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Geological and geochemical characteristics of Cünür volcanogenic massive sulfide mineralization (Kastamonu, Turkey)

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Research Article

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ABSTRACT

Çangaldağ Metamorphic Complex (CMC) in Central Pontides is an accretionary complex consisting of Jurassic units. Mafic, felsic metavolcanics, metamorphic equivalents of deep marine sediments and mafic meta - lava/sill intercalations are the most distinct units of the complex. Cünür Volcanogenic Massive Sulfide (VMS) mineralization is associated with metavolcanic units of CMC. Metavolcanic units in the mineralization area contain volcanic rocks with compositions ranging from sub - alkali basalt to andesite and dacite (50.3 - 74.6 % SiO_2). For 0.1 % Cu cut - off grade, 3,372,000 tons (t) of mineral resource with 0.28 % Cu, 0.50 % Zn and 0.19 ppm Au has been estimated. Ore paragenesis of the Cünür mineralization predominantly consists of pyrite, chalcopyrite and sphalerite, and lesser amounts of magnetite. The main ore textures are massive, semi - massive, disseminated, brecciated and fracture fillings. Pyrite - chalcopyrite grading and preserved silicified clasts within the massive ore indicate that mineralization has developed in relation to replacement processes. The most significant grade intercepts reported for the mineralization are 9 %, 9 %, 0.3 %, 3300 ppb and 79 ppm for Cu, Zn, Pb, Au, Ag, respectively. Cünür mineralization has similarities to bimodal - mafic (Noranda type) Cu - Zn dominated VMS deposits.

1. Introduction

Volcanogenic massive sulfide deposits (VMS) are one of the main sources of Zn, Cu, Pb, Ag and Au. Typically, VMS deposits occurring at or near the sea floor in submarine volcanic environments in the form of polymetallic massive sulfide lenses are generally classified according to their Au and base metal contents, the tectonic environment in which they were formed, or the host rock lithologies (Galley et al., 2007). Although VMS deposits can occur in many different tectonic settings such as mid - oceanic ridges or back - arc basins, oceanic arc or active continental margin arcs, continental rifting, the common feature of these formations is that all mineralizations occur in environments where extensional tectonics are effective (Galley et al., 2007; Piercey, 2011). Host rocks of VMS mineralizations can be both volcanic and sedimentary. It is a generally accepted that the formation of these ores is resulted from metal - enriched fluids associated with seafloor hydrothermal convection (Franklin et al., 1981; Franklin, 1993; Galley et al., 2007; Piercey, 2011).

Relative and radiometric age (host rock and ore ages) for the formation of VMS mineralizations in the Anatolian geography show the Triassic - Miocene interval (Yiğit, 2009; Eyüboğlu et al., 2014; Revan et al., 2014; Yıldırım et al., 2012*a, b*; Akbulut et al., 2016; Çiftçi, 2019; Günay et al., 2019*a*). The eastern part of the Pontide orogenic belt is an important metallogenic province associated with VMS. Eastern Pontide

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VMS mineralizations are associated with felsic calc - alkaline volcanism and clastic rocks and are classified as Kuroko type or Pontide - type. (Çağatay and Boyle, 1977; Akıncı, 1985; Çağatay, 1993; Çiftçi and Hagni, 2005; Abdioğlu and Arslan, 2009; Revan et al., 2013; Eyüboğlu et al., 2014; Köprübaşı et al., 2014; Revan et al., 2014). Central Pontide VMS mineralizations are associated with mafic tholeiitic volcanism and clastic rocks and are classified as Cyprus and Besshi type (Çakır, 1995; Altun et al., 2015; Akbulut et al., 2016; Günay et al., 2018, 2019*b*).

The Cünür VMS mineralization, which is the subject of this study, is the first discovered VMS deposit formed within felsic volcanics of Jurassic arc volcanism in the middle Pontides. The purpose of this study is to explain the geological and geochemical characteristics of the Cünür mineralization, to approach the origin of it, to compare and classify it with other VMS types known in the Pontide Orogenic Belt.

2. Regional Geology

The east - west trending orogenic belt in the north of Anatolia is named as Pontides. The Pontides consist of three tectonic units collocated in the Cretaceous times: the Strandja Massif, Istanbul and Sakarya Zone (Okay and Tüysüz, 1999; Okay, 2008; Göncüoğlu, 2010, Figure 1 - a). The common cover of these units, which include different lithological elements, starts with the Early Jurassic and continues with the Jurassic - Early Cretaceous platform sediments. After the late Cretaceous, flysch type sediments and units of the Inner - Pontide ocean thrust on the younger units (Göncüoğlu, 2010).

Middle Pontides including meta - granitoids and metamorphics have a complex structure. A large area consisting of many tectonic slices with approximately east - west trending and where the basement units are overlain by the Middle Jurassic and Albian - Turonian thrust and accretion complexes, is named as the Central Pontide Super Complex (CPSC, Okay et al., 2013; Aygül et al., 2015) or the Central Pontide Structural Complex (CPSC, Tekin et al., 2012; Çimen et al., 2016, 2017, 2018, Figure 1 - b). This structural complex includes Permo - Carboniferous basement rocks, metamorphosed ophiolite slices, ensimatic arc volcanics, deep - sea metasediments, rocks associated with the continental arc and Cenozoic cover rocks (Dönmez et al., 2014; Gücer et al., 2016; Ustaömer and Robertson, 1999; Çimen et al., 2016, 2017, 2018; Günay et al., 2019*a*). Within this large structural complex, the metamorphic unit consisting of island arc volcanics and clastic rocks is defined as Çangaldağ Metamorphic Complex (CMC) (Dönmez et al., 2014; Çimen et al., 2016; 2017; 2018; Günay et al., 2018, 2019). Mineral exploration studies carried out on CMC revealed that this complex is an important base metal province of middle Pontides. With the metallic mineral exploration projects carried out by the General Directorate of Mineral Research and Exploration (MTA), many Cu - Zn - Au mineralizations associated with both volcanics and clastic rocks were identified in the CMC (Konya, 1988; Dönmez et al., 2014; Günay et al., 2018, 2019*a*). The Hanönü and Zeybek massive sulfide deposits are located in the metaclastic rocks of the CMC. Hanönü mineral deposits are one of the largest VMS deposits in Turkey with a grade of 0.6 - 1% Cu and containing about 30 million tons of reserve. Cünür VMS mineralization is occured within the felsic metavolcanic units of Çangaldağ Metamorphic Complex.

CMC is an allochthonous mass with a length of approximately 50 - 55 km and a width of 1 - 30 km, in which the units coexist with each other in tectonic slices. CMC includes island arc meta - volcanic rocks with mafic and felsic character and metavolcanoclastics; dark gray to black phyllites formed from shale and siltstone and mafic sills or dykes cutting these clastic units, and to a lesser amount serpantininized peridotite as thin slices, pillow basalt and pelagic sedimentary units. Chlorite, epidote and actinolite minerals observed in volcanics of CMC indicate the metamorphism conditions under greenschist facies (Çimen et al., 2016; Günay et al., 2018, 2019). Early Cretaceous metamorphic age has been determined by Ar - Ar dating performed on micas in the phyllite samples associated with this complex (136 ± 4 Ma and 125 ± 1Ma, Okay et al., 2013). Middle Jurassic magmatic ages were obtained by zircon U - Pb dating performed on metadacites in the volcanic sequence (169 ± 2Ma, Okay et al., 2014; metarhyodacite / U - Pb zircon, 176 ± 2Ma, 163 ± 9Ma, Çimen et al., 2018). Geological and geochemical data of the volcanics in the CMC reveal the presence of an oceanic arc existed in the Middle Jurassic. The existence of this magmatic arc called Çangal island arc is accepted as a common view (Ustaömer and Robertson, 1999; Tekin et al., 2012; Okay et al., 2013; Dönmez et al., 2014; Çimen et al., 2018).

