

**LOCALIZATION OF MASSIVE, POLYMETALLIC SULPHIDE
ORES IN THE NORTHERN HARSIT RIVER AREA,
PONTID VOLCANIC BELT, NORTHEAST TURKEY**

by

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(16 figures and 4 tables)

RESUME.- Des gisements polymétalliques sulfurés, massifs et en "stockwork", et une minéralisation en manganèse d'origine exhalative se présentent dans les roches volcaniques de la région de la Rivière Harsit, dans le nord-est de la Turquie.

Le zonage morphologique et minéralogique présenté par ces minerais montre qu'un examen soigneux de certains gisements filoniens et exhalatifs peut conduire à la découverte de dépôts massifs qui y sont associés.

La minéralisation dans la région étudiée est associée à des roches sous-marines, acides, pyroclastiques de la phase terminale du cycle volcanique inférieur du Crétacé supérieur.

La roche encaissante est une formation de lave dacitique-rhyolitique, de tuf et de brèche. Dans cette série, Zr et Nb apparaissent en relation spatiale avec des centres volcaniques, eux-mêmes en liaison avec les zones minéralisées. La roche encaissante et la minéralisation sont, toutes deux, en relation étroite avec des failles orientées NW-SE et NE-SW tandis qu'une troisième faille, de direction N-S, peut aussi avoir joué un rôle dans la localisation du gisement. L'altération de la roche encaissante est générale au mur du dépôt massif, mais moins étendue dans le toit.

On peut distinguer quatre zones d'altération. Dans la roche encaissante, les teneurs en Mg, Ca et Na augmentent et celles en Al et K décroissent en s'éloignant de la masse minéralisée. A partir de celle-ci, la dispersion latérale des autres éléments est telle que $S, Ba > Cu, Zn > Mn, Fe$. Tandis que des niveaux à teneur anormale en S, Ba, Zn et Cu sont confinés dans la roche encaissante, des concentrations anormales de Mn et Fe apparaissent dans les tufs et les sédiments tuffacés du toit.

Des échantillons prélevés dans les environs de la mine de Harsit-Koprubasi ont révélé l'existence d'une zone anormale au-delà des limites des gisements reconnus.

ABSTRACT.- Massive and stockwork, polymetallic sulphide ores and exhalative manganese mineralization occur within the volcanic rocks of the Harsit River area, northeast Turkey. The morphological and mineralogical zonation shown by the ores indicate that careful re-evaluation of some vein-type and exhalative deposits may lead to the discovery of associated massive ore. The mineralization in the area is associated with submarine, acid, pyroclastic rocks of the terminal phase of the Upper Cretaceous, Lower Volcanic Cycle. The host-rock is a dacitic-rhyolitic lava, tuff and breccia formation. Within this unit Zr and Nb show spatial association with volcanic centres which, in turn, relate to mineralized areas. Both host-rock and mineralization show strong spatial association with NW-SE and NE-SW orientated faults, although a third fault trend N-S, may also have importance in localizing ore-deposition. Wall-rock alteration is widespread in the host rock of the massive ore deposits, but is less extensive in the hanging wall. Four alteration zones can be identified. Within the host rock Mg, Ca and Na increase, and Al and K decrease, outwards from the ore bodies. The lateral dispersion of other elements away from the orebodies is such that $S, Ba > Cu, Zn > Mn, Fe$. Although anomalous levels of S, Ba, Zn and Cu are confined to the host rock, anomalous Mn and Fe concentrations occur in the hanging wall tuffs and tuffaceous sediments. Samples from the vicinity of the Harsit-Koprubasi mine have revealed a distinctly anomalous area beyond the limits of the known orebodies.

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INTRODUCTION

The Pontid volcanic and metallogenic province extends approximately east-west along the Black Sea coast of N.E. Turkey from the vicinity of Samsun, in the west, to the Russian border (fig. 1). The region contains numerous massive and stockwork, polymetallic sulphide ore-deposits. They contain some 62 % Cu, 43 % Zn and 35 % Pb of the known potential of Turkey, together with significant amounts of Au and Ag. A number of publications relate to individual deposits or districts, they include : AKINCI (1974), BARNARD (1970), CAGATAY (1977), DURUKAL (1969), HAMAMCIOGLU & SAWA (1971), KOPRIVICA (1976), KRAEFF (1963), ÖNER & IWAO (1974), OVALIOGLU (1969), RYAN (1960), SAWA & ALTUN (1977), TAYLOR (1977), TUGAL (1969) and VUJANOVIC (1974).

