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The Massive Sulfide Deposit of Siirt Madenköy, South-Eastern Turkey

—Geology, Geochemistry and Mineral Raw Material Potential

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Abstract

The Siirt Madenköy massive sulfide ore deposit has been in operation since 2005. With its approx. 39 Mt reserves (2.40% Cu), it represents the largest Cu deposit and the largest mining operation in the country (1.5 Mt ore/year). The thickness of the adjacent rocks is composed of olivine-pyroxenite basalts pillow lava, which is spilite, interchangeable ore lenses of chalcopyrite and pyrite is about 170 m and reaches a depth of 350 m. The mid-Eocene aged porphyritic, strongly altered spilites are locally interspersed with diabase and covered by conglomerates. The ores appear massive, stock work and disseminated. Main ore minerals are idiomorphic pyrite, cataclastic chalcopyrite and fine-grained magnetite. The geochemical composition of the Cu ores of the Siirt-Madenköy deposit shows in places high levels of Cu, Fe and S, as important trace elements, As, Ba, Co and Ti are listed. In relation to Clarke values, Se, Bi, Cu, Mo and Co are strongly enriched, while Na, K and Ca as well as their coherent trace elements Rb, Sr and Cd are depleted due to hydrothermal alteration. The elemental distribution is characterized by log-normal distribution, proportionality effect, high Cu/Ni ratio and significantly positive correlation between the element pairs MgO-Ni, Cr-Ni and Co/FeO-Co. The dependence of Cu and SO_3 contents and Cu/FeO, SO_3/FeO ratios are to be interpreted as an indication of the common origin of Cu, Fe and S. In general, Cu, Zn, Pb and S content decrease with depth, whereas those of Fe_3O_4 increase. The variograms of the ore distributions are characterized by hole effect, trend and zonal anisotropy, which reflect alternation of ores with host rocks and changes in elemental contents. The Siirt Madenköy deposit is attributable to Cu and Zn ratios of the Cu class of ophiolitic massive sulfide deposits. Due to the very high Cu/Pb and Cu/Zn ratios, it can be described as an analogous deposit of the mid oceanic ridge, for example comparable to ores of Galapagos Ridge. The

Siirt Madenköy deposit is considered to be a syngenetic volcanogenic-exhalative massive sulfide ore deposit based on the results of the study. It belongs to the "Cyprus deposit type". Similar deposits are Küre and Ergani-Maden in Turkey, Ermioni in Greece and Outukumpu in Finland.

Keywords

Siirt Madenköy, Massive Sulfide Ore Deposits, Cyprus Type, Geochemistry, Mineral Raw Materials

1. Introduction

1.1. Geographical Location

Siirt Madenköy's massive sulfide deposit is located in South-Eastern Turkey, approximately 45 km northeast of the historic provincial town of Siirt (**Figure 1**), an important oil province in Turkey, with traces of ancient Upper Mesopotamian civilizations such as Assyrians, Urarteans, Persians and Ayyubids. The deposit can be reached from Siirt via a country road. The nearest railway Kurtalan is about 80 km west. The main body of the deposit is located at an altitude between 770 and 1290 m NHN [1]. The area has a continental climate with adequate vegetation (rainfall 638 mm/year) and temperatures between 43˚C (July) and −20˚C (February) [2]. The population density 58 persons/km^2 is far below the national average (100 persons/km^2). The population of the industrial poor area is predominantly active in agriculture.

1.2. Historical Overview

The mining activities in Siirt-Madenköy reach back to antiquity [1], but they are

Figure 1. Geographical location.

not clearly documented in time. Old slag heaps and galleries occupy these activities. The first contemporary geological works in Siirt Madenköy were undertaken by the Institute of Mineral Research and Exploration of Turkey (MTA) in 1947. These were followed by detailed work [3] [4] [5]. In 1971, the MTA institute resumed work and described the deposit in detail for the first time [6]. This work was followed by feasibility studies [7] [8]. The mining company was only added to copper ore or concentrate in the spring of 2005.

This article thoroughly discusses the deposit for the geochemical distribution of Cu, Pb, Zn, Fe (as Fe_3O_4) and S components in order to gain new insights into their occurrence in the deposit, to assist in previous geological investigations, and to provide guidance on future work. For this the frequency distribution, correlation analysis and variogram calculation are used. Subsequently, a stock calculation is carried out by profile method in order to determine important economic parameters of the deposit. It should be noted that the data after commissioning of the deposit in 2005 were not included in this work. These are the subject of further research work, as they are predominantly relevant to the determination of reserves (see "Reserve calculation") and this study was already completed.

2. Geological Background

2.1. Regional Geology

The Siirt Madenköy region is located between metamorphic Bitlis massif in the north and marginal folds of the Arabian plate in the south. It consists of north-south Palaeozoic metamorphic rocks (mica schist and marbles), ophiolithic rocks of the Upper Cretaceous (peridotites, volcanic and mudstones) and the Miocene marginal folds of the Arabian plate (conglomerates and sandstones) [9]. The boundaries between these series are always given by east-west almost parallel thrust tracks, which characterize the actual tectonics (see also [10] [11]). The ophiolithic series, also known as the South-East Anatolian Ophiolithic Belt, can be traced over a distance of about 700 km, from Hatay in the west to the Hakkarı on the Iranian border in the east. This series is regarded as the eastern continuation of the Cypriot Troodos massif and its raw material potential equalled with that of the Andes [12]. It contains numerous massive sulfide deposits of the type Cyprus, of which Helezor and Ergani-Maden in Elazığ, Mizak and Karadere in Diyarbakır and Siirt Madenköy in Siirt are the most important [13] [14] [15] [16] [17]. The formation of these deposits is associated with alpine orogeny [18], while [19] compares these with recent occurrences of mid-ocean ridges.

2.2. Geology of the Deposit

The geology of the Siirt Madenköy deposit, as noted above, has rock series of two distinct sequences: these are Permian marbles of the Bitlis massif and spilite, diabase and mudstones of the ophiolitic series of alpine orogeny. This structure is called a tectonic window [20].

The most common rocks of the deposit area are spilites, olivine pyroxenitic basalts, which occur mainly in the eastern and southeastern areas (**Figure 2**). They represent the oldest rock unit of the deposit, which are placed in the middle Eocene [8]. This greenish black, very fragile unit reaches a width of 450 m and is often interspersed with diabase veins. They are subdivided into dark and porphyritic (spotty) spilites [8], which merge into each other. In the center of the unit they lead heavily altered pillow lava, which reach a diameter of 2.50 m. They sweep northeast-southwest and drop northwest at 50˚ - 60˚. Their contact with the other rock series is mostly determined by fractions. Their gas chambers are filled with calcite, quartz and zeolite. The well-developed alteration consists primarily of solidification, chloritization and sericitization. The mineralization is bound to these altered rock areas [8] [21].

The spilites show a clear almond structure and ophiolitic or diabase-like texture under microscope [8] [20]. Their mineralogical composition consists mainly of slightly albitized and rarely idiomorphic plagioclases, as well as augite and mafic minerals such as magnetite, which is rare. The mafic minerals are mostly chloritized or sericitized. Their important secondary minerals are leucoxene and indingist.

Diabase occurs very rarely in the study area as passages in spilites and is younger. The surface diabase flows are mostly concentrated in the north and in the center of the deposit area (**Figure 2**). Their color changes from dark green to light green according to the degree of kaolinization or propylitization (see also [8]). They show a granular structure. Mineralogical they consist mainly of albite and augite. Incidentally, magnetite, hematite, rutile, ilmenite and quartz also occur.

In the west and northwest of the deposit area conglomerates are common. They are not graded [22] and show no stratification. Their transition to the neighboring rocks, for example to the mudstones, is gradual. In upper areas they carry volcanic pebbles, while in the lower areas they have recrystallised pebbles with round grains of pyrite and chalcopyrite. They carry fossils of *Nimmulites sp* and put them in Lutetium [8].

The north-westerly piles (scree) form the youngest rock formation in the deposit. It consists of a mixture of the surrounding rock series and reaches at most a few m thicknesses. In addition, there are still mudstones, which occur in the form of thin horizons and predominantly appear in the north (see also [7] and [23]). In addition, gypsum and breccia horizons can be observed in places.