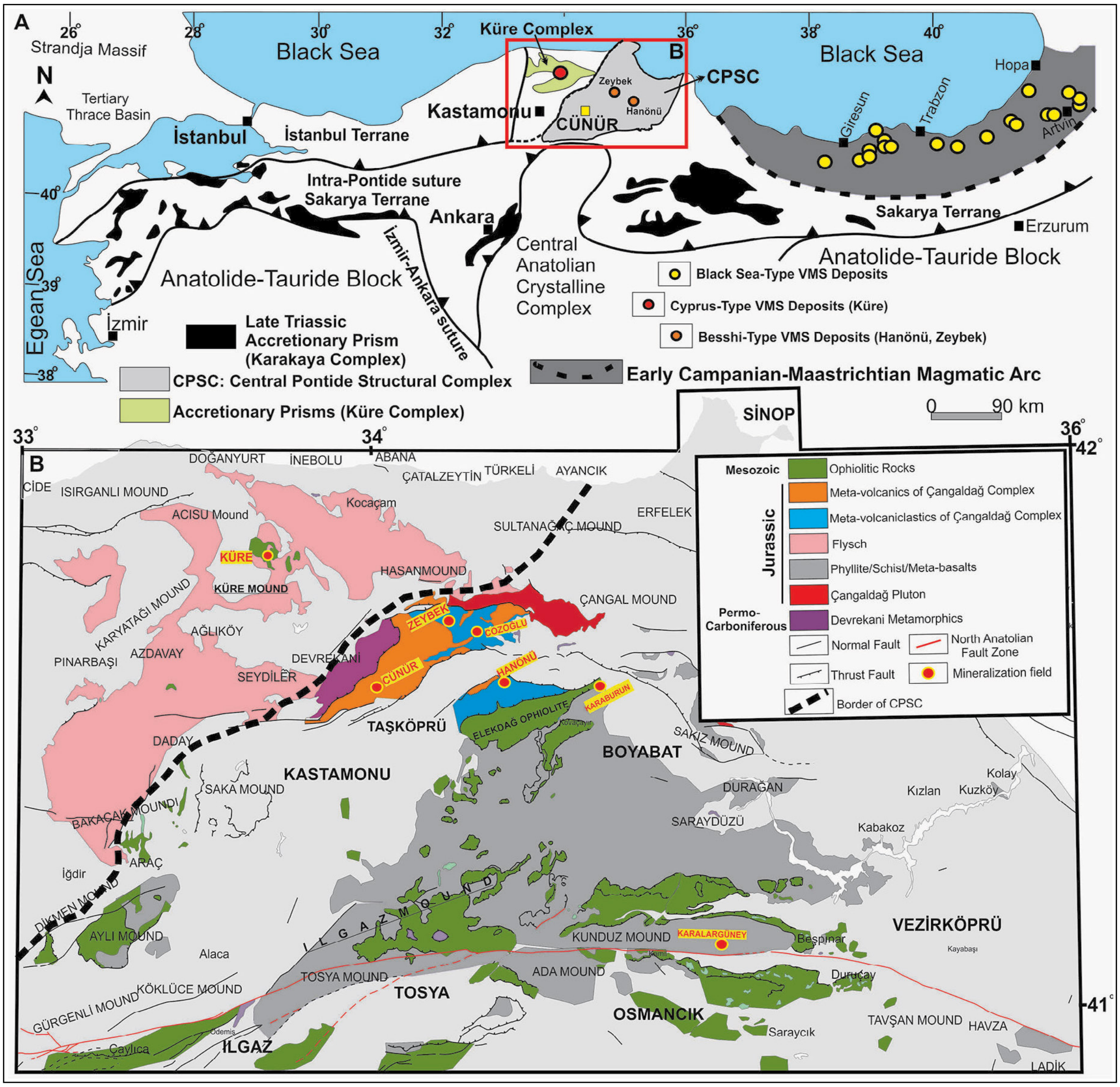

Figure 1- a) North Anatolian tectonic units (Okay and Tüysüz 1999; Göncüoğlu, 2010), the East Pontide magmatic arc and VMS mineralization points (Eyüboğlu et al., 2014), b) Simplified geology map of the Middle Pontides and Çangaldağ Metamorphic Complex (Uğuz et al., 2002), Middle Pontide VMS deposits (Günay et al., 2018, 2019*b*).

3. Material and Method

Analyzes of 50 rock samples and 31 mineralogy - petrography samples taken from the Cünür mineralization area (within the scope of the Mineral Exploration Project in Kastamonu and Surroundings) and 21369 samples for geochemical analysis, 343 mineralogy - petrography samples, 273 polished sections taken from 60 core mine drillings were carried out in MTA (General Directorate of Mineral Research and Exploration) laboratories. Ore containing zones are sampled at one - meter intervals. 2.570 density samples were taken from ore and host rocks and measurements were completed. 200 kg of samples were taken from the ore samples for full technological tests and analyzed in MTA laboratories (Günay, et al., 2019*b*; Archive No: 45892). For the geochemical analysis performed on the samples, the sample preparation methods selected by the sample characters were used and analyzes were performed with ICP - OES (Thermo, Agilint, Spectro brand), ICP - MS (Analytical Jena and Thermo brand), and XRF (Thermo and Axios brand) devices. After the samples were reduced to 1 cm grain size by coarse crushing, they were dried in an oven at 80 °C for about 12 hours and ground with a disc grinder to have a grain size of fewer than 75 microns. Samples for chemical analysis (XRF, Loss on ignition and major oxide element analysis) were prepared by concentrated ($HClO_4$ + HCI + HNO_3) at a ratio of (1: 2: 2) + 80 - 90 °C water bath (2 hours) + pure water or royal water dissolving (3: 1) ratio concentrated (HCI + HNO_3) + 80 - 90 °C water bath (2 hours) + distilled water process and analyzed. Using the same sample preparation method, trace elements (As, Co, Cu, Mn, Mo, Ni, Pb, Zn) and Ag element analyzes with AAS were performed with ICP - OES. For the Au element, the sample was prepared with (HNO_3 + HCI) + 300 °C Hot Plate method in the ratio of Royal Water (1: 3) and analyzed by ICP - MS. Values above 0.5 gr / ton for Au were analyzed by the Fire Assay method. The UniQuant semi - quantitative analysis method was used in the analyzes. Samples were checked with the appropriate SRMs (JA - 1, JA - 2, JA - 3, G1, JR2, 267, SI - 3, NCS DC 73303). The geochemical analysis results of selected host rock and ore samples associated with the Cünür VMS are given in Table 1 and Table 2.

4. Geological Characteristics of the Cünür VMS Deposit

The Cünür mineralization area within the CMC is represented by the Middle Jurassic metavolcanic rocks (meta - basaltic andesite, meta - dacite, meta - rhyodacite), which have mafic and felsic character, and phyllites (Figures 1 and 2). The presence of chlorite, epidote, albite, actinolite paragenesis and phyllites in mafic rocks both in macro scale and petrography studies indicate that low greenschist facies metamorphism conditions are effective for all rock groups regionally. While mapping lithologies associated with CMC, felsic metavolcanics, which are the host rocks of mineralization, and structurally controlled alteration areas were effectively targeted. The lithologies in the study area have tectonic contact with each other and are often thrust by imbrications and normal faults.

In the study area, meta - basaltic andesites constitute the dominant lithology in the northern and western parts (Figure 2). Chloritization and argillization are common in these rocks with sharp fractured surfaces and dominated by green tones. This unit occasionally exhibits compact aphanitic texture and dominantly has schistosity planes dipping towards (Figure 3a). In metabasaltic andesite, it is observed that mafic minerals and pyrites are altered due to the effect of supergene processes, and limonitization and hematite minerals are observed in fractures. Felsic metavolcanic rocks are composed of metamorphic equivalents of the dacites and rhyodacites. These units are frequently observed as small outcrops within the CMC. The felsic metavolcanites starting from the west of the Kevenlik ridge and extending to the vicinity of Büyük Hill, separated from other units by imbrications and thrusts, contain mineralization areas that constitute the study subject. These units can reach 3 km east - west in places, and north - south extensions up to 500 meters. Felsic metavolcanic rocks exhibit light gray color on weathered surfaces. Least and / or unaltered parts of these rocks are gray in color and have a silicified matrix: Meta - dacites are porphyritic in texture, meta - rhyodacites have generally an aphanitic texture. Porphyric textured metadacites are easily identified in the field with their euhedral - subhedral quartz minerals of 0.1 - 0.5 mm in size, found in a silicified and, partially clayey matrix (Figure 3b, c). On the other hand, meta - rhyodacites have a more glassy, aphanitic texture and contain disseminated pyrite (Figure 3d). Argillization, silicification and limonitization are observed in these felsic metavolcanics. Hematite minerals in felsic metavolcanics appear as fracture - crack fillings. The secondary minerals such as malachite and azurite in silicified zones along the fault planes play an important role in determining the mineralizations (Figure 3e). Phyllites are observed in tectonic contact with metavolcanic units in the southeast of the Kevenlik Ridge and about one kilometer northwest of the Cünür district. Phyllites are clastic units reflecting the low grade metamorphism of black - gray shale and silt stones. These units have very well developed cleavage and micro - folds, with light and dark parts showing a mottled appearance (Figure 3f). The Pliocene aged terrestrial sediments covering the CMC are exposed in the Cünür district and its surroundings. These units are represented by light yellow - beige massive nodular limestone, gray - black colored lacustrine sediments derived from thin - medium bedded silty - clayey material.

The Cünür mineralization has occurred within felsic metavolcanic rocks. These rocks, which are about east - west trending and have tectonic contact with other units, are shifted by an approximately north

Table 1- Representative major oxide (%) and trace element (ppm) compositions of metavolcanic rocks in the area of the Cünür mineralization.