The general relationship between volcanogenic sulphides and specific magmatic series has been well documented in recent years (GUILD, 1972a, b; JACOBSEN, 1975; MITCHELL & GARSON, 1976). The association is particularly strong with rocks from the orogenic belts of convergent plate boundaries. The sulphide ore-deposits of convergent plate boundaries may be broadly sub-divided into those associated with island arc volcanism and the Andean, or Cordilleran, porphyry deposits related to near-surface acidic intrusions. Although the two categories are distinctive they do often occur together. TITLEY (1975) has reported the occurrence of both in the Phillipines island arc, while in the Andean province, in Ecuador, volcanogenic, strata-bound sulphide deposits have been described by GOOSSENS (1972). Both categories occur in the Pontid metallogenic province, although this

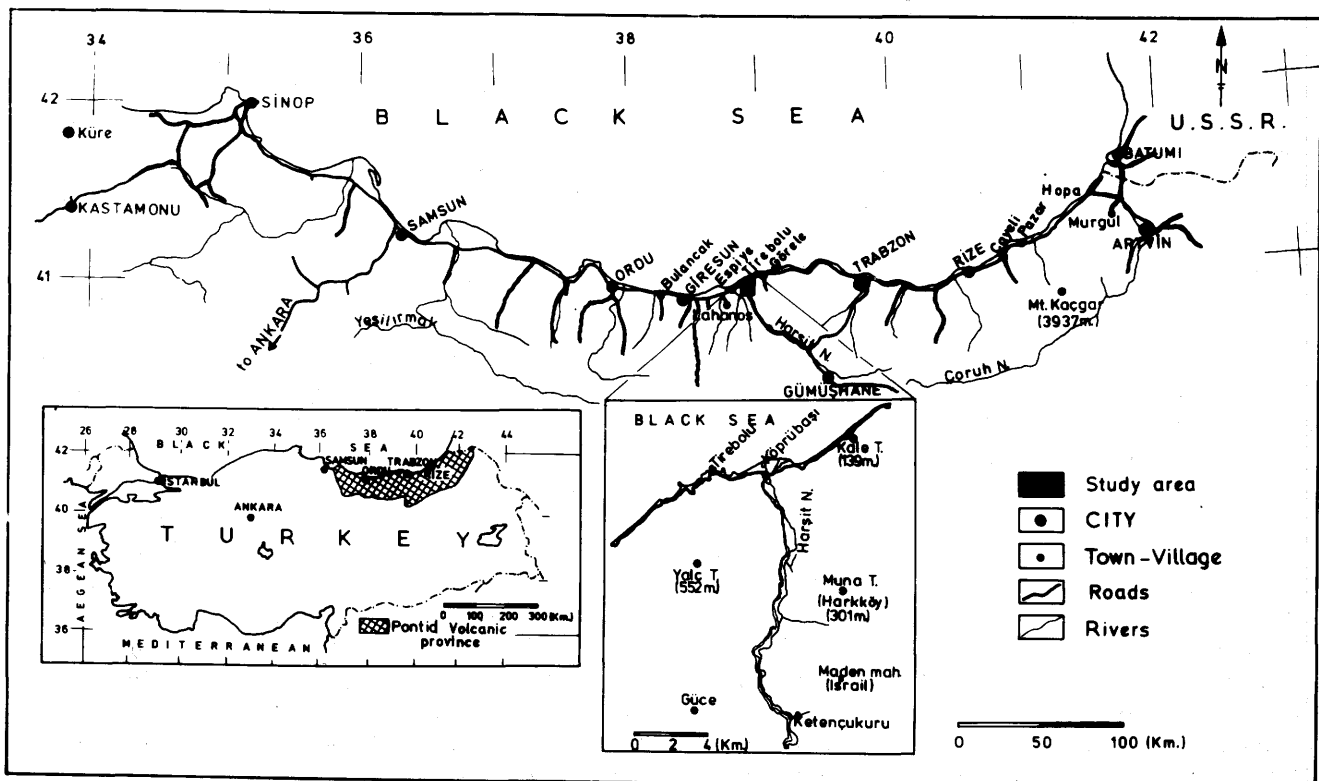


Figure 1.- The Pontid Volcanic Province showing the locality of the northern Harsit river (shown in more detail in fig. 2), after Egin et al. (1979).

