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GEOCHEMICAL PROXIMITY INDICATORS OF THE MURGUL VOLCANOGENIC COPPER DEPOSIT, EAST PONTIC METALLOTECT NE TURKEY

Nevzat ÖZGÜR* and Carlos M. PALACIOS**

ABSTRACT . - A study on the behaviour of F, Tİ, Mn, Cu, Au, and REE during hydrolhermal mineralization at the Murgul volcanogenic copper deposit reveals that Ti, Mn, and REE are strongly depleted in altered host rocks whereas F, Cu, and Au show remarkable positive anomalies in the altered mineralized areas. We propose the use of the elements F, Ti, and Mn as proximity indicators for exploration of concealed ore deposits of the same type in the East Pontic metallogenetic province of Turkey.

INTRODUCTION

The Murgul volcanogenic Cu-deposit comprises one of the principal copper ore districts of Turkey (Fig. 1). The open pits are located 7 km SE of the town Murgul. The area belongs to the East Pontic metallogenetic province in which a considerable number of base metal deposits are located (Çağatay and Boyle, 1977, 1980; Akın, 1979; Akıncı, 1980; Dieterle, 1986). This zone, however, has not been investigated intensively to find new ore deposits.

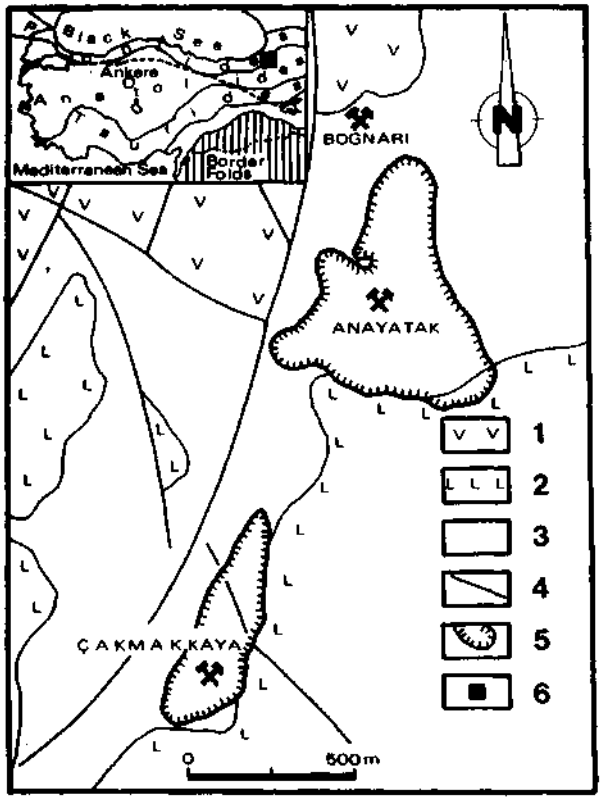

Fig. 1 - Geological sketch map of the Murgul deposit.
1 - Andesitic lava flows of the uppermost Cretaceous; 2- Hanging-wall felsic volcanics; 3- Pyroclastic host rocks; 4- Main faults, generally vertical movements; 5- Limits of the open pits (1983); 6- Investigated area of Murgul.

Detailed results of the geochemical investigations on the chemical solubility and depletion of Ti in the altered rocks under thermodynamic conditions will be reported in a separate paper. The aim of our paper is to discuss the geochemical behaviour of F, Ti, Mn, Cu, Au, and REE at the Murgul deposit during hydrothermal mineralization. We attempt to develop with these data an exploration model which could be applicable for practical use in this area. Previous geological investigations (Özgür, 1985; Dieterle, 1988; Schneider et al. 1988) of the deposits support the interpretations presented in this paper.

GEOLOGICAL SETTING

The East Pontic metallogenetic province represents a volcanic island arc system of Jurassic through Miocene age which hosts a great number of base metal deposits (Akın, 1979; Akıncı, 1980; Dieterle, 1986; Özgür and Schneider, 1988; Schneider et al., 1988). The East Pontides extend over an area of more than 350 km E-W and 60 km N-S and represent the mobile belt between the Pontic and Anatolian plate. The ratio of economically important base metal deposits changes along the general strike of the metallogenetic province from east (Cu >>Pb+Zn) to west (Pb+Zn >>Cu). The East Pontides consist of a 2,000 to 3,000 m thick sequence of volcanic rocks with minor intercalations and lenses of marine sediments (Fig. 2) which have been divided into three stratigraphic cycles (Maucher, 1960; Maucher et al., 1962):