Sample	KG-2	KG-6	KG-7	KG-13	KG-11	KG-12	KG-14	KG-15	KG-16	KG-23	KG-24	KG-26
Rock	Metabasalt		Metabasaltic-andesite		Medium-Felsic Metavolcanics							
SiO_2	55.5	50.3	61.5	69.9	70	69.5	72.10	69	64.7	71	68.7	74.6
TiO_2	2.4	2.4	0.5	0.5	0.3	0.4	0.30	0.4	0.4	0.3	0.3	0.3
Al_2O_3	13.8	13.8	14.9	12.7	15.1	13.4	11.60	15.8	15.6	13.8	12.9	11.1
Fe_2O_{3TOT}	13.8	14.9	8.1	3.6	3.7	3.7	3.80	3.2	4.9	3.2	3.6	1.7
MnO	0.2	0.2	0.2	0.1	0.1	0.09	0.10	0.09	0.1	0.1	0.1	0.09
MgO	3.6	4.5	4	2	2	6.2	1.50	2.1	4.8	1.2	1.3	0.2
CaO	2.9	6.1	2.7	2.2	0.5	0.6	1.00	0.4	1.1	3.1	5.5	3.4
Na_2O	4.4	4.7	4.2	5.9	5.4	1.2	5.60	7.2	6.2	4.2	4	4.9
K_2O	0.09	0.2	0.2	0.1	1	0.8	0.10	0.09	0.09	0.9	0.4	0.1
P_2O_5	0.6	0.2	0.1	0.1	0.1	0.1	0.10	0.1	0.1	0.1	0.1	0.1
LOI	2.55	2.45	3.2	2.2	1.7	3.7	2.20	1.45	2	1.7	2.9	2.45
Sum	99.84	99.75	99.6	99.3	99.9	99.69	98.4	99.83	99.54	99.6	99.8	98.94
Sc	19	22	21.9	1.3	2.5	3.1	2.1	5.2	3.3	0.9	1.1	1.4
V	224	448	224	56	56	56	56	56	56	56	56	56
Cr	45.1	20.2	18.5	137.1	119.4	76.6	268.4	157.6	182.5	111	86.9	252.3
Th	1	1.5	6.6	1.2	0.2	0.6	1.1	0.6	0.3	1.1	1	0.3
Ga	3.2	1.6	15.3	2.2	5.2	3.2	2.3	4.2	6.7	2.3	2.9	0.9
Rb	2.3	4.3	6.9	0.2	13.5	0.5	0.6	2.1	1.9	24.9	8.8	3.4
Sr	25.1	45.1	132.3	78.4	37.6	65.8	44.9	26.1	64.2	9.8	12.6	68
Y	65	32	33	5.9	7.6	4	3.8	6.3	7.7	5.1	18	4.6
Zr	43.2	36.2	48	55.7	77.1	86.4	95.7	106.5	77.9	46.3	46.3	90.2
Nb	4.2	1.4	5.7	1.4	1.6	2	1	2.6	1.6	1.5	1.2	1
Ba	85.2	24.2	20	22.3	308.7	145.8	20.7	30.4	28.1	88.6	48.1	22.2
Cs	2.2	1.2	5.3	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	0.5	0.2	<0.1
La	12	5	11.3	0.8	2.6	0.3	1.3	1.6	0.6	1.6	1.8	1.1
Ce	40	15	17.9	2.5	7.4	0.9	3.2	4.6	1.8	3.9	4.3	3
Pr	7	2	6.4	0.3	1.1	0.2	0.4	0.7	0.3	0.5	0.6	0.4
Nd	35	13	13.8	2.1	5.4	1	1.9	3.4	1.6	1	3	2.4
Sm	11	4	6.8	0.6	1.5	0.4	0.7	1	0.7	0.8	1	0.8
Eu	3	1	1.3	0.2	0.5	0.1	0.1	0.3	0.2	0.2	0.3	0.2
Gd	13	5	7	0.7	1.8	0.6	0.8	1.2	1.1	1	1.6	1.1
Tb	3	1	1.2	0.1	0.3	0.5	0.1	0.2	0.2	0.2	0.3	0.2
Dy	17	7	7.2	0.9	1.7	0.8	0.8	1.3	1.5	1	2	1.1
Ho	3	1	6	0.1	0.3	0.2	0.2	0.3	0.3	0.2	0.5	0.2
Er	9	4	4.8	0.6	0.9	0.5	0.5	0.7	0.8	0.6	1.6	0.5
Tm	1	0.3	0.7	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.2	0.2
Yb	6	3	3.5	0.4	0.6	0.4	0.3	0.5	0.6	0.6	1.2	0.4
Lu	1.2	0.5	0.4	2	1.2	1.3	0.1	0.1	0.1	0.1	0.2	0.1
Hf	9	2	1.7	1.15	1.2	2.3	2.45	1	1.23	1	2	2
Ta	0.2	0.2	2.3	0.1	0.1	0.2	0.1	0.2	0.2	0.1	0.1	0.08
Pb	2.3	3.1	14.5	5.1	4.2	2.7	6.5	3.9	5	4.3	3.6	4
U	0.1	0.2	4.9	0.3	0.2	0.1	0.2	0.1	0.3	0.3	0.1	0.1
Cd	0.2	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Tl	0.2	1	1.2	0.3	0.3	0.2	0.2	0.1	0.3	0.3	0.2	0.3
$(La/Yb)_N$	1.43	1.20	2.32	1.43	3.11	0.54	3.11	2.30	0.72	1.91	1.08	1.97

Table 2- Representative geochemical analysis results of Cu-rich zones in the Cünür mineralization.

Sample	Ag ppm	As ppm	Au ppb	Bi ppm	Co ppm	Cu ppm	Mo ppm	Ni ppm	Pb ppm	Sb ppm	V ppm	Zn ppm
KCS-1-98	79	11	150	18	<5	10.000	8	7	156	<5	<5	9.540
KCS-2/ J159	2.2	15	<20	<5	<5	10.000	5	11	57	<5	22	662
KCS-2/ J160	1.7	9	<20	<5	<5	10.000	<5	9	40	<5	41	2.110
KCS-5-J14	20.1	66	1300	<5	10	10.000	6	23	520	<5	43	4.100
KCS-5-J17	13.4	71	770	<5	9	12.000	8	15	540	<5	32	6.100
KCS-5-J18	8	36	350	<5	<5	10.000	<5	9	370	<5	18	2.600
KCS-5-J20	22.2	120	1.100	17	15	10.000	17	16	690	<5	37	8.000
KCS-5-J23	23.5	130	9.4	19	14	12.000	11	18	650	<5	45	6.600
KCS-5-J26	26.1	130	1.100	6	12	10.000	20	16	920	<5	32	11.000
KCS-5-J65	23.9	130	1.300	<5	10	15.000	35	8	760	9	19	15.000
KCS-5-J66	31.5	120	1.700	<5	10	10.000	31	10	1.500	12	21	17.000
KCS-5-J83	26.5	240	3.300	23	12	50.000	36	26	1.600	17	11	19.000
KCS-8-J330	2.7	99	85	<5	<5	13.170	32	<5	28	6	<5	2.198
KCS-8-J331	2.2	89	70	<5	<5	10.828	36	<5	32	6	<5	1.511
KCS-8-J333	3.3	98	95	<5	<5	11.766	31	6	57	6	<5	4.021
KCS-8-J334	3.2	133	85	<5	<5	12.994	43	<5	35	5	<5	3.991
KCS-8-J335	3.4	100	75	<5	<5	17.299	43	<5	48	6	<5	1.898
KCS-13-J289	4.6	369	150	7	<5	16.141	34	6	74	11	<5	9.298
KCS-13-J306	2	26	25	<5	<5	10.409	18	<5	108	<5	<5	322
KCS-21-J307	2.9	170	40	<5	<5	11.610	88	<5	53	<5	<5	2.268
KCS-21-J312	4.9	268	165	<5	<5	10.810	78	11	66	<5	<5	6.134
KCS-24-J266	39.8	967	685	71	8	92.652	67	5	160	49	<5	7.586
KCS-24-J267	8.5	580	135	24	6	19.266	19	6	39	31	<5	776
KCS-24-J268	26.5	1.369	660	68	7	41.609	51	<5	168	85	<5	2.260
KCS-24-J269	36.7	335	925	73	8	85.458	50	<5	86	32	<5	2.253
KCS-24-J272	36.9	416	1.750	65	9	89.320	43	<5	272	30	<5	941
KCS-27-J164	40.3	107	640	14	11	17.574	23	7	3.412	11	17	90.461
KCS-27-J174	37.1	113	930	13	11	17.376	34	8	2.857	12	17	91.679
KCS-39-J206	15	25	260	<5	<5	22.687	21	<5	276	<5	10	830
KCS-39-J210	9.6	39	180	<5	<5	13.205	30	<5	778	<5	6	16.220
KCS-52-J27	3.8	24	<20	15	<5	15.832	21	6	47	<5	5	182
KCS-59-J128	27.6	95	545	<5	<5	10.166	34	8	2.283	10	6	23.100
KCS-59-J129	11.5	216	890	18	<5	10.203	58	10	214	11	<5	2.339
KCS-59-J130	11.6	225	475	<5	<5	51.500	75	12	293	35	6	7.675
KCS-59-J132	15.8	408	575	<5	<5	54.500	118	14	225	41	6	10.643
KCS-59-J133	10.4	220	335	<5	<5	62.000	94	12	249	15	8	7.433
KCS-59-J134	9.5	142	285	<5	5	53.000	143	10	288	25	<5	9.026

- south trending left strike - slip fault passing through the western slope of Büyükdoruk Hill (Figure 2). The lines where mineralization is observed are generally located in the sections where felsic metavolcanic rocks are observed to be imbricated with other units. Starting from the east, there are silicified, hematitized and argillized alterations with pyrite - limonite, around the Horozbiçtigi Hill, Ahmetolduğu Hill, Kure Stream and Karabay Hill. These alterations are structurally controlled and occasionally appear as small slices of imbrication 5 - 30 meters wide. Quartz, sericite and pyrite mineral assemblages are observed on the northeastern and southwestern slopes of the Kure Stream. In these alteration zones, malachite, azurite, to a lesser extent bornite and covellite minerals, as well as local alunitizations are found.

Mineralization areas that may be of economic importance have been identified in two different areas. These are located in the Ahmetoldugu Hill (ZONE - 1) in the northeastern part of the Kure Stream and the extension of the Kevenlik Ridge and around the Karabay Hill (ZONE - 2). The Cünür mineralization has massive – semi - massive ore structure. The thickness of the largest massive sulfide lens consisting of massive ore in the field was determined as 22 m.