In the Siirt Madenköy deposit, numerous perturbations of various dimensions and properties have emerged [8] (**Figure 2**). Here, the northwest-southeast interference extending, which are considered as a result of vertical fractures and block movements outweigh. These movements have largely led to the shift of the geological formations and the mineralization zones. In particular, the areas of the conglomerates have been subjected to strong local reductions. The terrain observations show that the fractures were created only after the mineralization.

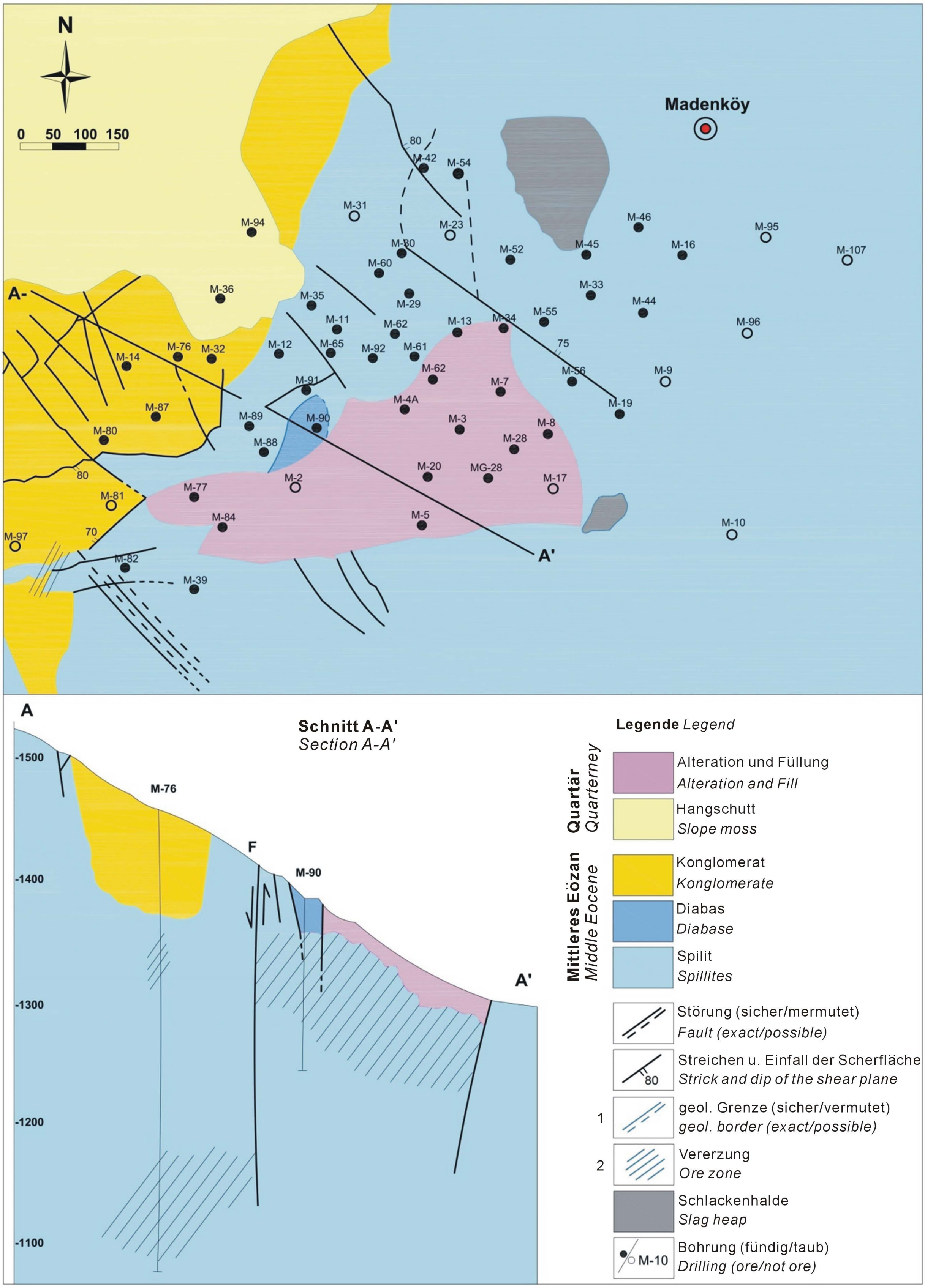

Figure 2. Geological map of Siirt Madenköy (revised after [8]).

2.3. Mineralogy

The mineralization in Siirt Madenköy is bound to the spilites according to [6] and [8], which have massive flow structures and lead cushion lava. These are particularly evident in the southwest of the deposit (**Figure 2**). The ore outbreaks are largely altered.

The mineralization in Siirt Madenköy constitutes a lenticular ore body extending northeast-southwest, consisting of numerous individual lenses of different dimensions at approximately 50˚ to the northwest (section A-A' of **Figure 2** and **Figure 10**). The total thickness of the ore body reaches about 150 m. Its length is about 700 m, while its width varies between 100 and 300 m. In the ore body is a significant vertical zoning to determine. From the bottom (magnetite) to the top (pyrite), the following resource zones are similar, similar to those of the Cyprus type massive sulfide deposits:

Pyrite,

Pyrite + chalcopyrite,

Pyrite + chalcopyrite + sphalerite,

Pyrite + chalcopyrite + magnetite,

Magnetite.

Pyrite is more or less everywhere, while magnetite occurs only in the deeper part of the mineralization. This indicates a primary depth difference characteristic of hydrothermal deposits, as indicated by [24] and [25]. The alteration of ore grades according to the depth in a deposit is an old fact of experience that some elements, such as Zn, increase in depth, or vice versa, such as Pb and Ag, which is why in old Pb mining, the occurrence of sphalerite as a "mining end" was viewed. This change in element contents with depth is interpreted as a consequence of the occurrence of higher temperature zones.

It is already macroscopically, without taking into account their genesis, to distinguish clearly massive, storied and impregnated mineralization. Of central importance is the massive mineralization common in lower areas of the deposit [6] [8]. It is composed of almost pure pyrite, chalcopyrite or magnetite or all of them. Their metal contents are highly variable depending on the composition of the ore, so that in places 16% Cu, 48% S or 92% Fe_3O_4 reach (see **Table 1**). This ore is often surrounded by all-over ore impregnation, which consists of randomly distributed single ore minerals and low metal contents lead. This type of ore predominantly consists of chalcopyrite [8] and fills in places cracks and crevices of country rock, which results in the net-like stock work mineralization. This intersperses both types of ore and occurs mainly in the lower areas of the ore zone, which is typical for volcanic massive sulfide deposits.

The mineralogical composition of these ore grades is identical, and generally consists of sulfidic ore minerals. Pyrite is the most widely used sulfidic mineral with grain sizes of 2 - 3 mm [20]. It is predominantly idiomorphic or hypidiomorphic, showing cataclastic texture and colloidal structure (**Figure 3**). Its cracks are filled with gangue minerals and are older than chalcopyrite, sphalerite

Table 1. Parameters of the frequency distributions of important elements in Siirt Madenköy (compiled from data after [8]).

Element wt%	Samp. n	Min. x_{min}	Max. x_{max}	Average x_a	Standard dev. s	Variation coeff. v	Mod m_o	Median m_e	Skewness g	Excess e
Cu	1369	0.20	16.60	2.23	2.33	104	0.75	1.29	+1.90	+ 4.53
Pb	55	0.50	4.20	1.08	0.57	32	0.74	0.97	+3.20	+15.52
Zn	330	0.50	13.11	2.60	2.14	82	1.04	1.98	+2.08	+4.96
*Fe_3O_4	353	20.00	92.55	42.91	14.88	35	35.00	40.08	+0.56	−0.35
S	904	20.00	48.69	33.10	6.59	20	36.80	33.69	−0.02	−0.71

*Fe analysed as magnetite (Fe_3O_4).