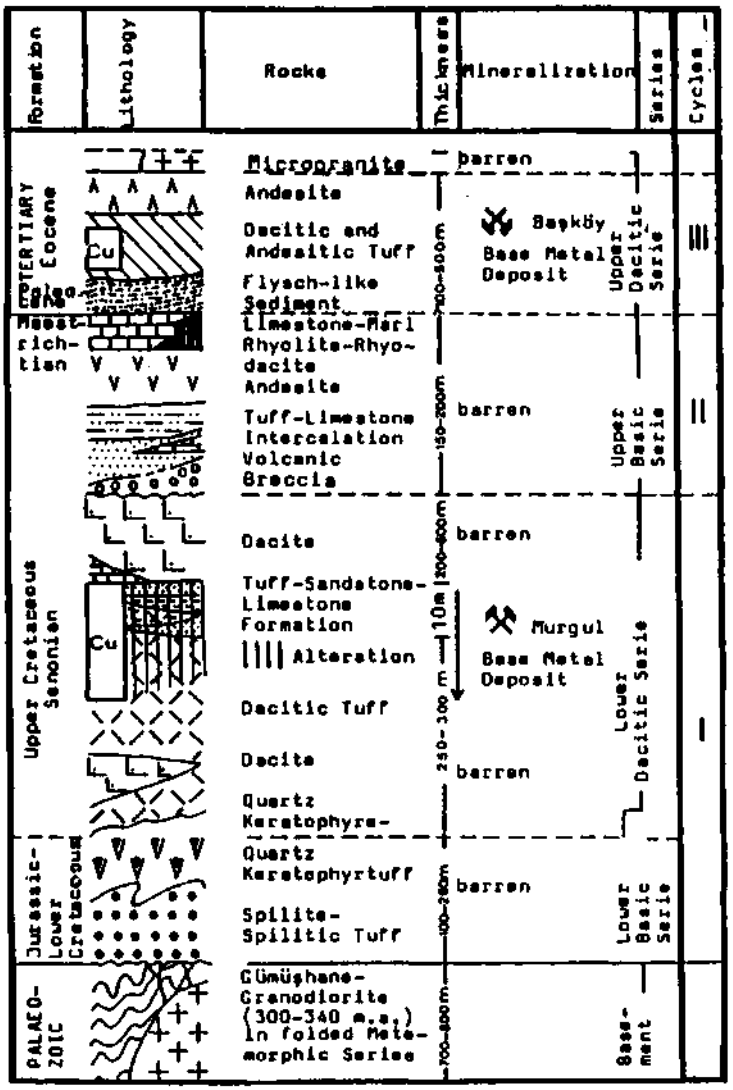

Fig. 2 - Schematic column of the stratigraphic sequence in the Murgul area.

1. The first cycle comprises a volcanic pile deposited between Jurassic and Upper Cretaceous. It is represented by initial basaltic activity (spilites) which changes progressively to felsic lava flows and thick pyroclastics in the middle and upper part.

2. The second cycle starts with volcanic breccias, tuffs and minor intercalations of marine sediments overlain by andesitic and rhyolitic lava flows, followed by limestones of uppermost Cretaceous age (Maastrichtian).

3. The last cycle consists of a basal sequence of marine sediments of Paleocene age which are overlain by andesitic and basaltic lava flows representing Tertiary volcanic activity.

The Murgul deposit is linked to the upper part of the first volcanic cycle and is associated with a 250 m thick felsic pyroclastic sequence. The top of the deposit is marked by a thin layer of marine sediments (Sawa and Sawamura, 1970; Mado, 1972; Buser and Cvetic, 1973) and is characterized by intense erosion and weathering (Özgür, 1985). This sequence is overlain by 200-500 m thick barren felsic volcanites. The age of mineralization in the pyroclastic sequence is pre-Maastrichtian according to paleontological observations (Buser and Cvetic, 1973).

THE MURGUL ORE DEPOSIT

The Murgul deposit consists of at least two primary orebodies (Anayatak and Çakmakkaya; Fig. 1) hosted in the same volcanic member, spanning a horizontal distance of about 500 m. According to former descriptions (e.g. Sawa and Sawamura, 1970; Mado, 1972) and our observations and interpretations of drilling profiles, the mineralization of both orebodies shows exactly the same feature. A third minor orebody, Bognari, came into production recently (Fig. 1) which has been interpreted by Mado (1972) as an erosional product of the upper part of the Anayatak orebody. The sulfide mineralization of both orebodies contains predominantly pyrite and lesser chalcopyrite. Minor quantities of galena, sphalerite, and fahlore occur locally only. Additionally, minor occurrence of aikinite, hessite, tetradymite, clausthalite, and free gold have also been determined by electron microprobe analysis (Willgallis et al., 1989).

The copper deposit consists of (1) widespread disseminated ore with varying Cu contents ranging from 0.2 to 0.7 percent, (2) stockwork ore with average Cu contents between 1.0 and 2.5 percent, and (3) small ore lodes with Cu contents from 5.0 to 10.0 percent (Schneider et al., 1988). The recoverable ore reserves are estimated at 40 million metric tonnes with an average content of 1.25 percent Cu, 0.1 percent Zn, 25 ppm Ag, and 0.2 ppm Au.

The ore mineralization may be divided into an early stage associated with a phyllic zone surrounded by a peripheral argillic zone, and a late stage related to a central pervasive silicification (Fig. 3). According to Schneider et al. (1988), the first stage of alteration led to destruction of the primary paragenesis of the pyroclastics and replacement of the host rock by quartz and pale greasy sericite. This stage reveals poor mineralization of disseminated pyrite and chalcopyrite (type one). The late stage of hydrothermal activity in this area of the deposit is represented by silicic alteration that appears as quartz replacement of the volcanic host rock, as cryptocrystalline varieties of jasper, and later on, as open-space fillings (quartz- ore veins). The sulfide mineralization of this stage represents the principal commercial ore (types two and three). The surrounding country rocks show pervasive argillization which characterized by an alteration assemblage containing quartz, montmorillonite, illite, dickite, and pyrite only.

SAMPLING AND ANALYTICAL METHODS

Various rock samples have been obtained from altered and mineralized zones; 53 samples from the surface (Tab. 1 and Fig. 4) and 87 from deep drilling holes (Tab. 2). For comparison, the less altered background rocks of the pyroclastic flows (18 samples) have been analyzed too (Tab. 1), which were taken between 500 and 700 m outside of the mineralized and altered area. The background pyroclastics include host member in which the alteration is on a regional scale generally weak.