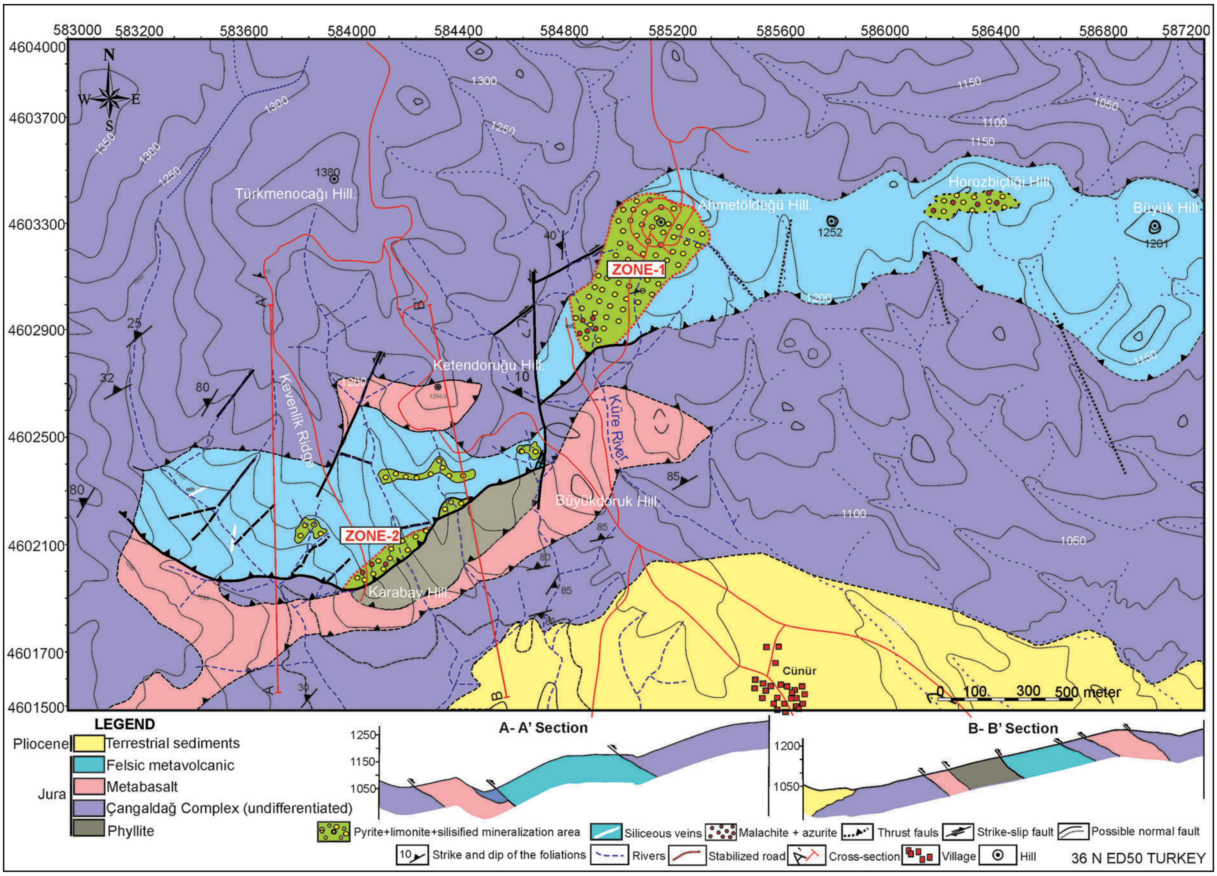

Figure 2- Cünür VMS mineralization and geological map of its surroundings.

Apart from this massive sulfide lens, which lateral continuity reaches 400 meters with decreasing thickness, many small - sized massive ore zones with a thickness of 1 - 15 meters have been identified by core drilling. The ores are found irregularly in the 50 - 370 meters elevation range throughout the field. Massive ores consist of sulfide ore, which is defined as pyritic masses of about 60% (Figure 4a, e). Massive sulfide masses in felsic metavolcanic rocks usually begin with crushed, argillized (montmorillonite, illite) zones and end with crushed, argillized zones (Figures 4a, b). These zones in the mineralization localise the mineralization, correspond to the imbrications. The observation of graded enrichments by pyrite - chalcopyrite minerals in massive sulfide bodies and the fact that the ore contains silicified rock fragments in places may indicate that mineralization has developed in relation to substitution. In felsic metavolcanic rocks, breccia fill and fracture - crack fill which have a continuity of meters and developed in metamorphism and tectonic processes and pyrite formations as veinlets, which include rarely chalcopyrite and sphalerite, are observed (Figure 4c, g). The presence of pyrite - chalcopyrite minerals in secondary siliceous zones as well as coarse (1 - 5 mm) pyrite crystall formations in fracture - crack deposits may indicate remobilization that develops in post - mineralization processes.

4.1. Rocks and Mineralogical - Petrographic Characteristics of Ore in the Cünür Mineralization Area

Mafic metavolcanic rocks, which constitute the dominant lithology in the study area, have intersertal - hypohyaline texture and can mostly be defined as metabasaltic andesite or metabasite. The mineral paragenesis of these rocks consists of amphibole (actinolite), plagioclase, quartz, chlorite, epidote and lesser amounts of opaque minerals (Figures 5a and b). Amphibole minerals are reticular - fibrous, prismatic in places, small - grained and hypidiomorph plagioclase crystals are predominantly sericitized. Platy chlorite and epidote minerals in clusters, in addition small amounts of fine - grained, semi - euhedral quartz and

Figure 3- Field photographs of lithological units in the mineralization area. a) Metabasaltic andesite, b) limonitized altered metadacite, c) altered metadacite with semi-euhedral quartz minerals, d) aphanitic textured, silicified metariodacite containing disseminated pyrite, e) fractured zones containing azurite and malachite, f) phyllite (view direction north).

carbonate minerals are generally found as fracture - fillings. The mineral assemblage of albite, chlorite, and epidote in basaltic andesites indicates metamorphism under greenschist facies conditions at low temperature and moderate pressure.

Felsic metavolcanites are predominantly hypocrystalline porphyritic in texture and contain feldspar, quartz and opaque mineral (pyrite) phenocrysts in a felsic matrix composed of feldspar and quartz (Figure 5 c, d). Feldspars are in the form

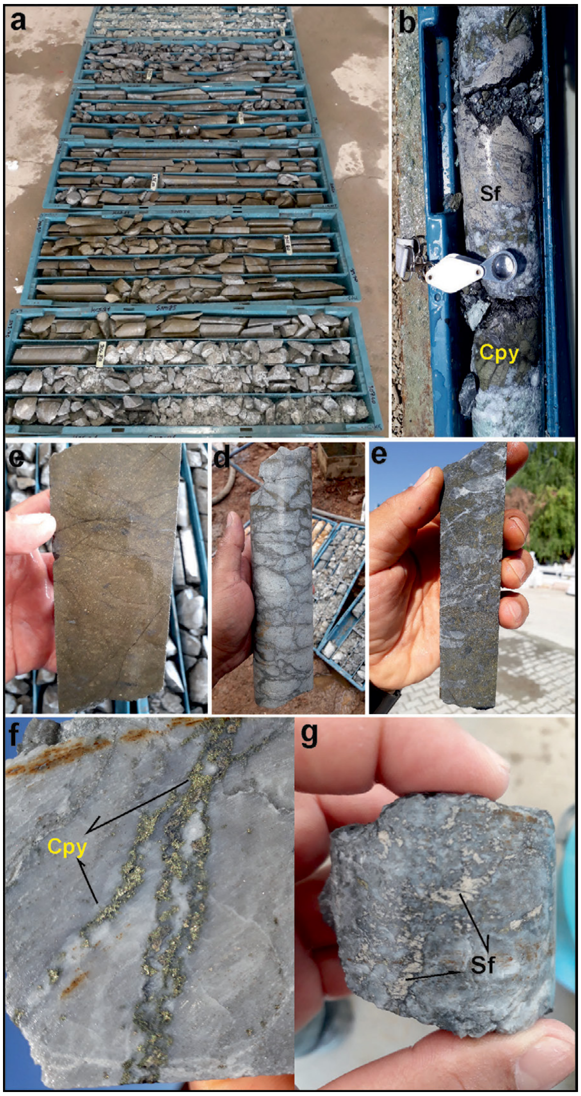

Figure 4- Core photographs associated with the Cünür mineralization. a) Massive sulfide ore with a thickness of 22 meters, consisting of massive ore, b) the appearance of zones rich in chalcopyrite and sphalerite minerals, c) the close view of the massive ore d) tectonic breccia fill secondary pyrite mineralization developed over silicified metariodacite, e) Substitution texture containing siliceous zones in semi-massive ores f) and g) appearance of chalcopyrite and sphalerite minerals filled with fractures and cracks in the silicified host rock.

of fine - grained hypidiomorphic crystals and are predominantly argillized and sericitized. Generally, absorbed quartz and opaque minerals are observed as euhedral, subhedral forms. In these rocks, opaque minerals consisting of euhedral - subhedral pyrites are found as disseminated at a rate of 10 - 20%. Secondary calcite fillings, small amounts of chlorite, epidote, hematite minerals are observed along the fractures in felsic metavolcanic rocks, and predominantly argillisation is observed (Figure 5 c, d). The presence of fine grained epidote minerals in thin sections may indicate that these rocks contain mafic phenocrystals. The change in MgO contents of 0.2 - 6.2% in the geochemistry analysis results of felsic metavolcanic rocks supports the presence of mafic phenocrystals in these rocks.

Black - gray colored and very fine - grained phyllites are seen in lepidogranoblastic texture. These rocks have very fine - grained plagioclase and quartz as main minerals as well as secondary mineral paragenesis of calcite, mica (sericite flakes), and chlorite (Figure 5 e, f).

Pyrite, chalcopyrite and sphalerite are the main mineral paragenesis of the Cünür sulfide mineralization. Apart from magnetite and galena minerals which are rarely seen, bornite, digenite, covellite, chalcocite are found in small amounts as secondary minerals. Quartz is the main gangue mineral and calcite formations are observed in veins and pockets. Pyrites, the most common sulfide mineral, form the first phase in the paragenetic sequence of ore minerals in the Cünür mineralization (Figure 6). The second widespread ore phase is composed of chalcopyrite and sphalerite minerals as anhedral fillings between pyrite grains. Generally, chalcopyrite coexisting with sphalerite is rarely seen as inclusions within sphalerite. Intergrowth textures indicate that a phase with chalcopyrite and sphalerite developed following the early sulfide phase in which pyrite was formed.