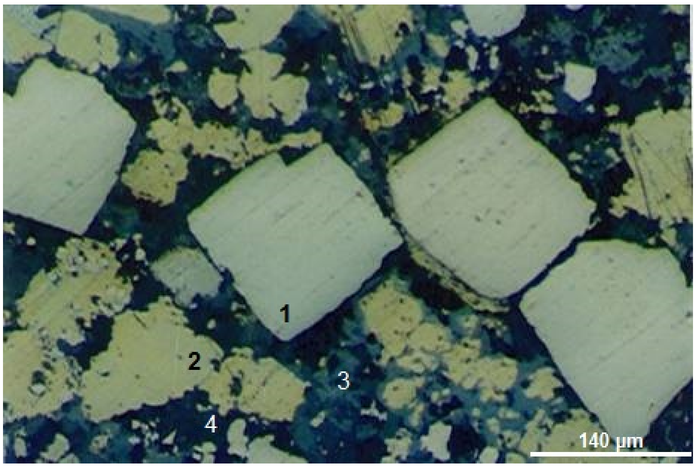

Figure 3. Mineralogical composition of massive ore: 1 idiomorphic pyrite, 2 chalcopyrite, 3 sphalerite (with chalcopyrite inclusions) and 4 gangues or holes. Nicols crossed.

and magnetite. He leads ilmenite and magnetite inclusions in places [8]. Occasionally pyrite from converted pyrrhotite can also be observed.

Magnetite is the second most abundant mineral after pyrite and increases in depth to pure magnetite (see **Figure 6(a)**). It is mainly idiomorphic or hypidiomorphic with pyrite and chalcopyrite. Its grain sizes reach a diameter of 0.30 mm. Rarely does he appears as a lamb. At margins he is often martitized or rarely converted into leucoxene. Its ilmenite, rutile and pyrrhotite inclusions are common [20].

With pyrite and magnetite, cataclastic copper gravel also occurs (**Figure 3**). It is fine-grained, marginally limonitized, shows chalcocit and coveline transitions. Occasionally, sphalerite inclusions can be seen. Incidentally, numerous other oxides, hydroxides, sulphates and carbonates can be found. These are mainly sphalerite, galena, marcasite, pyrrhotite, bornite, coveline, chalcocite, linseed and Fahlerz. Quartz, chlorite, barite, siderite and carbonates must be listed as gangues [6] [20].

3. Material and Methods

The basis of this study is the analytical data of the cores from Siirt Madenköy.

For the detailed statistical, geostatistical investigations and reserve calculations approx. 2000 analysis values of the 49 wells drilled by the MTA institute on the deposit until 1982 of the total of 61 deep wells (about 17.000 m) were used. The average core output is 65%. Some computationally determined important statistical parameters of respective components are summarized in **Table 1**. It can be seen that Cu and Zn are the most dispersed. This is shown by their high coefficients of variation (v = 104 and 82%, respectively). Due to the very low and therefore partly inaccurate analysis values of all components, a lower limit value (min. = cut off), which could be mined, was used (**Table 1**, column 3). Thus, the number of analysis was reduced (**Table 1**, column 2), but the mean values of 2.23% Cu, 1.08% Pb, 2.60% Zn, 42.91% Fe_3O_4 and 33.10% S are more realistic. On the other hand, extremely high values according to [26] were checked for outliers and switched off (mean ± 4 standard deviations), which did not belong to the population. For the evaluation of the data the methods of the frequency distribution, correlation analysis and the location-dependent variables (variograms) were applied. These are the analytical values of the 6 representative samples from 4 different core drillings for the geochemical trace element studies. The determination of the main and trace elements in ore samples was carried out by X-ray fluorescence analysis on powder tablets at the TU Berlin, as the orodispersible tablets were not suitable because of high S contents. The measurable results of the samples analyzed on 39 elements are shown in **Table 2** (see Geochemistry), whereby the contents of the elements Cs, Hg, Th, Tl and U were below the detection limit. Experience has shown that the relative error of these analytical methods, depending on the element, is between ±3% (Cr, Ni) and 10% (Na, Mg).

4. Results and Discussion

4.1. Geochemistry

Mineralogical investigation methods are not sufficient to separate Cu ores of different origin from each other with sufficient accuracy. For this reason, geochemical investigation methods are used in addition.

The chemical composition of the ores is of particular importance for the valuation of a deposit. It can give important clues to its genesis, facilitate the processing of the ores and gain valuable elements. An overview of the chemistry of the ores of Siirt Madenköy, compared to the similar deposit Ergani-Maden, is given in **Table 2**.

The geochemical analyses of copper ore samples from the Siirt Madenköy deposit show a moderate degree of mineralization, averaging 1.33% Cu (**Table 1**). The contents of all main elements vary very much. The high levels of FeO (31.83%) and SO_3 (27.62%) indicate high magnetite and pyrite concentrations. Na does not appear in any of the investigated ore samples in clearly detectable concentrations, while K has been detected in only 2 samples. Also Ca and Mg are very impoverished. This may be related to the basic character of the rocks and

Table 2. Composition of Cu ore from Siirt Madenköy and its relation to Ergani-Maden [27].

Drilling Sample no.	M-19 208	210	M-36 209	290	M-56 204	M-65 209	Arithm. averages	
							Siirt Madenköy	Ergani-Maden, n = 22
Oxides, wt%								
SiO_2	31.18	13.30	4.85	6.06	16.30	10.69	13.73	21.80
Al_2O_3	2.61	9.47	0.47	0.38	8.84	0.53	3.72	6.98
FeO[1]	25.99	30.96	34.01	32.61	37.05	30.36	31.83	23.13
MgO	0.13	8.92	0.03	1.94	11.19	2.79	4.17	12.83
CaO	0.04	0.78	0.05	0.07	1.08	2.57	0.77	0.73
Na_2O	bdl[2]	bdl	bdl	bdl	bdl	bdl		
K_2O	0.46	bdl	0.02	bdl	0.01	bdl	0.08	0.05
TiO_2	0.07	0.81	0.05	0.01	0.56	0.02	0.25	0.10
P_2O_5	0.03	0.05	0.04	0.03	0.12	0.02	0.05	0.03
SO_3	30.64	9.79	43.85	39.96	4.20	37.30	27.62	9.87
BaO	0.02	0.003	11.78	0.03	0.08	0.09	2.00	0.005
$Sum_{(Oxydes)}$	**91.17**	**74.08**	**95.17**	**81.09**	**79.43**	**84.37**	**84.21**	**75.98**
Cu	1.88	0.13	1.81	2.43	1.58	0.13	1.33	2.01
Pb	0.002	0.001	0.71	0.06	0.003	0.001	0.12	0.002
Zn	0.003	0.007	4.56	0.003	0.003	0.13	0.79	0.02
Minor el., ppm								
Ag	3	bdl	28	bdl	bdl	bdl	15	
As	215	bdl	1575	554	bdl	bdl	781	10
Bi	28	26	53	49	72	32	43	
Br	1	2	bdl	bdl	2	4	2	
Cd	bdl	bdl	110	bdl	bdl	4	57	
Cl	33	bdl	6	bdl	bdl	bdl	20	101
Co	344	307	612	406	201	140	335	283
Cr	33	69	43	46	42	25	43	615
Ga	bdl	16	bdl	bdl	12	bdl	14	7
Mn	2	998	bdl	32	1,061	662	551	690
Mo	59	88	92	83	20	111	75	14
Ni	16	27	14	bdl	30	bdl	21	264
Rb	9	4	14	6	6	3	7	5
Sb	4	bdl	148	6	bdl	bdl	53	
Se	29	22	49	53	38	27	36	

Continued

Sn	2	bdl	72	bdl	6	bdl	27	
Sr	3	16	634	bdl	17	14	13	10
V	17	119	bdl	9	141	8	59	86
W	1	11	bdl	bdl	8	4	6	
Zr	8	97	20	3	96	5	38	7
Element ratios								
FeO/TiO	328	38	680	3260	66	1520	982	231
Pb/Zn	0.67	0.14	0.16	2	0.10	0.01	0.51	0.10
Cu/Ni	1175	48	1292	bdl	527	bdl	760	76
Co/Ni	22	11	44	bdl	7	bdl	21	1.1

[1]Total ironoxide as FeO; [2]bdl: Below dedection limit.

the hydrothermal alteration. The concentrations of valuable materials, such as those of Ag, Pb and Zn are very low, which is also to be expected due to the rarity of galena and sphalerite. In general, Siirt Madenköy's Cu ores are poor in trace elements. Significantly high enrichments in relation to their Clarke values show Bi (217 times), Co (13 times), Cu (241 times), Mo (50 times), and Se (363 times), with As (0.16%) and Ba (10, 25%) sometimes reach high concentrations (Table 2). The high fluctuations of the components are due to the different types of ore.