Rare earth elements (La, Ce, Sm, Eu, Tb, Yb, and Lu) and gold were determined by instrumental neutron activation at the Hahn-Meitner Institut fur Kernforschung, Berlin, with a routine precision better than ± 9 % for most elements (Dulski and Moller, 1975) using GSP-1 of the U.S. Geological Survey as the reference standard.

Ti, Mn, and Cu were determined by atomic absorption spectrometry, and F by ion-sensitive electrode at the Institut fur Geologie, Geophysik und Geoinformatik, Freie Universitat Berlin, with a precision better than ± 5 %. For all analyses, BCR-1 and GSP-1 rock standards have used.

Element / Sample	F (ppm)	Ti (ppm)	Mn (ppm)	Cu (ppm)	Au (ppb)	ΣREE (ppm)	Element / Sample	F (ppm)	Ti (ppm)	Mn (ppm)	Cu (ppm)	Au (ppb)	ΣREE (ppm)
1	740	850	50	30	n.d.	n.d.	37	410	1250	150	10	3	33.8
2	655	900	100	90	n.d.	n.d.	38	430	1500	205	10	4	66.8
3	545	3650	550	45	n.d.	n.d.	39	425	500	40	4500	n.d.	n.d.
4	555	550	50	2600	n.d.	n.d.	40	575	800	50	1650	n.d.	n.d.
5	860	700	100	75	n.d.	n.d.	41	1100	1100	50	185	n.d.	n.d.
6	1035	650	50	55	n.d.	n.d.	42	965	650	50	60	n.d.	n.d.
7	490	1300	100	90	n.d.	n.d.	43	180	500	50	190	80	15.1
8	265	650	100	310	n.d.	n.d.	44	n.d.	n.d.	n.d.	n.d.	30	37.9
9	490	550	50	300	n.d.	n.d.	45	n.d.	n.d.	n.d.	n.d.	70	35.0
10	665	650	100	305	n.d.	n.d.	46	225	500	50	275	60	19.4
11	55	125	50	160	n.d.	n.d.	47	135	500	100	30	30	16.0
12	625	800	110	320	n.d.	n.d.	48	165	1150	10	5	2	45.6
13	1965	n.d.	50	4950	n.d.	n.d.	49	n.d.	n.d.	n.d.	n.d.	20	7.0
14	1690	200	100	6750	n.d.	n.d.	50	1280	800	950	10	2	37.2
15	85	500	35	3700	n.d.	n.d.	51	745	550	50	115	6	28.7
16	335	300	50	13000	n.d.	n.d.	52	30	500	40	225	80	1.9
17	1650	100	50	80	n.d.	n.d.	53	415	550	50	7250	4	20.0
18	140	150	100	10000	n.d.	n.d.	54	240	3000	965	35	3	37.3
19	460	700	100	70	n.d.	n.d.	55	380	5750	810	15	3	31.2
20	630	1000	120	60	n.d.	n.d.	56	345	3550	1370	40	2	33.7
21	930	300	50	175	n.d.	n.d.	57	285	3100	4800	70	2	45.6
22	165	2300	400	5	n.d.	n.d.	58	215	3750	1000	15	2	38.6
23	415	2600	370	80	n.d.	n.d.	59	345	4250	1700	20	2	40.7
24	1810	400	355	355	n.d.	n.d.	60	230	4250	1130	50	2	43.2
25	1030	500	90	90	n.d.	n.d.	61	300	2400	550	10	3	49.4
26	340	250	300	2300	n.d.	n.d.	62	360	225	35	45	2	21.5
27	315	350	100	465	n.d.	n.d.	63	305	1000	35	370	2	22.4
28	2515	700	60	385	n.d.	n.d.	64	700	2000	600	45	3	44.6
29	1370	1250	75	110	n.d.	n.d.	65	455	3000	545	15	4	58.9
30	1235	1400	210	15	n.d.	n.d.	66	290	1750	40	15	2	26.5
31	435	600	55	380	2	18.4	67	800	n.d.	n.d.	n.d.	n.d.	n.d.
32	1980	500	100	400	n.d.	n.d.	68	595	1000	40	25	2	20.1
33	770	1100	565	6	2	52.8	69	153	n.d.	n.d.	n.d.	n.d.	n.d.
34	440	250	100	210	n.d.	n.d.	70	176	3750	1700	15	2	34.9
35	230	700	50	85	2	16.7	71	265	2500	925	610	2	49.2
36	535	1400	40	120	2	31.9							

* for locations see Figure 3.
n.d. not determined.

Table 2 - Element data of the altered drill holes (A and B) from both ore bodies of Anaystak (samples 70 to 118) and Çakmaktkaya (samples 119 to 158) *