In massive ores, the grain size of pyrite minerals is much smaller than semi - massive and other formations, and the ratio of chalcopyrite is much higher. Pyrite crystals in massive ores have a grain size of approximately 5 - 800 µm and appear in euhedral, subhedral, and mostly anhedral forms (Figure 7 a). Pyrites recrystallized in fractures and cracks of the host rocks, on the other hand, have grain sizes in the range of 1 - 5 mm macroscopically in places. Chalcopyrite and sphalerite are found, filling the voids after pyrite crystallization, settling in the fracture - cracks of pyrites and surrounding them, and rarely, chalcopyrite inclusions are observed in sphalerite (Figure 7 b - d). Bornite minerals found in the fractures and cracks of pyrites are transformed into digenite, covelline, and chalcosine. In polished sections dominated by anhedral pyrite minerals, there are rarely galena

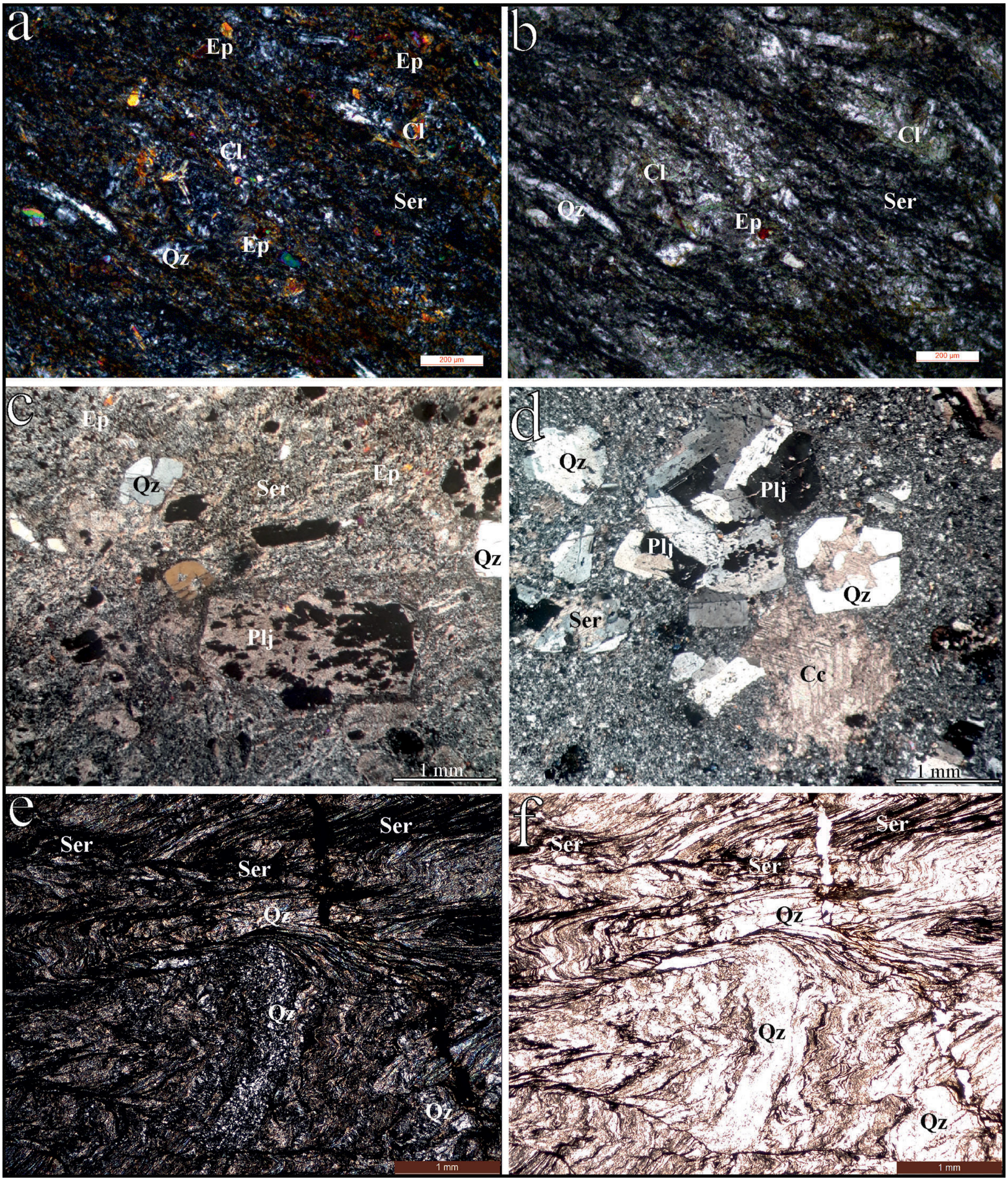

Figure 5- In the Cünür mineralization area, the thin-section images of the chloritized, epidotized, and silicified mafic metavolcanic rocks. a) Cross polarized light, b) plane polarized light); clayed, carbonated, and silicified felsic metavolcanic rocks, c) cross polarized light, d) plane polarized light); phyllite, e) cross polarized light, f) plane polarized light) (Cc-calcite, Cl-Chlorite, Ep-epidote, Ser-sericite, Qz-quartz, Plj-plagioclase).

minerals settled in fractures of pyrite minerals (Figure 7 e). Magnetites are generally in the form of small accumulations, sometimes as disseminated grains. Fine - grained anhedral and sometimes sub - euhedral magnetites of 15 - 60 µm grain size are seen in the spaces of pyrite minerals (Figure 7 f). Pyrite minerals in areas where secondary silicification associated with mineralization are coarse - grained, sharp - angular,

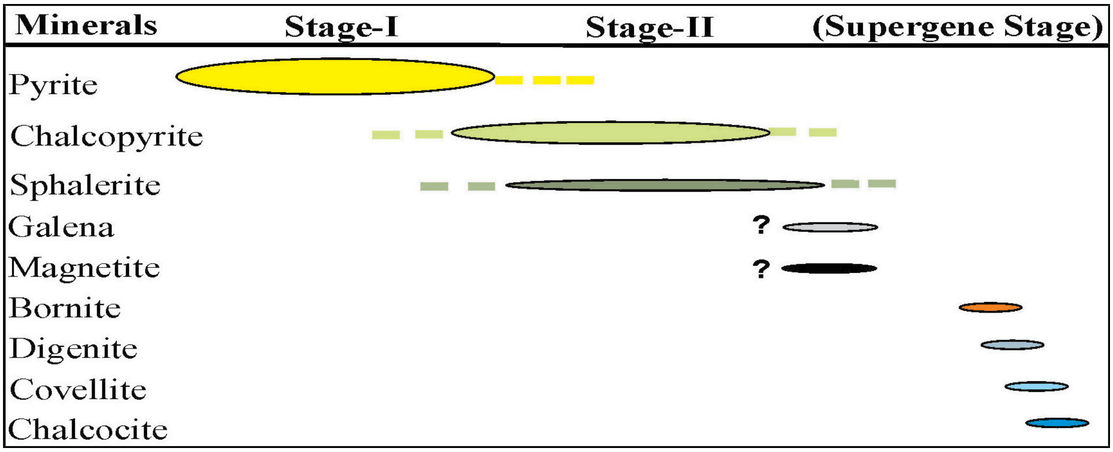

Figure 6- The Cünür mineralization paragenetic sequence table.

fractured and cracked, and chalcopyrite, in addition, sphalerite and chalcopyrite minerals are observed to be developed in their fractures (Figures 7 g, h). This indicates that remobilization has developed in the post - primary mineralization processes.

4.2. Geochemical Characteristics of Metavolcanic Rocks

For the geochemical classifications of metavolcanic rocks outcropping in the Cünür mineralization area, those with loss on ignition values were used, and the major oxide and trace element contents of these rocks are given in Table 1. The loss on ignition of the samples ranged from 1.7% to 3.7%. Samples include volcanic rocks with a composition ranging from partially hydrothermally altered sub - alkaline basalt to andesite and dacite (50.3 - 74.6% SiO_2). This situation indicates that the rocks may have been affected by hydrothermal alteration, low - grade metamorphism or seafloor hydrothermal alteration. Although loss on ignition is partially low, it has been observed that rocks are affected by hydrothermal alteration and metamorphism and partially lost their original textural and mineralogical characteristics. With the effect of hydrothermal alterations, most major elements and LIL (large ion lithophile, excluding Th) elements behave mobile, while HFS and RE (high field strength and Rare earth) elements behave mostly immobile or less mobile (Winchester and Floyd, 1977).

In order to make a more accurate classification approach for metavolcanic rocks in the study area, the Nb / Y - Zr / TiO_2 variation diagram of Winchester and Floyd (1977) was used (Figure 8a). In this diagram, it is seen that the samples have a composition ranging from sub - alkaline basalt series to andesite and dacite. Metavolcanic samples plot within the calc - alkali and island arc tholeiites fields on the Hf / 3 - Th - Ta tectonic discrimination diagram of Wood (1980) (Figure 8b).

N - MORB - normalized spidergram (Figure 9a) demonstrate that samples are generally enriched in LILE (excluding Sr), HFSE and REE relative to N - MORB (Normal Mid - Ocean Ridge Basalts). HFS elements (Nb, Ta, Zr, Hf) are typical with their relative tendency to be depleted relative to LIL and LRE elements. The greater enrichment of LIL and LRE elements than basaltic samples in the transition from sub - alkaline basaltic samples to more evolved andesitic and dacitic samples typically can be corresponded to the fractional crystallization processes in their evolution.