Numerous minor and trace elements can be replaced by the predominant minerals such as pyrite, chalcopyrite, magnetic gravel, galena, sphalerite and magnetite. The determination of the actual concentrations of the investigated trace elements in the individual mineral phases requires single-mineral analyses, which will be the subject of further research.

There is no significant relationship between SiO_2 contents and the contents of the main components or trace elements analysed (Table 2). The concentration of the plurality of elements is opposite to that of the SiO_2. This means the displacement of the silicates by sulfide or oxides. In contrast, MgO, TiO_2, Ni, and V show a marked dependence on Al_2O_3, which is related to the diadochiene relationships between these elements in pyroxenes and mica. Despite the distribution of chalcopyrite and pyrite, FeO has no clear relation to Cu and SO_3, which can be explained by different modal conditions of magnetite, pyrite and chalcopyrite. However, Cu and SO_3 levels are parallel to each other and to those of Co and Se. This means that Cu, Co, and Se are chalkophilically bound and that Se has largely replaced S. In addition, contents of Ba, Pb and Sr are significantly related due to the similar ionic radii (0.137, 0.124 and 0.112 nm) and diadochiene relationships and indicate their hydrothermal origin.

Also, the ratios of certain oxides or elements provide important information. For example, the FeO/TiO_2 ratio of about 127 for basic rocks is high, possibly related to hydrothermal alteration, that is, Ti removal. The ratio of Cu to Ni (633) is extremely high compared to that of the magmatic sulfide deposits of basic rocks (about 10) [28]. In contrast, that of Cu/S (0.12) is lower, suggesting pyritic power.

The comparison of the average analytical values of the Siirt Madenköy copper ore samples with those of the Ergani-Maden deposit shows a certain similarity of both deposits (**Table 2**). For example, the concentrations of Cu, FeO and SO_3 are very high. The deposit Siirt Madenköy is compared to Ergani-Maden Cu poorer (see also [8]). The higher FeO and SO_3 contents in Siirt Madenköy indicate rich magnetite or pyrite mineralization, leading to low levels of SiO_2, Al_2O_3 and MgO. The ores of Siirt Madenköy, on the other hand, contain numerous trace elements such as As, Ba, Bi, Mo, Pb, Se and Zn in higher concentrations than Ergani-Maden (compare [29]).

Massive sulfide deposits can be classified with special features in mind [30]. These are, for example, metal contents, age and country rock type. Also, the method of the Cu ratio (CR = 100Cu/(Cu + Zn)) and the Zn ratio (ZR = 100 Zn/(Zn + Pb)) is an important definition factor for distinguishing types of deposits such as Cu and Zn types [31]. Since it starts from metal contents, it is often used. At the Siirt Madenköy deposit, this factor indicates an average of 79 Cu and 81 Zn ratios for a Cu type Siirt Madenköy deposit (Cu ratios = CR > 60), as shown by [32]. These values are indicative of Cyprus type massive sulfide deposits and indicate saturation of the ore resolutions at Cu and Zn. For Siirt Madenköy this means, for example, the Zn saturation of the pyrites and the chlorides by the hydrothermal alteration. This is the case for the low-Pb massive sulfide deposits of the Cyprus type [31].

The distributions of the mean values of Cu, Pb, Zn and Fe of the forty-nine core drillings are shown in the concentration triangles of **Figure 4(a)** and **Figure 4(b)**. It can be seen that Cu is most concentrated relative to Pb and Zn (**Figure 4(a)**), while the Pb/Zn ratios remain approximately the same. As a result, the Siirt Madenköy deposit, as defined by [33], is assigned to the Cu type of bulk sulfide deposits, which is consistent with the result of the Cu ratio [32]. This is associated with the ophiolitic country rocks of the Cyprus type massive sulfide deposits [34], as indicated by [17] and suggesting very low levels of TiO_2 and P_2O_5 as an indication of mid-ocean ridges. Hereby, a Co/Ni ratio of 0.29 to 1.97 is emphasized for massive sulfide deposits with serpentinitic country rocks and for those with basaltic values of 1.09 to 8 [35]. This ratio is between 6.7 and 44 in Siirt Madenköy in the analysed ore samples, which is much higher.

Figure 4(b) shows the ratio of oxidic (e.g. magnetite) and sulfidic ores (e.g. pyrite and chalcopyrite), so that the average contents of Cu, Fe_3O_4, and pyrite in the wells are very different. This reflects the distribution of rich local ore concentrations and poor ore or impregnation ores. This also illustrates the supremacy of the S over Cu and Fe_3O_4 (ignoring the non-magnetic Fe), where S has low scattering, which means extensive or relatively regular occurrence of the sulfidic ores (not shown, see **Figures 7(b)** and [32]). Terrain observations, mineralogical composition of the ores and the microscopic findings, such as those of **Figure 3**, also support these views.

The **Figure 5** shows the position of the deposit Siirt Madenköy in the Cu-10Pb-Zn triangle according to [36]. In it are shown for comparison recent mineralization from the different oceanic environments. It can be seen that the massive sulfide deposit Siirt Madenköy is characterized by average Cu/10Pb and Cu/Zn ratios. The location of the representative point (SM) shows the area of the Cu class of massive sulfide deposits [30]. This can be achieved, for example, with the mineralization of the Galapagos Spreading Center (GAL), the Middle Oceanic Ridge (MOR), the Ergani-Maden (EM) and Küre (Mağaradoruk, KM) massive

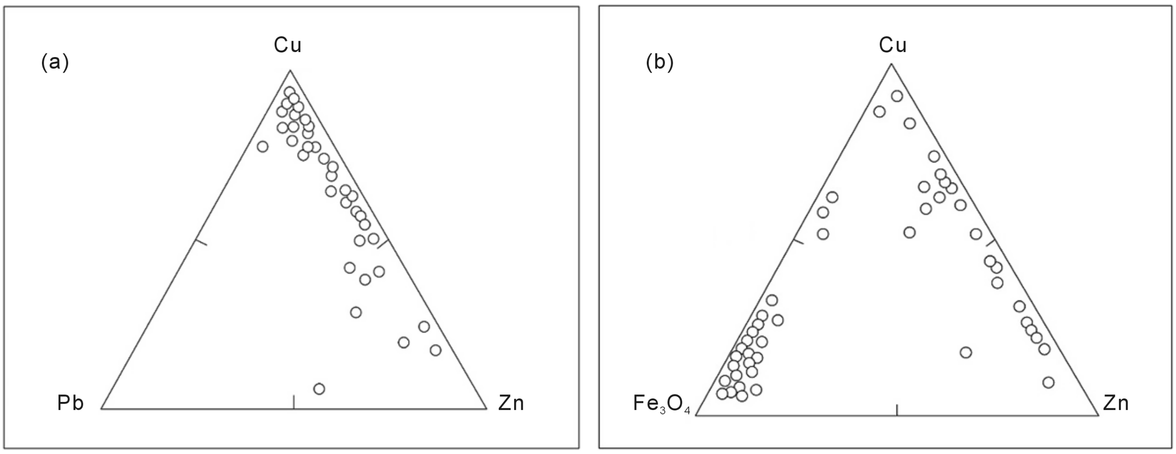

Figure 4. Distributions of the average of relevant elements in drillings in the Pb-Cu-Zn triangle (a), and in the Fe_3O_4-Cu-Zn triangle (b).