Element Sample	F (ppm)	Ti (ppm)	Mn (ppm)	Cu (ppm)	Au (ppb)	ΣREE (ppm)	Element Sample	F (ppm)	Ti (ppm)	Mn (ppm)	Cu (ppm)	Au (ppb)	ΣREE (ppm)
72	425	375	100	95	n.d.	n.d	116	480	1250	n.d.	11	n.d.	n.d.
73	n.d.	10	n.d.	24400	430	1.5	117	800	2640	300	16	n.d.	n.d.
74	460	460	1550	55	n.d.	n.d.	118	710	2500	n.d.	29	20	33.1
75	395	1230	n.d.	100	n.d.	n.d.	119	140	430	50	45	130	8.0
76	465	550	n.d.	85	n.d.	n.d.	120	75	n.d.	350	305	n.d.	n.d.
77	420	1600	100	1580	130	21.2	121	141	340	50	360	n.d.	n.d.
78	415	660	n.d.	15	n.d.	n.d.	122	50	80	150	430	n.d.	n.d.
79	260	730	300	35	n.d.	n.d.	123	260	100	50	300	n.d.	n.d.
80	605	1340	n.d.	12	n.d.	n.d.	124	50	10	n.d.	22500	n.d.	n.d.
81	235	1300	100	46	8	29.5	125	45	100	n.d.	21500	n.d.	n.d.
82	130	570	n.d.	930	n.d.	n.d.	126	30	10	n.d.	11000	1700	n.d.
83	175	750	50	850	n.d.	n.d.	127	95	120	n.d	23700	n.d.	n.d.
84	340	1560	n.d.	20	n.d.	n.d.	128	45	30	n.d.	3800	n.d.	n.d.
85	450	1000	50	150	n.d.	n.d.	129	40	10	100	660	160	n.d.
86	400	1180	n.d.	44	28	30.3	130	270	400	50	380	n.d.	n.d.
87	540	1620	n.d.	160	n.d.	n.d.	131	20	30	n.d.	8400	n.d.	n.d.
88	320	700	100	40000	n.d.	n.d.	132	225	200	50	22000	n.d.	n.d.
89	675	1150	350	75	15	31.8	133	210	380	n.d.	3400	n.d.	n.d.
90	420	920	n.d.	460	n.d.	n.d.	134	35	10	n.d.	10000	300	n.d.
91	850	1350	500	335	n.d.	n.d.	135	335	780	n.d.	1270	n.d.	n.d.
92	435	840	n.d.	13500	n.d.	n.d.	136	300	390	n.d.	9400	780	15.0
93	520	910	250	9000	160	21.8	137	125	260	n.d.	13000	390	9.8
94	1235	5200	n.d.	42	n.d.	n.d.	138	190	380	n.d.	8300	n.d.	n.d.
95	710	1100	250	23000	n.d.	n.d.	139	125	200	n.d.	8100	n.d.	n.d.
96	635	1180	900	1450	n.d.	n.d.	140	270	500	n.d.	6200	130	12.4
97	620	460	n.d.	152	n.d.	n.d.	141	265	560	n.d.	11800	6000	15.0
98	960	1620	n.d.	26	17	36.6	142	180	470	500	12000	260	13.2
99	780	750	300	80	n.d.	n.d.	143	170	270	650	1040	n.d.	n.d.
100	680	1160	n.d.	31	n.d.	n.d.	144	420	400	350	675	n.d.	n.d.
101	1100	1300	250	55	n.d.	n.d.	145	140	220	250	2300	n.d.	n.d.
102	635	2030	n.d.	30	n.d.	n.d.	146	305	305	50	39500	n.d.	n.d.
103	265	3040	250	19	n.d.	29.8	147	180	170	n.d.	920	n.d.	n.d.
104	795	1830	n.d.	10	n.d.	n.d.	148	90	100	50	13500	n.d.	n.d.
105	880	800	100	55	n.d.	n.d.	149	30	40	n.d.	1990	n.d.	n.d.
106	475	1200	n.d.	20	n.d.	n.d.	150	200	500	150	2200	n.d.	n.d.
107	495	1700	n.d.	16	n.d.	n.d.	151	565	1570	100	60	n.d.	16.1
108	930	3390	650	420	11	39.7	152	640	1580	100	200	n.d.	n.d.
109	625	n.d.	n.d.	n.d.	n.d.	n.d.	153	150	n.d.	50	3550	n.d.	n.d.
110	690	950	200	75	n.d.	n.d.	154	180	400	100	13500	n.d.	n.d.
111	695	690	n.d.	74	n.d.	n.d.	155	420	1320	350	40	n.d.	19.6
112	435	1380	n.d.	22	n.d.	n.d.	156	120	240	n.d.	34000	n.d.	n.d.
113	620	1160	n.d.	25	n.d.	n.d.	157	230	470	n.d.	60	n.d.	19.6
114	820	1250	250	90	27	31.1	158	100	70	n.d.	3200	n.d.	n.d.
115	510	1380	n.d.	3700	n.d.	n.d.							

* for locations see Figure 3.
n.d. not determined.