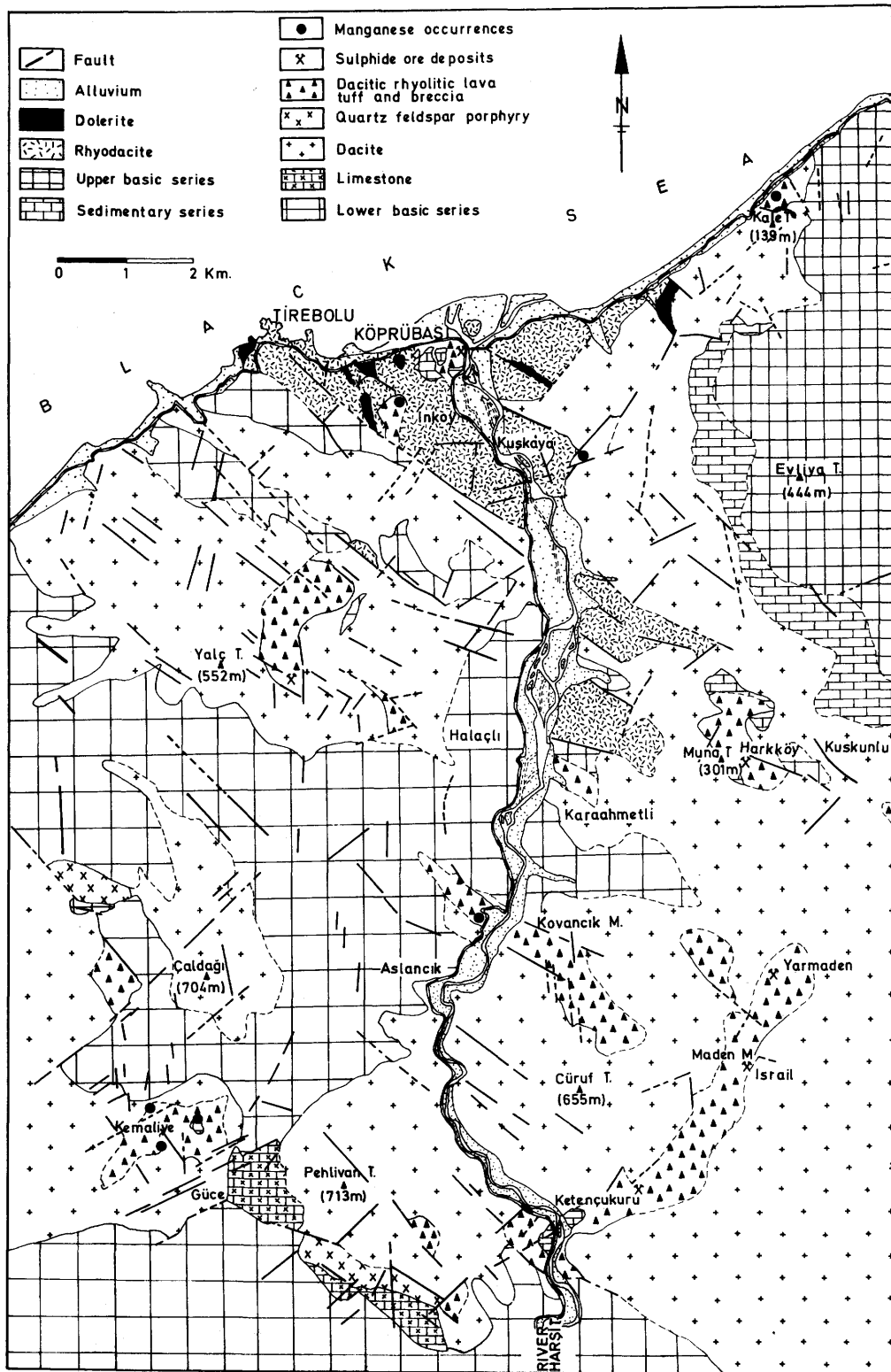


Figure 2.- Geological map of the northern Harsit river area, after Egin et al. (1979).

communication is concerned only with orebodies associated with the volcanic rocks.

In the Pontid volcanic belt the ores are associated with specific horizons of a volcanic cycle. The volcanic rocks generally dip to the north at low angles, although they are disrupted by block faulting. Surface outcrop of ore is limited. Techniques which might localize buried or "blind" ore deposits are thus necessary for effective exploration of the area. Formulation of such techniques is considered here on the basis of information derived from a study of the volcanic rocks and associated ore-deposits of the northern Harsit river area.