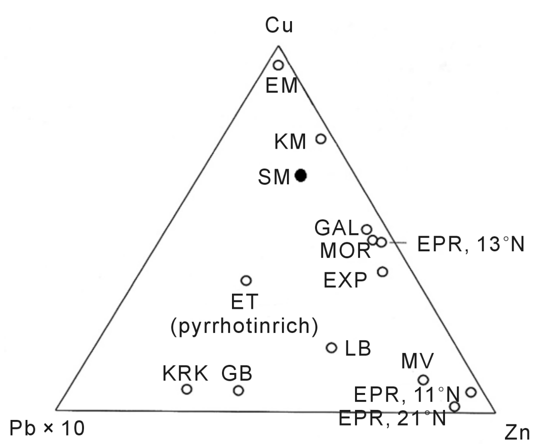

Figure 5. Comparison of mean Cu, Pb and Zn contents of the holes in the Cu-10Pb-Zn-triangle with massive sulfide deposits of different oceanic environments [36] and [37]. Abbreviations: SM = Siirt Madenköy, EM = Ergani-Maden, EPR = East Pacific Rise, ET = Escanaba Trough, EXP = Explorer Ridge, GAL = Galapagos Spreading Center, GB = Guayamas Basin, KM = Küre Mağaradoruk, KRK = Kuroko ore deposits (back-arc basin), LB = Lau Basin, MOR = Middle Oceanic Ridge, MV = Juan de Fuca Ridge (Middle Valley).

sulfide deposit, but with relatively higher Pb-Zn. Maintain, compare, and differ significantly from the Kuroko deposits (back-arc basin). As a result, the Siirt Madenköy deposit is considered to be one of the slow-spreading ridges massive sulfide deposits [37]. This is also supported by the elemental contents of Table 2 (see [28]).

4.2. Statistical and Geostatistical Researches

4.2.1. Frequency Distribution

From Table 1 it can be seen that the data are characterized in part with pronounced scattering. This is particularly noticeable for Cu and Zn contents, which are due to irregular mineralization, for example due to different ore grades requiring denser sampling.

The frequency distributions of individual components, with the exception of S and Fe_3O_4, are normally distributed, as their mathematically determined parameters show in Table 1. Their distribution images are left asymmetric or show positive slopes (mean > median > mod) and bulges (excess > 3).

As an example, the frequency distribution of the mean Cu, Zn and S contents of the holes are shown on the Figure 2 in Figure 6(a). The positive slopes of the distributions of all 3 illustrated elements, the Cu, Zn and S, by the accumulation of data below the mean (left asymmetric) to express. This points to the poor ore, this means the low Cu, Zn and S contents indicate that the ore impregnations and storied ores are more widespread than the massive ores. Thus, the deposit Siirt Madenköy is to be designated as a type of pain, which also coincides with the field observations (see also [8]).

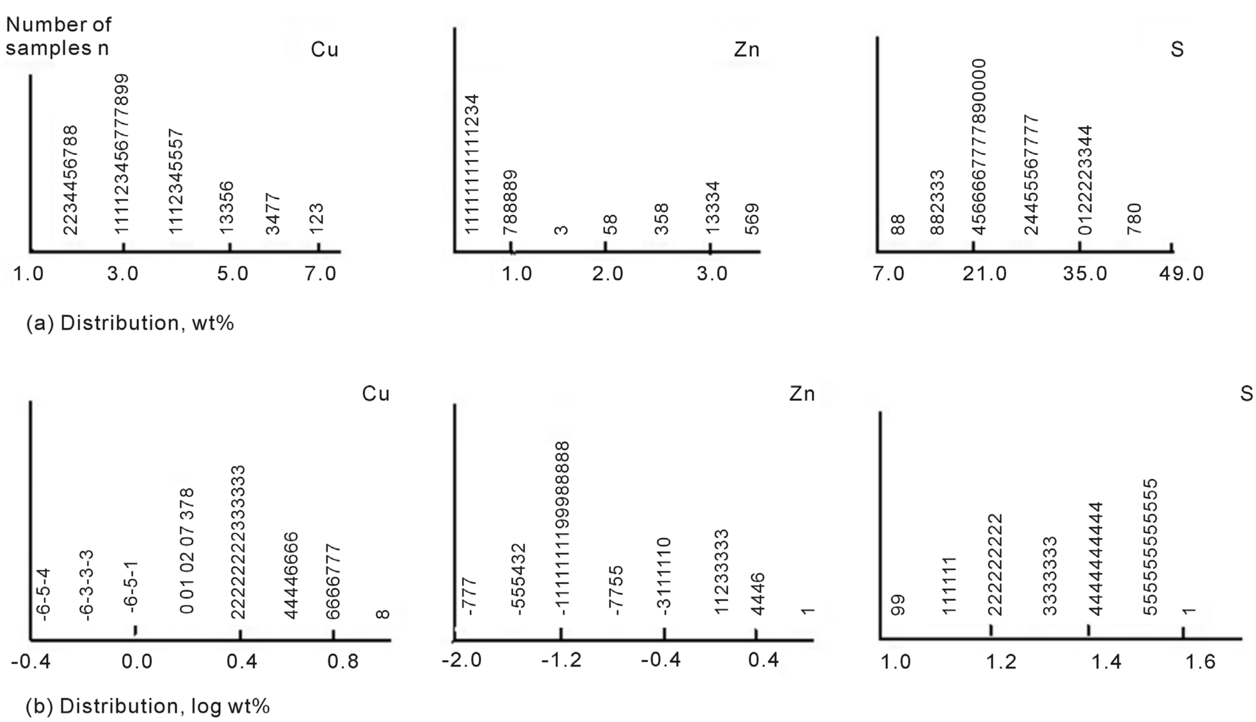

Figure 6. Frequency distribution of the average of Cu, Zn and S contents of the drillings (a), and their log distributions (b).

In contrast, their logarithmic distributions are characterized by the approximately symmetrical accumulation of the analysis values around the mean value of Figure 6(b). This is to be interpreted as a log-normal distribution of the analysis values, whereby the S-distribution tends to negative skewness and thus indicates richness type (pyritic power). The log-normal distribution of the elements in rocks and ores is indicative of magmatic differentiation and bonding of the elements to certain minerals, such as copper gravel [38] [39] [40]. These results also apply in general to element distributions in the individual holes according to depth [32] (see also Figure 7(a) and Figure 7(b) and Figure 10).

Frequency distributions of the Cu, Pb and Zn contents show positive (pointed) curves (Table 1), while those of the S and Fe_3O_4 are slightly negative (flat). The peak distribution is mainly due to a mineral as a consequence of the elemental bonding [41]. This means, for example, that Cu is bound almost exclusively to chalcopyrite, Pb to galena and Zn to sphalerite. In contrast, S is distributed on chalcopyrite and pyrite, Fe on chalcopyrite, pyrite and magnetite. Their shallow distributions reflect mineral phases or ore composition and confirm site observations and microscopic findings.