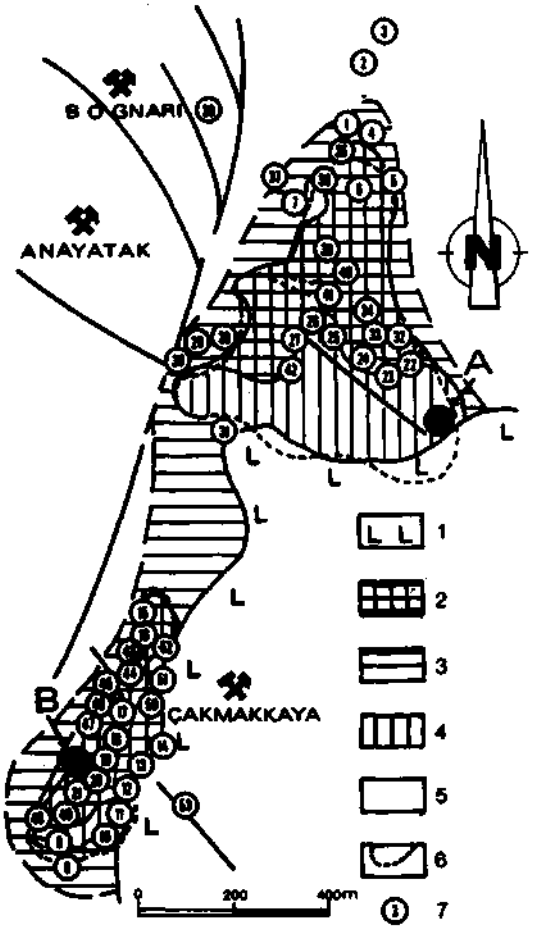

Fig. 3 - Map showing hydrothermal alteration zones and sample locations from the surface of both orebodies.
1- Hanging-wall felsic volcanics; 2- Silicic alteration; 3- Argillic alteration; 4- Phyllic alteration; 5- Pyroclastic host rocks; 6- Limits of the open pits (state of mining: 1983); 7- Location of the samples for the analyses.

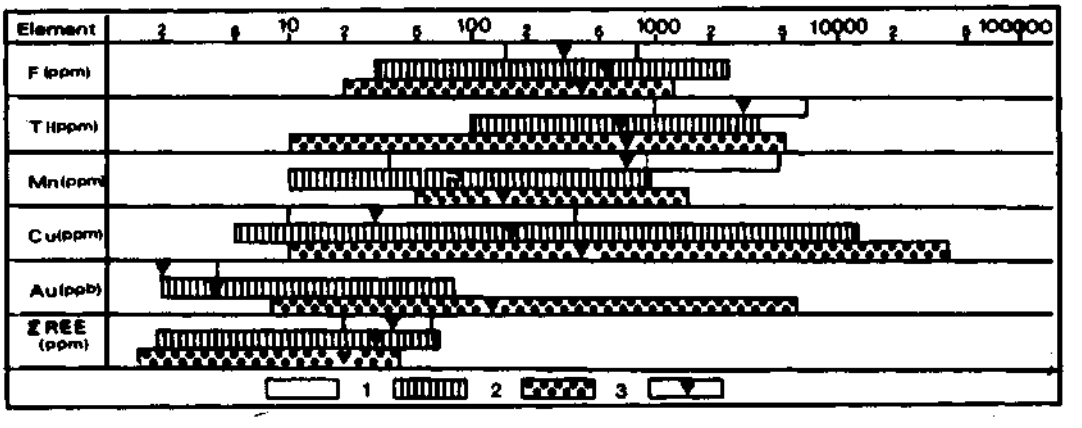

Fig. 4 - Background and range of the content of the elements in 1- Less altered background rocks, 2- Host pyroclastics, and 3- Drill holes; ▼ - background value.

The less altered samples formed the basis for determinating regional backgrounds of each element For the statistical evaluation, a computer program "Geo-500" together with "Stasy" and "Easy" of Company PIC, Munich/West-Germany, was applied to determine geochemical parameters and anomalous values. Additionally, the method of Lepeltier (1969) was constituted to establish anomalous populations.

RESULTS

Data on the elements F, Ti, Mn, Cu, Au, and REE in the altered volcanic host rocks indicate extensive geochemical dispersion halos and anomalies within the area of both orebodies (Figs. 5 and 6). The contents of F, Cu, and Au increase in the altered areas remarkably whereas Ti, Mn, and REE exhibit a distinct depletion.

Cu is enriched in phyllic and silicic alteration areas with concentrations greater than 220 ppm. This element is present with a background of about 30 ppm in the less altered pyroclastics (Fig. 4) and shows a higher value of 60 ppm in argillie zones (Fig. 5 and 6).

The two and three dimensional distributions of fluorine in altered pyroclastic host rocks are shown in Figs. 5 and 6. Fluorine in less altered pyroclastics has a background value of 325 ppm (Fig. 4). Geochemical halos in the phyllic and silicic alteration zones exhibit values of 320 to 500 ppm and more than 500 ppm F are observable. Locally, the fluorine contents in both altered zones reach extreme values of up to 2515 ppm (Fig. 4).

Gold has a background value of 2 ppb in the less altered pyroclastic country rocks (Fig. 4). Gold distribution within the both orebodies displays anomalous areas (Fig. 7) represented by values between 2-80 and more locally values greater than 80 ppb (Fig. 4). Particularly remerkable is the distribution of higher Au values which are linked to parts of silicic alteration in a greater distance to the surface. Some sectors have shown local economic concentrations.

In contrast to the positive anomalies represented by F, Cu, and Au; Ti, Mn, and REE were intensely depleted in the altered and mineralized areas. The less altered pyroclastics show a Ti background value of 3000 ppm (Fig. 4). In the mineralized areas, Ti is obviously depleted (Figs. 5 and 6), especially in the areas of phyllic and silicic alteration which indicates a estimated background value of 650 ppm in the host rocks. Similar behaviour is shown by Mn (Figs. 5 and 6) which can reach concentrations of about 10 ppm whereas the regional background was estimated at 705 ppm (Fig. 4).

As reported by Schneider et al. (1988), the REE have been leached from altered host rocks. Fig. 8 shows the distributions of the REE values of the investigated areas. It is notable that the silicified host rocks display the more important negative REE anomalies.