Localization of the deposits depends on a thorough knowledge of the morphology and zonal sequence of the volcanogenic sulphide ores, on identification of the host-rock formation, on structural control of host-rock and mineralization, and on recognition of wall-rock alteration patterns. Although there may be numerous massive sulphide deposits in areas such as that occupied by the northern Harsit river, they are small. They thus form small targets unlikely to be sufficiently localized by regional geochemical surveys. Detailed litho-geochemical analysis is therefore more likely to be of use, particularly in extending knowledge of individual deposits localized by geological parameters.

Table 1.- Stratigraphic sequence in the northern Harsit river area, Pontid volcanic belt.

Pleistocene-Recent	Sea and River Terraces
	Granitic Intrusions (In extreme south)
Tertiary	Dacite-Rhyodacite
Upper Volcanic Series	Upper Basic Series ?Dolerite Sheets
	Tuffaceous Sedimentary Series
Mesozoic	Dacitic-Rhyolitic Lava, Tuff and Breccia. <u>Mineralisation</u>
Lower Volcanic Series	Dacite Lavas and Quartz Porphyry Intrusives
	Limestone
	Lower Basic Series

MINERAL DEPOSITS OF THE NORTHERN HARSIT RIVER AREA

The volcanic rocks of the eastern Pontid belt have been described by EGIN *et al.*, (1979). The main elements of the sequence, as seen in the northern Harsit river area are shown in Table 1. They are intruded by Tertiary acidic rocks.

The volcanogenic ores are associated with the terminal phase of the Upper Cretaceous, Lower Volcanic Cycle. The host-rock is the dacitic-rhyolitic lava, tuff and breccia formation described by EGIN *et al.*, (*loc. cit.*). This unit is comprised largely of the pyroclastic products of submarine volcanism but includes rhyolitic lava domes seen, for example, at both the Harsit-Koprubasi and Harkkoy deposits (fig. 2). Three types of ore deposit are associated with this unit in the eastern Pontids. They are (a) massive and stockwork, polymetallic sulphide ores, (b) polymetallic sulphide and Cu-Au vein deposits, and (c) exhalative manganese deposits.

MASSIVE SULPHIDE DEPOSITS

The massive sulphide deposits of the northern Harsit river area exhibit morphological and mineralogical zonation strikingly similar to those shown by the Japanese Kuroko ores described by LAMBERT & SATO (1974) and ISHIHARA (1974). Individual deposits commonly consist of two or more orebodies. This is seen at the Harsit-Koprubasi mine where three discrete orebodies have been identified by EGIN (1978). The deposits may be polymetallic, containing Fe, Cu, Pb and Zn sulphides, together with sulphosalt and sulphate minerals. Deposits of this type include Harsit-Koprubasi and Harkköy. Some orebodies are mainly pyritic, with only minor Cu, Pb and Zn sulphides and sulphosalts. These are exemplified by the mineralisation at Israil & Yalc (fig. 2).

The sequence described below, and shown schematically in figure 3, has been determined from observations in the Harsit-Koprubasi and Harkkoy mine areas. The lowest mineralized horizons are dome-shaped masses of rhyolitic lava containing disseminated pyrite. These are overlain by tuff and breccia containing discontinuous lenses and veinlets of dolomite and/or gypsum. They are followed upwards by quartz-pyrite veinlets, an extensive pyrite-chalcopyrite stockwork and some disseminated ore. The upper-part

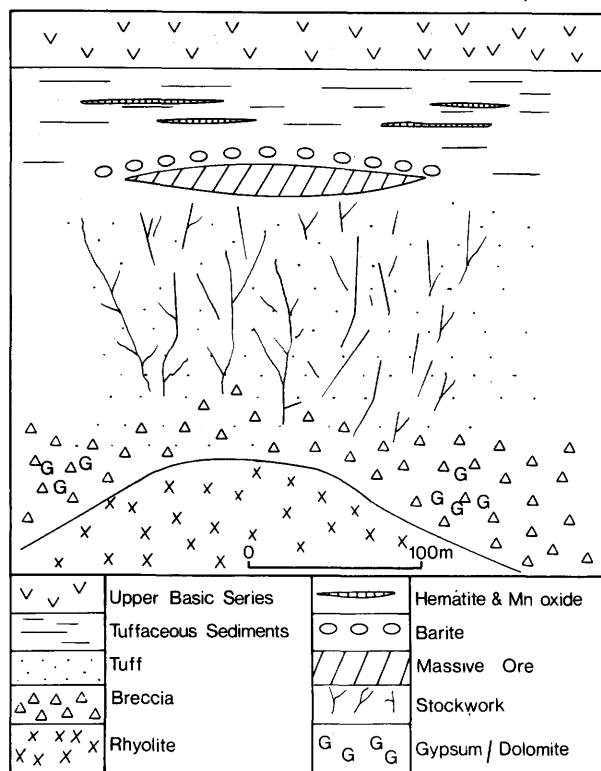


Figure 3.- Schematic cross-section of a typical volcanogenic sulphide deposit from the northern Harsit river area.