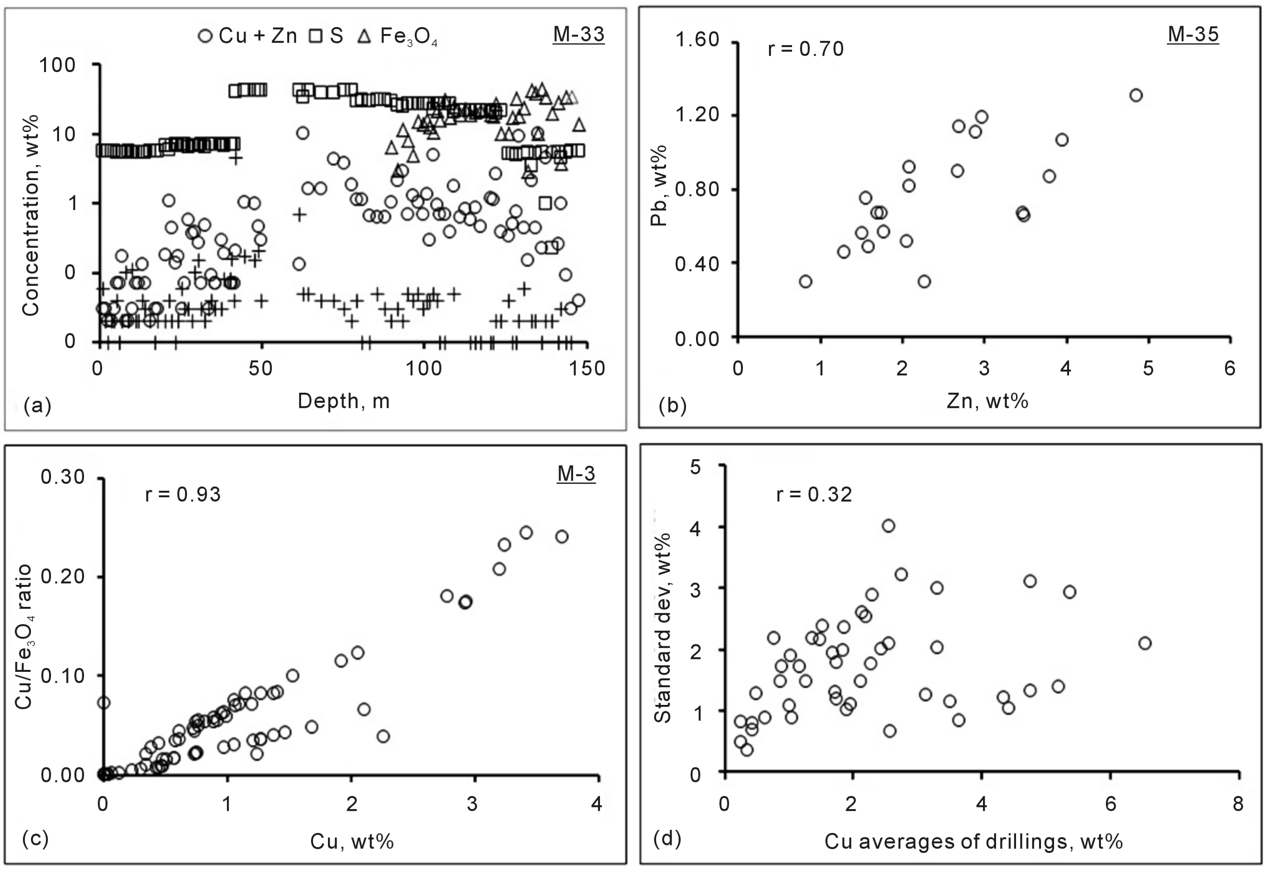

Figure 7. Variation between depth and Cu, Zn, S and Fe_2O_3 in drilling M-33 (n = 98). (a) Correlation between relevant elements Zn and Pb in drilling M-35 (n = 21); (b) Correlation between Cu content and Cu/Fe_3O_4 ratio in drilling M-3 (n = 73); and (c) Proportionality effect of Cu content in drillings (n = 49); (d) Significant correlation coefficients for 99 % confidence for $F > 19$: $|r| > 0.55$.

4.2.2. Correlation Analysis

In Siirt Madenköy, there are no significant interelement correlations (Table 3). This means that there was no saturation of the elements in the deposit. From Table 3 it can be seen that the chalcophilic elements Cu-Zn, Cu-S and Zn-Pb correlate significantly positively with each other, while Fe_3O_4 correlates negatively with S. It can be deduced that as a result of hydrothermal formation processes, e.g. occur due to the secondary depth difference, sulfidic and oxidic ores in opposite directions. While sulphidic ores, such as pyrite, concentrate in the upper regions of the deposit, oxidic ores, e.g. As magnetite, in lower layers of the mineralization (Figure 7(a)). Accordingly, the high Cu and S contents counteract the depth, which causes pyrite concentration. However, this relationship of the analysed elements to the deposit depth is highly variable. Here, different depth horizons occur, where depending on the depth sulfide (top) or oxidic ores (below) are bound, which are found in the field as ore lenses. However, the Cu dependence on the drilling depth is not significant. It decreases where Fe occurs (Figure 7(a)).

Also noteworthy is the horizontal distribution of the average ore grades. They decrease from the northwest of the ore body to the southeast, so that, for example, the average Cu content of about 5% (hole M-80) to less than 1% (hole M-56) goes back (Figure 2).

The best positive correlation among the analysed element pairs in the holes is a correlation coefficient of r = 0.70 between Zn and Pb contents of the M-35 well (Figure 7(b)), which is to be considered as a consequence of hydrothermal processes. However, this relationship is variable in the deposit. The regularities between element pairs may have been disturbed by hydrothermal alteration [21], which has led, for example, to the dilution or displacement of elements in ore and rock. In contrast, the course of the Cu/Fe_3O_4 ratios and Cu contents is linearly positive (Figure 7(c)). This is because Cu has more concentrated in the deposit relative to Fe_3O_4, and high Cu contents correspond to relatively low Fe_3O_4 contents.

For the ore grade in a deposit and application of geostatistical methods, the proportionality effect is an important factor [42] [43]. In Siirt Madenköy, a significant (r = 0.32) proportionality effect occurs (Figure 7(d)). It can be concluded that the coefficient of variation (Table 1) is constant (see also [43]). This means that it will not be easy to obtain a constant average ore grade during

Table 3. Correlation coefficients of the investigated element pairs in ore (n = 2203). Significant correlation coefficients at the 99% confidence for $F > 300$: $|r| > 0.15$.

Cu				
0.11	**Pb**			
0.38	0.36	**Zn**		
0.19	−0.06	0.16	**S**	
0.02	−0.04	−0.04	−0.49	**Fe_3O_4**

mining. This requires the application of the comprehensive and expensive universal rigging in the reserve calculation.

4.2.3. Structure Analysis (Variograms)

A structural analysis in the Siirt Madenköy deposit can be carried out on the basis of the absolute variograms, since the ore zones are approximately homogeneous and the proportionality effect is not pronounced. This means that the variograms of the rich zones and the zones of the smelling will be similar. The log-normal variogram type can lead to high erratic errors related to the log-normal distribution of Cu contents.

For the analyses, the vertical variograms of the Cu in the selected drillings (Figure 8(a) and Figure 8(b)) and horizontal variograms in the northeast-southwest and northwest-southeast directions were calculated (Figure 8(c) and Figure 8(d)). The calculated variograms are assigned to the spherical variogram model. The general formula for this is

$$\gamma(h) = c_0 + c_1\left(1.5\text{h/a} - 0.5\text{h}^3/\text{a}^3\right) \tag{1}$$

Herein mean

c_0: nugget effect (estimation error, %),

c_1: variance of the analysis values (% 2),

h: increment in m and,

a: threshold (optimal sample or well spacing) in m.

The variograms examined in the Siirt Madenköy deposit show an optimal sample spacing of approximately 5 m for all elements (Figure 8(a) and Figure 8(b)). This means that the samples are no longer dependent on each other from this distance. The nugget effect c_0 varies according to the element and the drilling due to the irregular ore distribution. In general, they are below 2%^{2} for all investigated elements and are considered normal for a copper deposit, whereas for Cu variograms, as in Figure 8(a), higher values are also found (see also [32]). The sill c_1, as the statistical variance of the sample values, is variable. This is due to the sometimes strongly varying ore contents of massive, storied and impregnated mineralization.

The calculated variograms also give indications of ore-host rock conditions, such for example change storage (hole effect). Some variograms indicate a pronounced alternating storage of the poor or rich ore zones, *i.e.* ore lenses, with the bedrock down to the depth, as reflected in the wavelike structure of the variograms (Figure 8(a)).