DISCUSSION

The geochemical data from the Murgul deposit indicate that fluorine, titanium, and manganese are excellent indicators of volcanogenic sulphide deposits in the East Pontic metallogenetic province. The Murgul deposit has been genetically interpreted as a subvolcanic type associated with Upper Cretaceous island arc volcanic activity (Akın, 1979; Özgür, 1985; Özgür and Schneider, 1988; Schneider et al., 1988).

The dispersion halos of F, Ti, Mn, Au, and REE outline perfectly the presence of a hydrothermal mineralization and alteration pattern in altered host pyroclastics. This has-been corroborated additionally by Çağatay and Boyle (1977) and Dietcrle (1986) in Madenköy, Sırtköy, and Kutlular ore deposits in the western part of the East pontic metallogenctic province which arc linked to similar type of pyroclastic host rocks in nearly the same stratigraphic horizon. They belong genetically to the subvolcanic hydrothermal mineralization too.

The increase of fluorine during hydrothermal alteration is a well known phenomenon: the fluorine contents of the primary host rock are increasing within the mineralized area because the element is concentrated by the ascending hydrothermal fluids. Due to the similar radii of F and (OH), fluorine can replace (OH) in the lattice of micas and clay minerals. This is well documented at the Murgul deposit in which the greater F values are concentrated within the phyllic and parts of the argillic zones (Figs. 5 and 6). The size of the deposit in the pyroclastic host rock stratigraphy seems to dictate the magnitude of the elemental haloes as evidenced by the fluorine distribution around Anayatak orebody in contrast to that

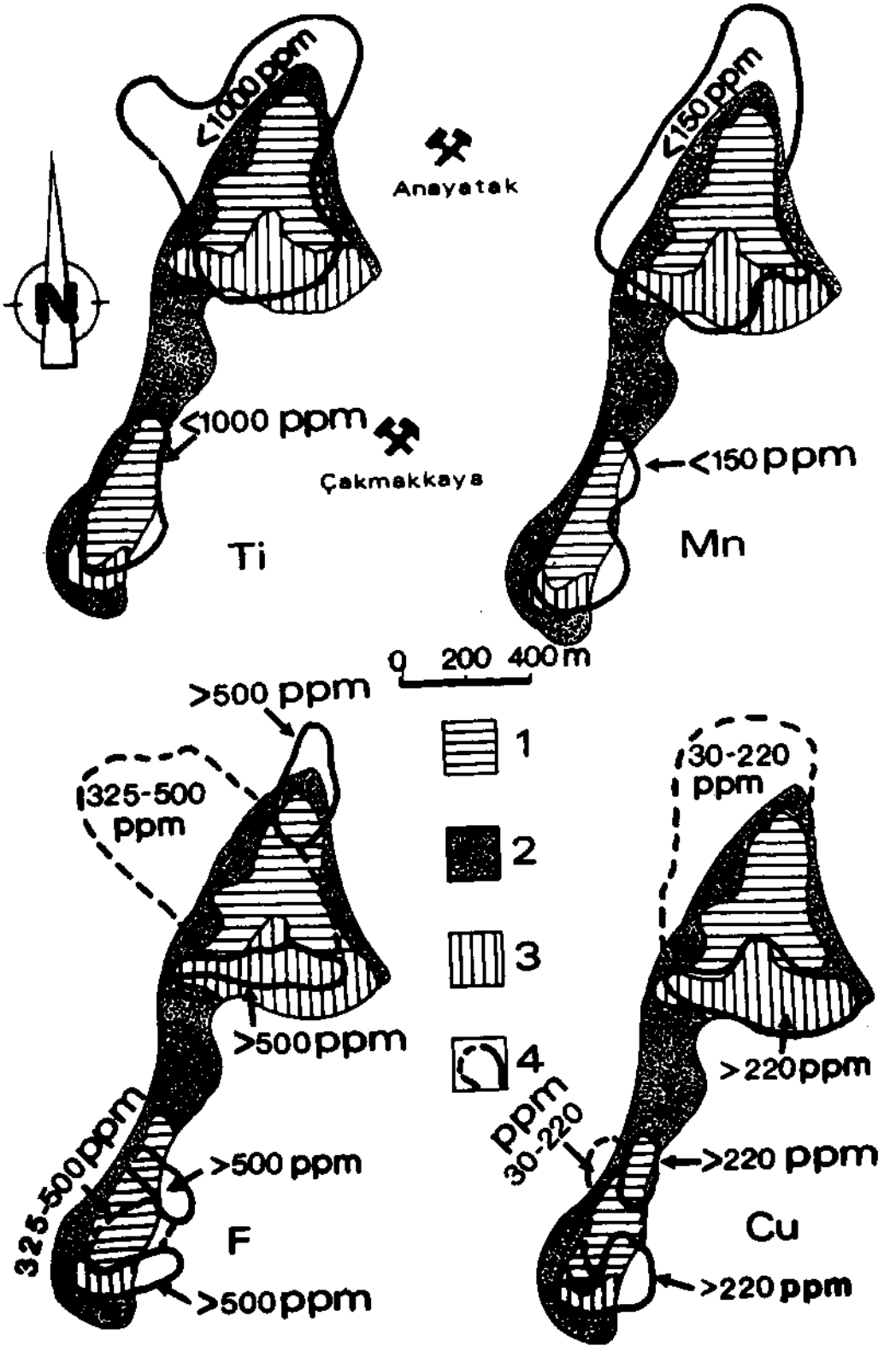

Fig. 5 - The distributions of Ti, Mn, F, and Cu in the Murgul deposit.
1- Silicic alteration; 2- Argillic alteration; 3- Phyllic alteration; 4- Boundary of anomalies.