Chondrite - normalized (Sun and McDonough, 1989) REE spidergrams are presented in Figure 8b. There is no enrichment or depletion in these diagrams, the samples show a near - flat trend from LREEs to HREEs (La / YbN = 0.5 - 3.1), typically showing a trend in line with MORB and island arc tholeiite values. In addition, the REE patterns of andesite and dacite samples, which evolved as in the multi - element spider diagrams (Figure 9a), show enrichment in rare earth elements according to the patterns of the sub - related basaltic samples, thus indicating that felsic volcanics are typically derived by fractional crystallization processes.

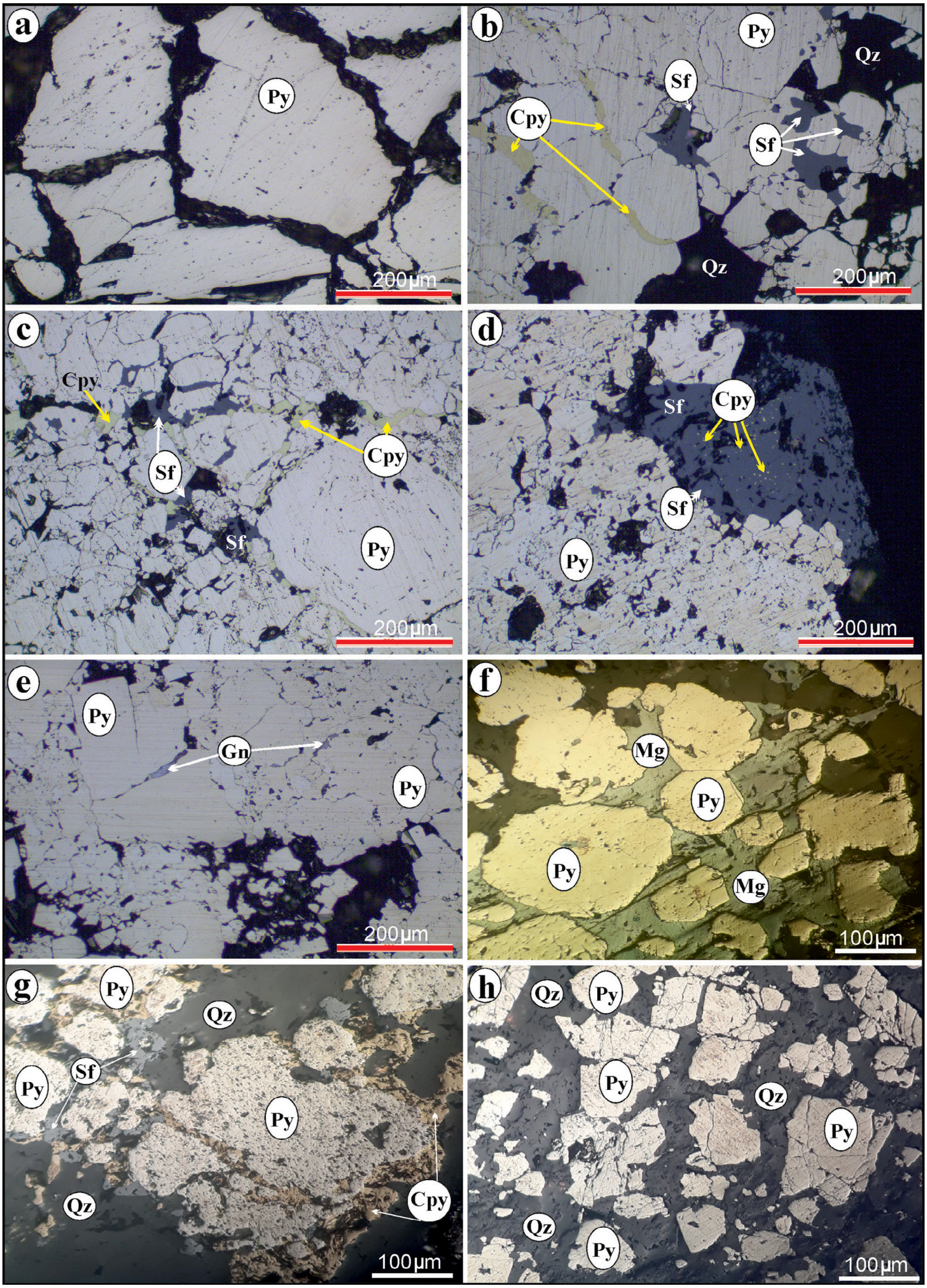

Figure 7- The polished sections images of the Cünür mineralization; a) coarse crystalline fractured pyrite minerals, b) and c) in massive ore rich in chalcopyrite, chalcopyrite and sphalerite minerals that filled fractures-spaces between subhedral and anhedral pyrites and replaced pyrites, d) chalcopyrite inclusions in sphalerite, e) galena minerals seen in anhedral pyrite mineral fractures, f) in zones of pyritic massive ore, euhedral-subhedral pyrite and magnetite minerals filling its spaces, g) and h) in siliceous zones, chalcopyrite-sphalerite filling the gaps of pyrites and pyrites (Cpy- chalcopyrite, Mg- magnetite, Py- pyrite, Sphalerite, Gn- Galen).

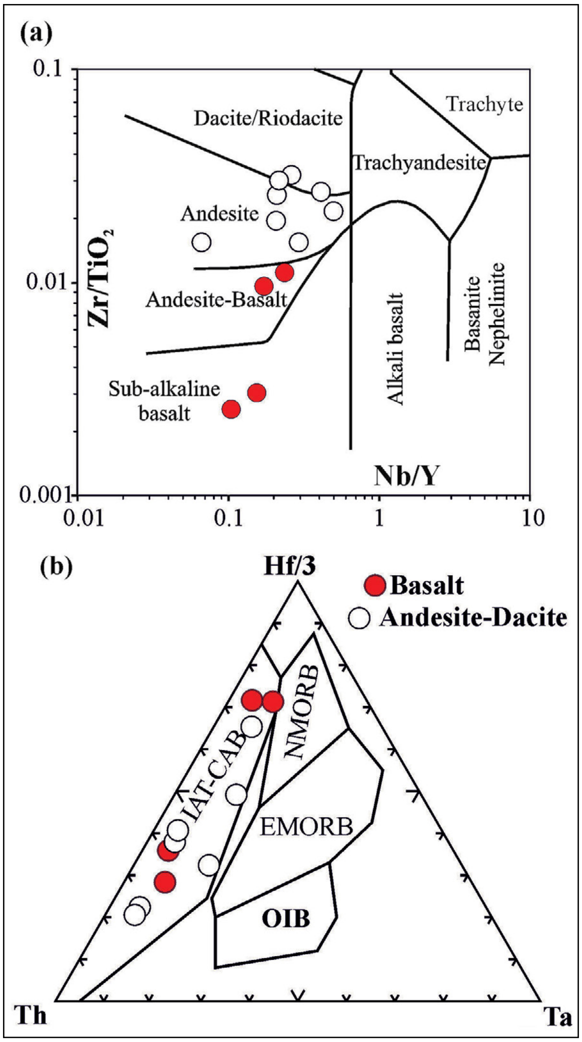

Figure 8- In the Cünür mineralization area, a) Zr/TiO_2 versus Nb/Y classification diagram of metavolcanic rocks (Winchester and Floyd, 1977), b) classification of metavolcanic rocks in Th-Ta-Hf/3 paleotectonic discrimination diagrams (Wood, 1980).

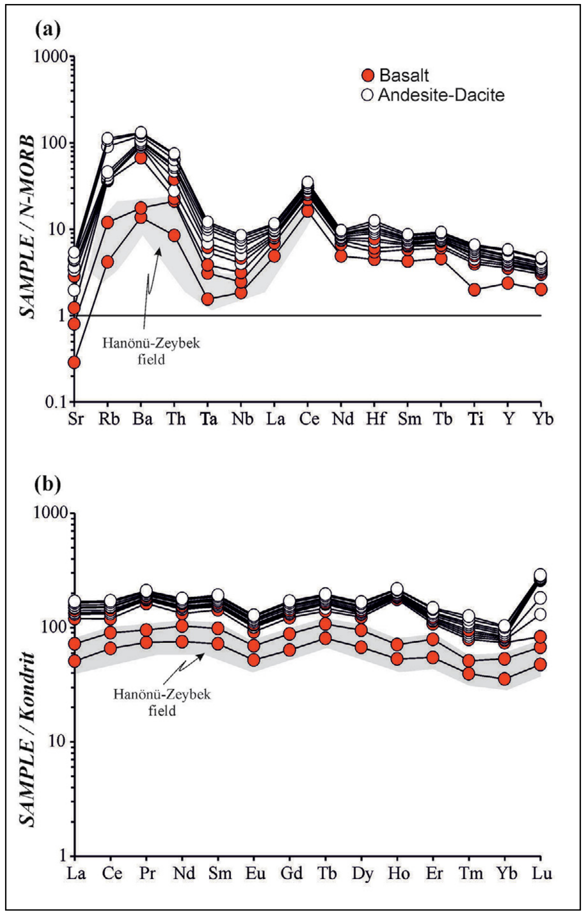

Figure 9- The spider diagrams of metavolcanic rocks normalized to a) N-MORB and b) chondrites (normalized values are taken from Sun and McDonough, 1989).