However, some drillings show an increase in depth variogram values (Figure 8(b)). This applies to all investigated elements in individual holes, as shown in [32]. The increase in variogram values in one direction, as here for example, with depth, *i.e.* "the trend", means the increase of ore grades in the given direction [42]. This also confirms the correlation of the ore grades with the drilling depth (see Figure 7(b)). This means that the mean contents depend on the step size h [43]. For geostatistical investigations, this means that, in theory, no simple

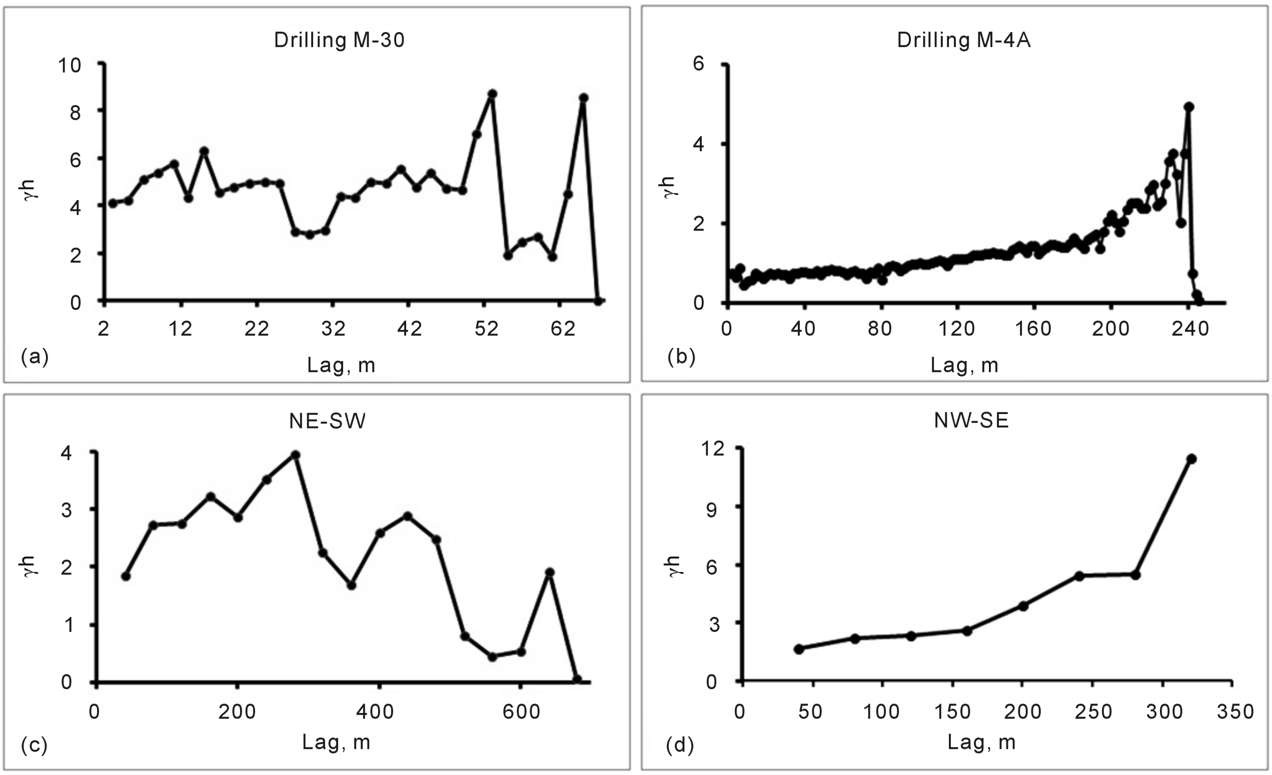

Figure 8. Vertical variograms in drillings and horizontal variograms in diverse directions (see Figure 2).

kriging is to be used for reserve calculation in the deposit. Instead, more sophisticated methods, such as universal kriging, must be used [44]. An alternative would be the decomposition of the orebody into parts of approximately homogeneous ore grades with sufficient numbers of samples.

Variograms also give indications of the structure of the entire deposits. In the Siirt Madenköy deposit, variograms in northeast-southwest and northwest-southeast directions were calculated from the mean grades of the Cu, Zn, and S to determine structural properties of the orebody, such as trend and zonality [32]. The determined variograms show a clear alternation of the ores in a northeast-southwest direction for Cu distribution (**Figure 8(c)**). In contrast, there is a slight trend from northwest to southeast (**Figure 8(d)**). Their nugget effects come close to the variograms in the selected wells with values of approximately 1.5%^{2} (see **Figure 8(a)**, **Figure 8(b)**). However, they have lower thresholds. This means that the mineralization is more horizontal regularly than in depth. The threshold, e.g. the optimum drilling distance is variable and is estimated at about 150 m. This is approximately the same for the two computed directions, while their thresholds differ significantly (**Figure 8(c)** and **Figure 8(d)**). This can be explained by a pronounced zonal anisotropy, which is due to the interlacing of different types of ore [42] [44].

5. Reserve Calculation

The Siirt Madenköy massive sulfide deposit is an important source of raw material for Turkish mining. It is one of Turkey's major copper deposits, which is currently under mining in Kastamonu and Çayeli near Rize. Similar Cu deposits Ergani-Maden/Elazığ and Murgul/Artvin, are already mined.

The Siirt Madenköy deposit has been extensively investigated by MTA. In the 70s of the last century, a total of 61 deep holes were drilled down to 450 m (M-29) depth and created numerous trenches. The holes are arranged according to a drilling grid and perpendicular down. The drilling distances are on average 50 m. The core drilling output is 65% on average. The reason for this low core output is the widespread alteration and the archbreccia. In total, over 2000 core samples have been withdrawn, of which

2038 on Cu,

330 on Zn,

337 on Pb,

905 on S, and

1178 on Fe_2O_3.

analysed and continuously tested for their density and humidity. The average dry density of the ores is 3.5 t/m^3, which was also used in the reserve calculation. For a thorough investigation of the deposit these basics are sufficient. In addition there are the numerous slot samples from tunnels and graves.

For reserve calculation, the method of vertical parallel cuts was selected (Figure 9). The profile method is suitable for the lenticular orebody and the MTA drill grid. In addition, the storage device can be represented geometrically well by this method. As an example, Figure 10 shows the location and distribution of the mineralization in the vertical direction.

The total reserves Q has been constructed on the basis of the MTA drill program (see Figure 9) carried out by the MTA until 1984 at the University of Firat according to the general formula,

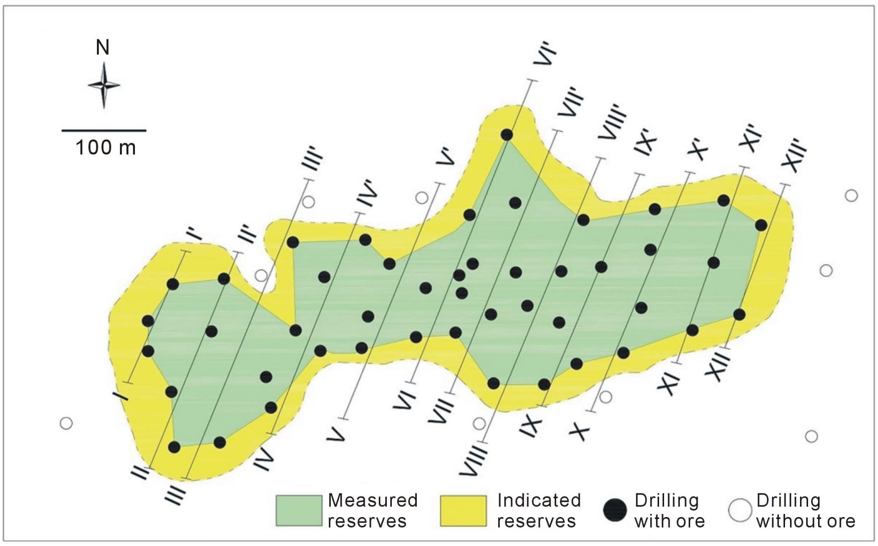

Figure 9. Position of parallel profiles for reserve calculation and classification (see Figure 2).