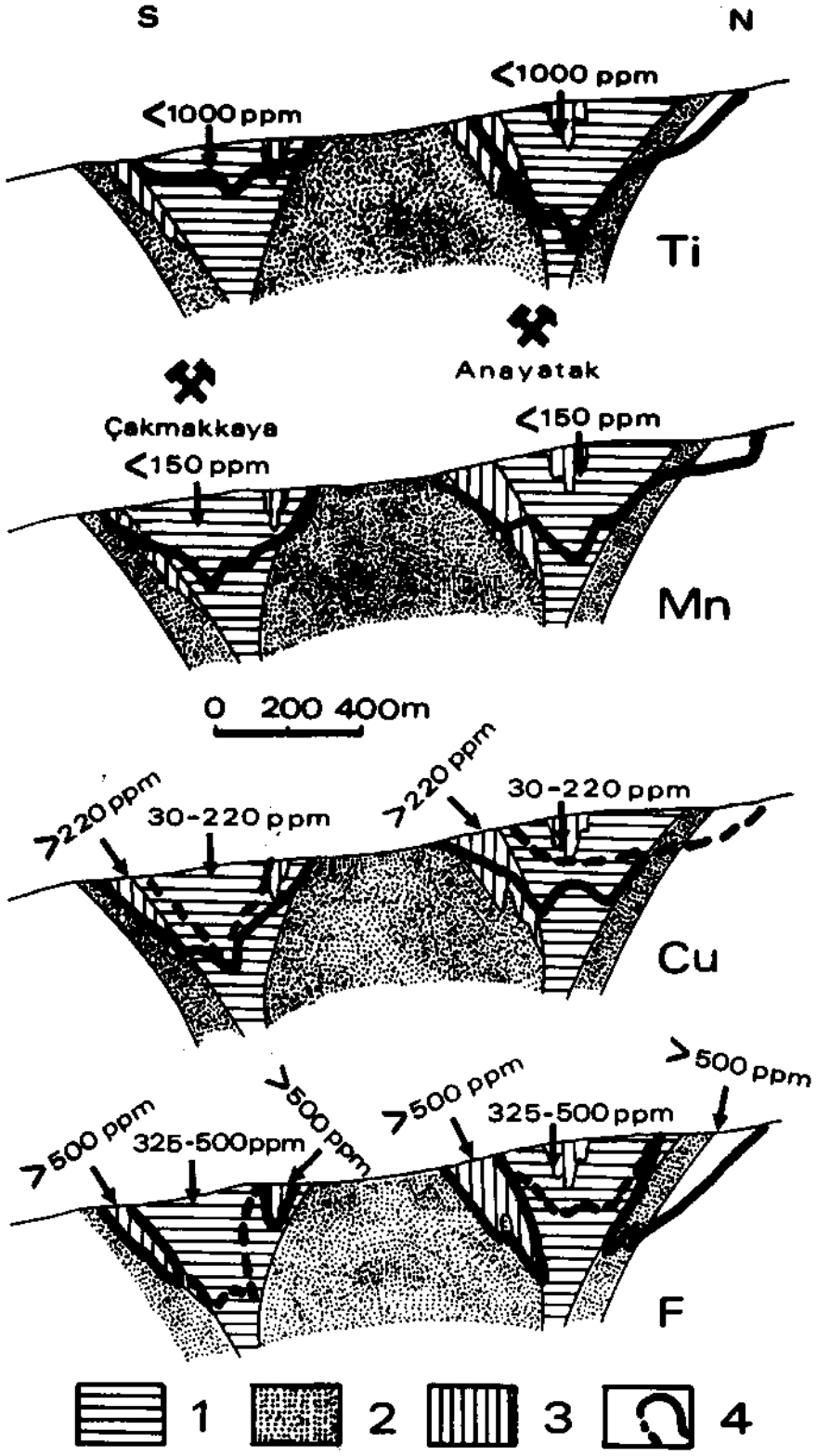

Fig. 6 - Cross sections showing the distributions of Ti, Mn, F, and Cu in the Murgul deposit.
1- Silicic alteration; 2- Argillic alteration; 3- Phyllic alteration; 4- Boundary of anomalies.

around Çakmakkaya which is to led the lack of the rock samples from Çakmakkaya due to hanging wall volcanics and soils. In addition to above, the analyzed host pyroclastics are derived from the silicic alteration area of Çakmakkaya. Therefore, these rock samples indicate low fluorine contents in comparison to Anayatak orebody.

The two and three dimensional distributions of manganese (Figs. 5 and 6) show strong negative anomalies within both ore bodies. This could be generated by the breakdown of Mn-bearing minerals (biotite, feldspars, and possibly glass). Thus, manganese was released from the rocks during alteration.

In the original pyroclastics, titanium is present in sphene and rare rutile or anatase. These minerals are not stable under the thermodynamic conditions during hydrothermal alteration. Therefore, titanium is leached from the altered areas too. Gold was especially enriched in silicic alteration zones (Fig. 7) which could be attributed to a hydrothermal remobilization of the Au contents of the host rocks.

