skarn deposit (Ezine/Canakkale-West Turkey), Scientific Research and Essays, 6(3), 592-606.
- [10]. Okay, A.I., Satir, M., Maluski, H., Siyako, M., Monie, P., Metzger, R. and Akyuz, S., 1996, Paleo-and Neotethyan events in northwest Turkey. In: Yin A, Harrison M(eds) Tectonics of Asia. Cambridge University Press, Cambridge, 420-441.
- [11]. Krushensky, R.. 1976, Neogene calc-alkaline extrusive rocks of the Karalar-Yesiller area Northwest Anatolia: Bulletin of Volcanology, 40. 336-360.
- [12]. Ercan, T., Satir, M., Steinitz, G., Dora, A., Sarifakioglu, E., Adis, C., Walter, H.J. and Yildirim, T., 1995. NW Anatolia Tertiary volcanism in Biga Peninsula, Gokceada, Bozcaada and Tavsan peninsulas characteristics, Journal of Min. Res. Expl. Inst. of Turkey, Ankara, 117, 55-87.
- [13]. Birkle, P. and Satir, M., 1995, Dating, Geochemistry and geodynamic significance of the Tertiary magmatism of the Biga Peninsula, NW-Turkey. Geology of the Black Sea Region, Journal of Min. Res. Expl. Inst. of Turkey, Ankara, 171-180
- [14]. Yilmaz Sahin, S., Orgun, Y., Gungor, Y., Goker, A.F., Gultekin A. H. and Karacik, Z., 2010, Mineral and Whole-rock Geochemistry of the Kestanbol Granitoid (Ezine-Canakkale) and its Mafic Microgranular Enclaves in Northwestern Anatolia: Evidence of Felsic and Mafic Magma Interaction, Turkish Journal of Earth Sciences (Turkish J. Earth Sci.), 19, 101-122.
- [15]. Orgun, Y., Altinsoy, N., Sahin S.Y., Gungor, Y., Gultekin, A.H., Karahan, G. and Karacik, Z., 2007, Natural and anthropogenic radionuclides in rocks and beach sands from Ezine region (Canakkale), Western Anatolia, Turkey. Appl Radiat Isot. 65(6):739-747.
- [16]. Fytikas, M., Innocenti, F., Manetti, P., Peccerillo, A. and Villari, L., 1984. Tertiary to Quaternary evolution of volcanism in the Aegean region. Geol. Soc. Spec. Pub 17, 687-699.
- [17]. Siyako, M.,Burkan, K. and Okay, A., 1989. Tertiary geology of Biga and Gelibolu Peninsulas and hydrocarbon facilities. Bulletin of Turkey Petroleum Geologist Association 1, 183-199.
- [18]. Arik, F. and Aydin, U., 2011, "Geochemical features of the Aladag Fe-Cu-Zn-Pb skarn deposit" (Ezine/Canakkale-North West Turkey), Goldschmidt 2011 Conference, Prague, Mineralogical Magazine, 452.