4.3. Ore geochemistry

In this study, ore samples, which geochemistry was used, were taken from parts of the massive ores where the effects of textural and petrographic alteration and recrystallization processes were not observed. Samples with Cu values higher than 1% of the Cünür mineralization are presented in Table 2. The highest values obtained for base and precious metals were determined as 9% for Cu and Zn, 0.3% for Pb, 3,300 ppb for Au and 79 ppm for Ag. The Cünür mineralization has the highest values of 15 ppm for Co, 143 ppm for Mo, 26 ppm for Ni, 85 ppm for Sb and 45 ppm for V. 227 samples taken from the ore zones in the cores of the drillings made in the field of Cünür mineralization and analyzed have an average of 8,860 ppm Zn, 6,231 ppm Cu, 335 ppm Pb, 24 ppm Ag and 299 ppb Au metal content. With the geochemical data obtained from the core drillings in the Cünür mineralization area, 3,372,000 tons of 0.28% Cu, 0.50% Zn, and 0.19 ppm Au content, with a Cu cut off grade 0.1%, were determined (Günay et al., 2019*b*).

5. Discussion

5.1. Petrogenetic Indicators of Volcanic Rocks in the Cünür Mineralization Area

The unstable trace element trends (Figure 9a), normalized to the MORB (mid - ocean ridge basalts) values of the most mafic sub - alkaline basaltic samples found in the Cünür mineralization area, typically indicate subduction - enriched mantle source areas. The tendency of Nb and Ta elements to be depleted relative to neighboring LIL and LREE (light rare earth elements) elements indicate mantle source areas metasomatized with subduction component. In contrast, the same trend in rocks of the andesitic and dacitic composition suggests that these rocks have underwent evolutionary processes in magma chambers from sub - alkaline basaltic volcanism, associated with processes of fractional crystallization and / or assimilation and crustal contamination (AFC processes).

Th / Yb versus Nb / Yb diagram is used to reveal the source characteristics of metavolcanic rocks (Figure 10). Nb and Th elements can be used as a normalization factor to reflect the changes in the mantle, while the Yb element can be used as a normalization factor to minimize the effects of fractional crystallization, crystal accumulation, and crustal contamination (Pearce et al., 1984). As can be seen in Figure 10, samples are separated from the EMB - OIB mantle area with Th values rising from sub - alkaline basaltic samples to evolved samples. Increased in Th contents typically represent the presence of subduction component for sub - alkaline basaltic volcanism products, while typically indicate the effects of fractional crystallization for evolved samples. On the diagram, rocks of sub - alkaline basaltic composition associated with the Cünür mineralization cluster in the same / close area with the Hanönü Massive Sulfide (HMS) and Zeybek Massive Sulfide (ZMS) mafic sills and dykes samples (Günay et al., 2018, 2019). This data indicates that the sub - alkaline basalts in the Cünür mineralization area are derived from a mantle source enriched by subduction - zone components, such as rocks of HMS and ZMS. It can be said that the felsic metavolcanics associated with the Cünür mineralization were formed as a result of the evolution of sub - alkali basalts derived from an enriched mantle source.

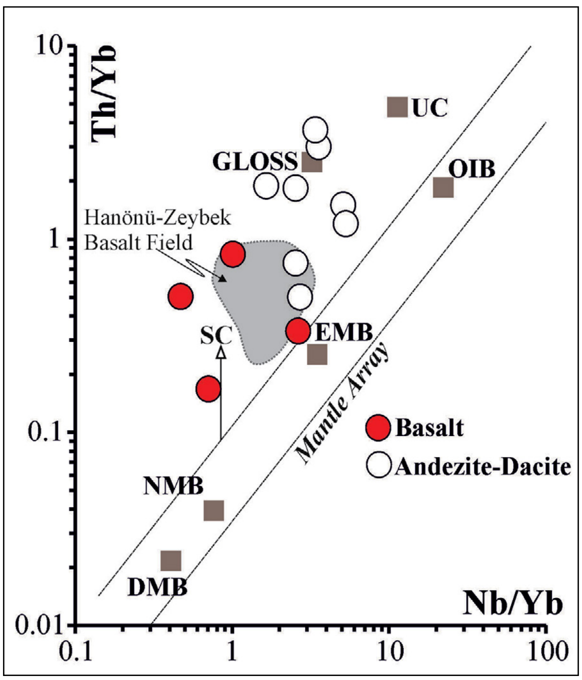

Figure 10- Nb/Yb - Th/Yb binary variation diagram of metavolcanic rocks associated with the Cünür mineralization. NMB (N-type Mid-Ocean Ridge Basalts), EMB (Enriched Mid-Ocean Ridge Basalts), DMM (Depleted Mid-Ocean Ridge Basalts), OIB (Ocean Island Basalts) values were taken from Sun and McDonough (1989), UC-value was taken from Taylor and McLennan (1985). GLOSS values are taken from Plank and Langmuir (1998) and Plank (2014). HMS (Hanonu massive sulfide) and ZMS (Zeybek massive sulfide) data were taken from Günay et al. (2018) and Günay et al. (2019), respectively.

Another approach can be developed over the structural relationships of the Çangaldağ Metamorphic Complex. The members of this metamorphic complex locate with each other in tectonic contact. The members of this complex were formed in two different paleotectonic environments and are present together in accretion. These are mafic volcanics intercalated with deep - sea sediments associated with the Hanönü and Zeybek massive sulfide deposits and an island arc with Jurassic bimodal volcanism products. While the Cünür mineralization takes place within the island arc units associated with bimodal volcanism, this mineralization and mafic volcanics intercalated with deep - sea sediments are found together in tectonic contact. In this context, CMC is an accretionary product in which units formed in two different paleotectonic environments are together.

5.2. Classification of Cünür Mineralization and Status in Other Pontide Belt VMS Formations

Massive sulfide deposits are commonly classified using the Cu - Zn - Pb triangle diagram (Franklin et al., 1981; Franklin et al., 1993; Galley et al., 2007). Relatively higher Cu or Zn content compared to sedimentary exhalative (SEDEX) type mineralizations distinguishes volcanogenic massive sulfide mineralizations from SEDEX type formations. In the Cu - Zn - Pb triangular diagram, Cünür mineralization with high Zn - Cu content is located in the Cu - Zn

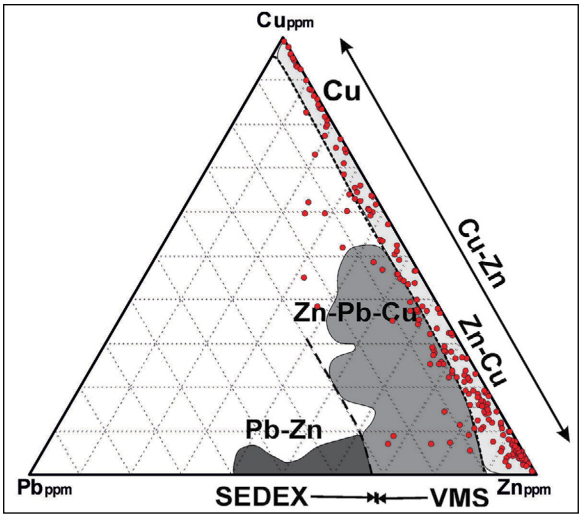

Figure 11- Classification of Volcanogenic Massive Sulfide deposits of the Cünür mineralization according to the Cu-Pb-Zn triangle diagram (Franklin et al., 1981).

group of volcanogenic massive sulfide deposits (Figure 11). SEDEX - type mineralizations with high Pb content are generally found in sedimentary rocks associated with continental rifting. The Cünür mineralization has high Cu - Zn, low Pb content and is a typical VMS formation as the country rocks are the product of bimodal volcanism.

One of the common methods used in the classification of VMS mineralizations is the classification in which paleotectonic environments are taken into consideration. For the Cu - Zn group VMS mineralizations, four different classification criteria have been determined: Noranda type (within mafic - felsic volcanic successions), Mattabi type (similar to Noranda type but with abundant Pb), Cyprus type (within ophiolites), and Besshi type (in sediments in volcanic areas) (Franklin et al., 1981; Franklin, 1993; Lydon, 1984*a, b*). Noranda type VMS mineralizations are located in the lithologies that tholeiitic and calc - alkaline mafic / felsic rocks are dominant. In Noranda type mineralizations, the ore is included in felsic volcanic rocks, while the dominant volcanic rocks in the mineralization area are mafic in character (Franklin, 1993). The Cünür mineralization has characteristics similar to the Noranda type VMS mineralizations with its ore and host rock properties and is different from other VMS formations in the Pontides.

Cu - Pb - Zn content of volcanogenic massive sulfide deposits presents changes according to the relationship of mineralization with the host rock lithologyand the tectonomagmatic settings in which they formed. The VMS deposits are classified into five different groups based on host - rock composition: Mafic, Bimodal - Mafic, Mafic - Siliciclastic, Bimodal - Felsic, Bimodal - Siliciclastic (Barrie and Hannington, 1999). Among these groups, Bimodal - Mafic type VMS mineralizations have host rock lithology that is more than 50% mafic, more than 3% felsic, and a small amount of siliciclastic. In this type of VMS formations, the characteristic of mafic volcanism is tholeiitic. Felsic volcanics are in transition to highly siliceous rhyolites or calc - alkaline rhyolites. Bimodal - mafic type VMS mineralizations are characteristic with high Cu - Zn contents. Considering this new classification based on dominant host rock lithologies for VMS mineralizations, the Cünür mineralization exhibits similar characteristics to bimodal - mafic volcanogenic massive sulfide formations within VMS mineralizations. As in the bimodal - mafic type VMS formations, the host rocks in the Cünür mineralization area are predominantly composed of mafic volcanics. However, the mineralization is within the felsic volcanics and they are accompanied by less silicified volcanoclastic units. It is similar to bimodal - mafic type VMS formations in that the Cünür mineralization has high Cu and Zn content compared to Pb content. However, for volcanogenic massive sulfide mineralizations, this classification criterion alone does not define the tectonomagmatic environment in which mineralization occurs.