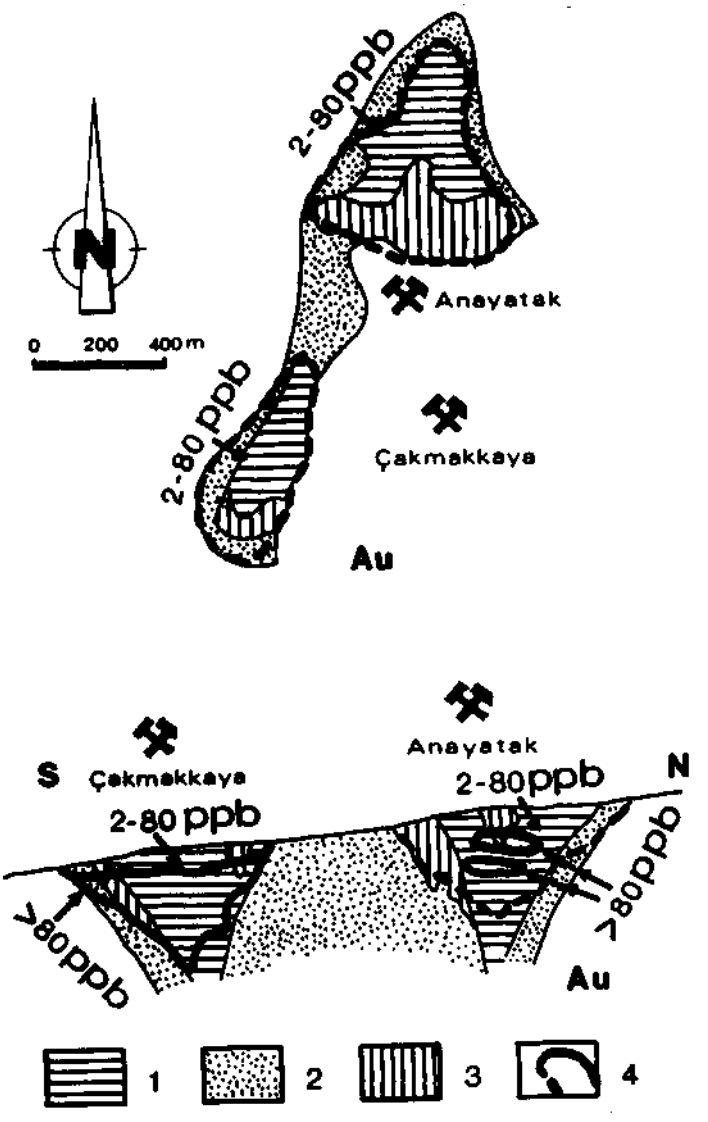

Fig. 7 - Gold distributions at the Murgul ore deposit.
1- Silicic alteration; 2- Argillic alteration; 3- Phyllic alteration; 4- Boundary of anomalies.

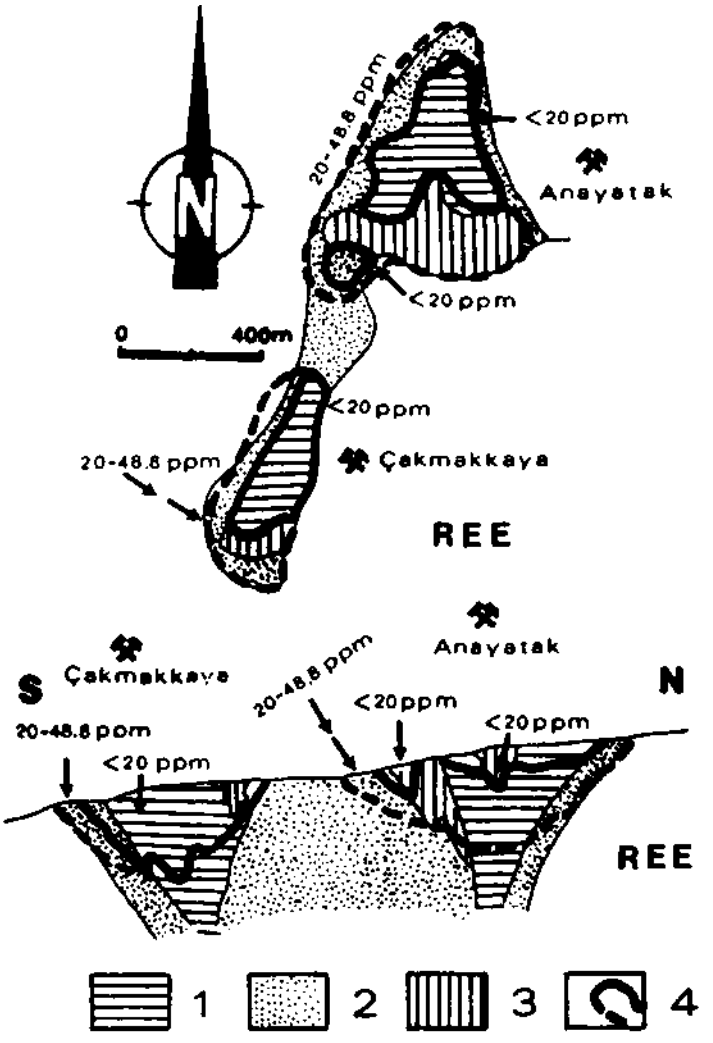

Fig. 8 - REE distributions at the Murgul ore deposit.
1- Silicic alteration; 2- Argillic alteration; 3- Phyllic alteration; 4- Boundary of anomalies.

The mineralization of Murgul seems to be strata-bound observing the semistratigraphic position of all deposits in the East Pontic metallogenetic province which arc linked to the volcanic sequence of Senonian age. Therefore, manganese, titanium, and fluorine could be applied as proximity indicators for the concealed deposits of the same type throughout the entire East Pontides.

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