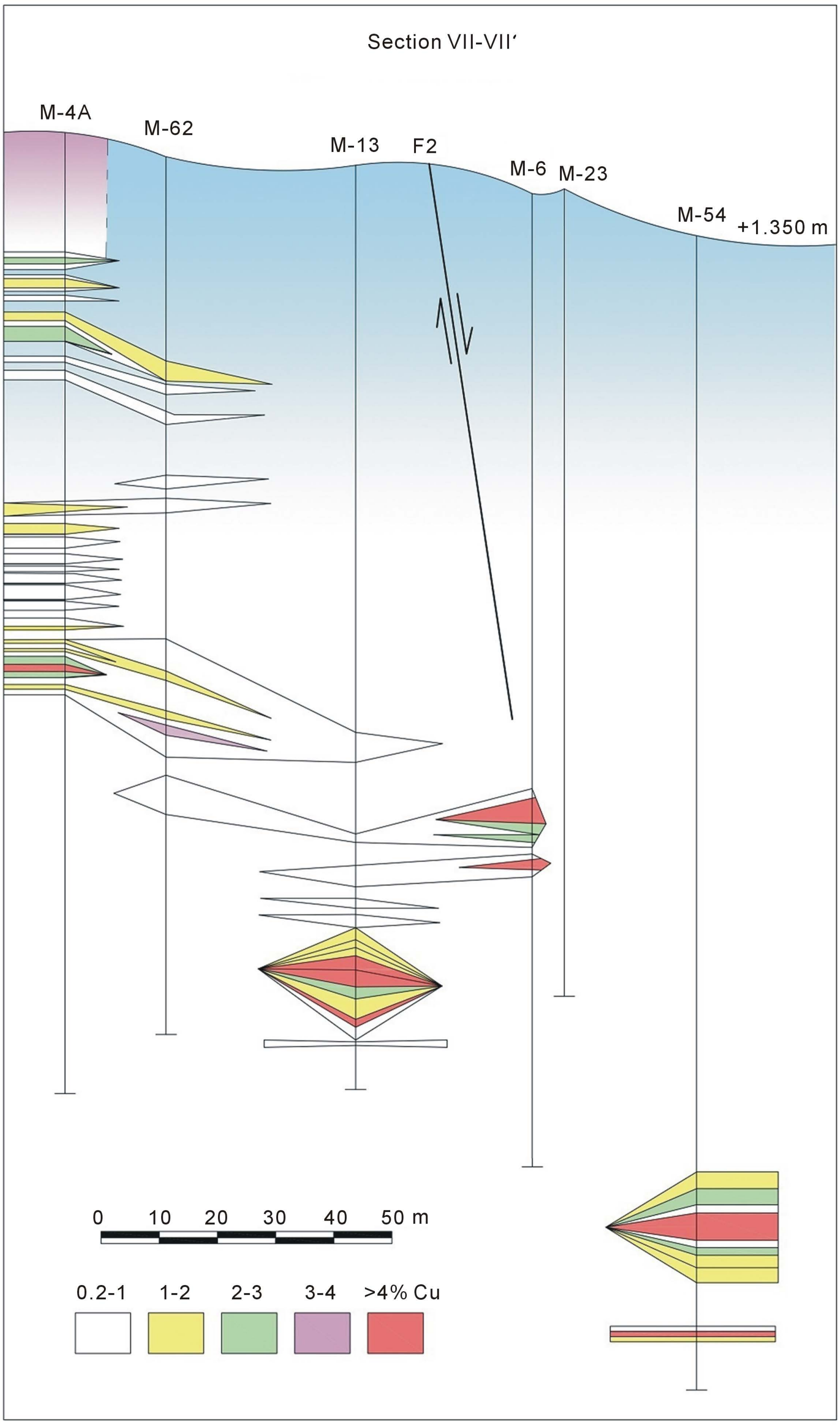

Figure 10. Vertical profile VII-VII' for reserve calculation (see **Figure 2** und **Figure 9**).

$$Q_{\text{total}} = L \cdot \frac{\sum_{i=1}^{n} F_i}{n-1} \cdot \rho[\text{t}] \tag{2}$$

determined [32]. In that mean,

L: length of the worship [m],

F_i: average mineralized area of two profiles [m^2],

n: number of vertical cuts, and

ρ: density of ore [3.5 t/m^3].

Here, the marginal quantities of reserves by cone formula,

$$q = 1/3.F.h.\rho[t] \tag{3}$$

where F is the base area [m^2], h is the height of the cone [m] and ρ is the density of the ore [t/m^3].

The calculations showed a reserve of 14.2 million tonnes (safe and likely). The recyclable material results in 288,000 t Cu (2.01%), 78,000 t Zn (0.54%) and 27,000 t Pb (0.20%). These supplies are divided into approximately 13 million tonnes through mining operations, and exploration wells are exploring safe reserves estimated at approximately 1.3 million tonnes by geological assumptions (see **Figure 9**). These reserves, calculated by the profile method, were checked for correctness by the triangular prism method (14.8 Mt) [32]. These stocks and metal grades are also in good agreement with those of the 15 million tonnes reported by MTA [8].

It should be added that the Siirt Madenköy deposit was further intensively explored after its commissioning in 2005. The number of deep wells has been increased to 74 [45]. The ore body was examined 241 times in total by control drilling, 2 new galleries were set up and numerous investigations were carried out [46] [47] [48]. This increased total reserves to 39.8 Mt, with a mean Cu content of 2.40%. Of these, 31.1 Mt are considered to be safe, 6.4 Mt as probable and 2.2 Mt as possible supplies. The results of this exploration work could not be included in this study, as they were solely inventory investigations, constantly changing, and this study had already been completed.

The wavy plate-shaped ore body is located according to previous geoscientific investigations at an altitude between 1160 and 1332 m and falls with about 50˚ to the north [8] [32] [48]. The ore is mined in a process combination in opencast mining and civil engineering (partial-load fracture) with a capacity of 1.5 Mt/a [45] [47]. The overburden/ore ratio is approximately 77/1 [48] in open pit mining. In spite of its fine adhesion (<53 μm) saleable Cu and S concentrates are extracted economically from the extracted ore [49]. In 2012, approximately 46,800 t of Cu concentrate were produced with a Cu content of 20% - 22% (<2.7% Zn). In the same year, the annual production of the pyrite concentrate was 89,000 t with an S content of 44% [1] [49]. At the time, about 500 people worked in the mine [45]. In 2016, the mine suffered major damage from landslides.

6. Conclusions

The synthesis of Siirt Madenköy's genetic processes, their geological interpretation, present results and comparisons with similar deposits indicate that Siirt Madenköy is a syngenetic, volcanogenic-exhalative massive sulfide deposit. It belongs to the "deposit type Cyprus". The main indications are the chloritization and sericitization, which are limited to the recumbent, and the absence of clastic sediments, which bear their unmistakable resemblance to those of the deposit type Cyprus. The undercutting of the ground ore impregnating ores and the collomorphic mineralization accompanied by framboidal pyrite formation, which reflects colloidal precipitation, may be added as further features of this type of deposit. Furthermore, the occurrence of Fe-rich sulfides such as pyrite and magnetic gravel, the high levels of trace elements Cr, Ni and Co and low to Zn and Pb are emphasized. The formation of valeriite in the chalcopyrite corresponds to approx. 200 m sea depth and a temperature of approx. 350˚C.

It is characteristic for the low-Pb type massive sulfide deposits of the Cyprus type that Cu is very enriched in relation to Pb and Zn at almost constant Pb/Zn ratios. This is the case in Siirt Madenköy and means the Zn saturation of the pyrites and chlorides by the hydrothermal alteration. This is also consistent with the high result of the Cu ratio. Accordingly, the Siirt Madenköy deposit is classified as a Cu class of massive sulfide deposits. This is related to the ophiolitic country rocks of the Cyprus-type massive sulfide deposits, where the very low levels of TiO_2 and P_2O_5 indicate the mid-ocean ridge formation environment.

In light of these findings, Siirt Madenköy's massive sulfide deposit is comparable to recent massive sulfide mineralization from the oceanic environment. Due to the very high Cu/Pb and Cu/Zn ratios, it can be characterized as an analogous deposit of the mid oceanic ridge, this means back-arc-basin. It differs from the deposits of the Kuroko and Besshi type due to their high Cu/Pb and low Zn/Pb ratios. The analytical values of the ores of Siirt Madenköy partly correlate well with those of the ores from the "spreading-ridge-area", being comparable to ores of Galapagos Ridge. These implications and the association of ophiolites, tholeiite basaltic volcanics, and pillow lava with mineralization make the Siirt Madenköy deposit one of the slow spreading ridge deposits.

The above geochemical results of the present study corroborate the thesis on the "volcanogenic-exhalative" genesis of the Siirt Madenköy deposit. Similar deposits are Küre and Ergani maggots in Turkey, Ermioni in Greece and Outukumpu in Finland.

Due to its economic importance and recent history, the Siirt Madenköy deposit is an important research object. The details of deposit geology, patrology and mineralogy of the spilites have not yet been explored. Detailed geochemical, electron microscopic and isotopic geochemical investigations on ore and minerals can provide valuable knowledge. These can be important, for example, for further exploration, clarification of existing questions and making comparisons. Analysis of fluid inclusions and radiometric age determination could help to clarify the educational milieu and to answer open questions such as the age of magmatism, mineralization, and adrenal alteration.

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