The Hanönü and Zeybek VMS mineralizations in CMC (Middle Pontide) were defined as mafic - siliciclastic (Besshi type) type (Günay et al., 2018, 2019*b*). The host - rock lithology of mafic - siliciclastic type VMS mineralizations is mainly composed of mafic volcanic or intrusive rocks and turbiditic silicilastic rocks with lesser or no felsic volcanics. Küre VMS mineralizations exhibiting mafic - siliciclastic type characteristics, have been defined as Cyprus Type VMS formation due to their host rock and paleotectonic setting features (Çakır, 1995; Altun et al., 2015; Akbulut et al., 2016). These VMS deposits known in the Central Pontides have mafic - siliciclastic features and can be defined as Besshi (Hanönü, Zeybek VMS deposits) and Cyprus (Küre VMS deposit) type. Cyprus type mineralizations genetically indicate oceanic rifting, while Besshi type mineralizations indicate continental rifting or divergent sections of oceanic rifting. The Eastern Pontide VMS deposits are consistent with bimodal - felsic (Kuroko or Eastern Pontide type) type VMS mineralizations according to the relationship of mineralization with the host rock and the tectonomagmatic setting in which they occur (Eyüboğlu et al., 2014; Revan et al., 2014). This type of mineralization has >50% felsic volcanic rocks and <15% siliciclastic rocks, and is defined as VMS mineralizations with widespread barite and the highest Zn and Ag content (Barrie and Hannington, 1999).

Primitive mantle normalized spider diagram of the average metal content of the Central and Eastern Pontide VMS deposits is presented in Figure 12. In this diagram, the metal contents of Bimodal Mafic, Bimodal Felsic, and Mafic Siliciclastic VMS formations are given by normalizing to the primitive mantle (Barrie and Hannington, 1999). The metal contents orientations between the Eastern Pontide VMS deposits and Central Pontide VMS deposits differ significantly. The Eastern Pontide VMS formations are considered between the Bimodal Mafic and Bimodal Felsic VMS formations with their metal contents and high Pb, Zn, Au content is characteristic.

The Hanönü and Zeybek VMS mineralizations in the Central Pontides are similar to the Cu metal dominant Mafic - Siliciclastic type VMS mineralizations with metal variations and host rock composition. Although the Küre VMS mineralization exhibits metal variations similar to mafic siliciclastic type VMS formations, it has characteristically high Cu and Au content.

The Cünür VMS mineralization differs from the Central and Eastern Pontide VMS formations in terms of both host rock properties and metal content. Although mafic - intermediate metavolcanic rocks are dominant in the Cünür area, mineralization takes place in felsic metavolcanics, the dominance of Zn metal compared to other mineralizations and the difference of the tectonomagmatic environment in which mineralization host rocks are formed (dominant lithology volcanic rocks with the felsic character) are the most important differences that distinguish the Cünür mineralization from Middle (dominant lithology metaclastic - mafic metavolcanic rocks) and East Pontide VMS (dominant lithology felsic volcanic rocks) mineralizations.

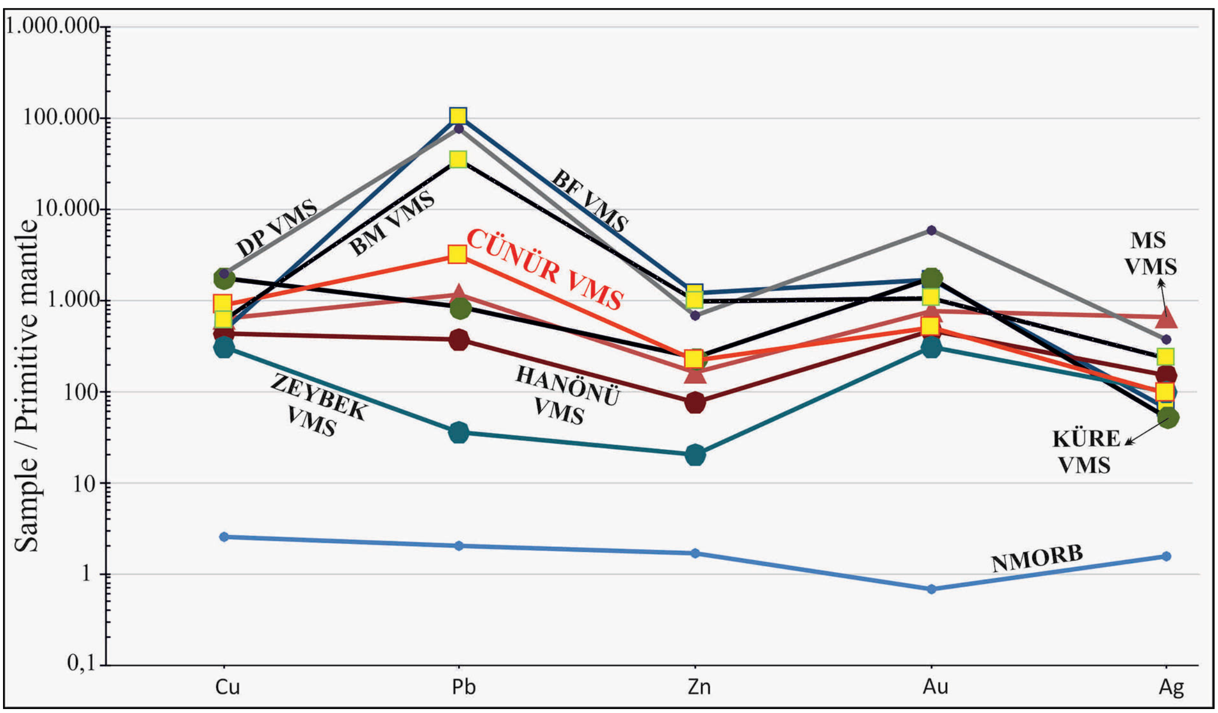

Figure 12- The illustration of metal values of different types of VMS deposits normalized to Primitive mantle in spider diagrams [Primitive mantle values from Wolf and Anders, (1980); Taylor and McLennan, (1985); N-MORB values from Doe, (1994); Keays and Scott, (1976); Hamlyn et al., (1985); Metal contents of Mafic siliciclastic (MS) type VMS beds, Bimodal Mafic (BM) type VMS beds and Bimodal Felsic (BF) type VMS beds from Barrie and Hannington, (1999); Metal contents of the Hanonu and Zeybek VMS deposits from Günay et al. (2018; 2019*b*); the Kure VMS metal contents from Altun et al. (2015); Metal contents of the Eastern Pontide (DP) VMS deposits from Revan et al., 2013)].

The Re / Os data of Küre, Hanönü, and Zeybek Middle Pontide VMS mineralizations indicate that mineralization age is the Middle Jurassic (Küre host rock, 180 Ma, Akbulut et al., 2016; Hanönü - Zeybek ore, 178 My, Günay et al., 2019*a*). The Eastern Pontide VMS formations are younger, and the age data of volcanic units associated with mineralization point to the Late Cretaceous (ore host rock, 91 - 82 Ma, Eyüboğlu et al., 2014). The Cünür mineralization is in the felsic metavolcanics of the Cangaldag Metamorphic Complex. The recent studies for these volcanic rocks indicate the Middle Jurassic age range (metadacite / U - Pb zircon, 169 ± 2My, Okay et al., 2014; metariodacite / U - Pb zircon, 176 ± 2My, 163 ± 9My, Çimen et al., 2018). Although there is no clear syngenetic finding in terms of mineralization host rock relationship, the fact that the mineralization host rock is metavolcanics with felsic character and the mineralization is dominated by Cu - Zn reflects that mineralization developed in relation to the island arc volcanism on the oceanic crust. From this approach, the age of mineralization should be Middle Jurassic, that is the host rock age, or younger.

6. Results

Metavolcanic units in the Cünür mineralization area have compositions ranging from sub - alkaline basalt to andesite and dacite (50.3 - 74.6% SiO_2).

The geochemical characteristics of sub - alkaline basalts in the Cünür mineralization area indicate that these rocks are derived from a mantle source enriched by subduction components. The evolution of sub - alkaline basalts derived from such a source has led to the formation of felsic volcanic rocks associated with the Cünür mineralization.

The Cünür Volcanogenic Massive Sulfide mineralization takes place in the felsic metavolcanic rocks of Çangaldağ Metamorphic Complex.

Geochemical data obtained from 60 core drillings in the Cünür mineralization area revealed the existence of 3,372,000 tons of resources that have 0.28% Cu, 0.50% Zn, and 0.19 ppm Au content with a Cu cut off grade 0.1%.

The highest values obtained for the base and precious metals in dross mineralization are 9% for Cu and Zn, 0.3% for Pb, 3.3 ppm for Au and 79 ppm for Ag, 15 ppm for Co, 143 ppm for Mo, 26 ppm for Ni, 85 ppm for Sb, 45 ppm for V.

The Cünür mineralization is in the Cu - Zn group of volcanogenic massive sulfide deposits, with higher Zn - Cu content compared to Pb content. Considering the ore and host rock properties, the Cünür Cu - Zn mineralization resembles bimodal - mafic type volcanogenic massive sulfide formations.

Paleotectonic environment properties of dominant host rocks and genesis of the Cünür mineralization indicate the Noranda type VMS occurrence within the Cu - Zn group VMS formations. The Cünür mineralization is different from other VMS formations in the Central and Eastern Pontides with its genetic features.

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