of the stockwork occasionally contains sphalerite, galena and sulphosalts. Lenticular, massive ore occurs overlying the stockwork. Its lateral extent is usually less than that of the stockwork, the lenses having dimensions of 100-150 m in diameter and a thickness of 0.2 to 15 m. The massive ore consists mainly of sphalerite, chalcopyrite, pyrite and galena with a quartz and barite gangue. Towards the top of the massive ore, orpiment, colloform and framboidal pyrite, and the sulphosalts tetrahedrite-tennantite and bourmonite also occur. Discontinuous barite lenses are found in the succeeding tuffs. They are overlain by hematite and goethite bearing tuffs, in thin lenses, which extend laterally beyond the massive ore. Manganese oxide and hydroxide bearing tuffs and tuffaceous sediments complete the sequence.

The complete sequence is not exhibited by one deposit, but the Harsit-Koprubasi and Harkkoy deposits contain most of the elements. The deposits are mainly concealed, most of the sequence being established from borehole cores. The valley of the Yersuyu River extending northeast from the Harsit

River towards Ketencukuru, however, reveals a good section. In this locality the emplacement and subsequent disposition of the hostrock is controlled by NE-SW and NW-SE faults respectively (fig. 2). On the west bank of the river Harsit, a NW-SE striking fault, downthrown a few hundred metres to the east, exposes the host rock. NW-SE step faulting forms a graben in the Harsit river valley, exposing rhyolitic lavas in the valley bottom which contain disseminated, euhedral pyrite crystals. To the northeast, in the Yersuyu river valley the lavas give way upwards to breccias, which in turn are succeeded by tuffs containing 5-10 m thick, massive dolomite lenses. The succeeding tuffs are about 100 m thick and contain a stockwork of pyrite-chalcopyrite which changes to a stockwork of pyrite-chalcopyrite-sphalerite-galena towards the top of the sequence. At the head of the valley, at Ketencukuru, a small outcrop of massive ore, 1 m in thickness, is succeeded by 0.5 to 1 m of massive barite overlain, in turn, by further tuffs.

Similar sequences are well demonstrated elsewhere in the eastern Pontids by deposits such as Lahanoş (TUGAL, 1969) and Madenkoy/Cayeli (CAGATAY, 1977). The host-rock of these deposits always displays widespread alteration, characterized by argillization and extensive silicification. The hanging wall tuffs, in contrast, exhibit only limited alteration with formation of sericite, montmorillonite and mordenite.

VEIN-TYPE SULPHIDE DEPOSITS

Although not the principal concern of this study, these deposits deserve brief mention. AKINCI (1974) has made an extensive study of veins in the Bulancak area showing that they are fissure-filling Pb-Zn-Cu sulphide deposits. He demonstrated that the ore-fluids rose along NW-SE trending faults. The influence of major lineaments on the disposition of veins has also been shown by POLLAK (1968), GUMUS (1970) and SNELGROVE (1971).

SAWA & ALTUN (1977) have described vein and stockwork deposits from the eastern Black Sea region but have placed them in a different genetic class to the massive ores, although they occur in rhyolitic domes and have pyrite-chalcopyrite associations. Such deposits clearly resemble the stockwork zone of the ore-deposits described above. Recognition of such stockworks as part of, or associated with, massive sulphide ore lenses is fundamental in exploration for the latter. This is exemplified in the Ketencukuru area. These deposits had previously been described by KIEFT

(1956) as pyrite-chalcopyrite vein deposits. The description given above indicates that the "veins" form part of the stockwork underlying a massive sulphide lens.

MANGANESE MINERALIZATION

Manganese deposits are numerous in the eastern Pontids but with the exception of the Peronit orebody, they have been uneconomic. The deposits occur in the same host-rock as the massive sulphide ores. They are massive, and are associated with fine opal or chalcodony and radiolarian cherts, as seen near Guce, or they are nodular and botryoidal as seen near Kale Tepe (fig. 2). They are intimately associated with tuffs, cherts and cherty sediments which probably owe their formation to submarine volcanism, as proposed by SHATSKIY (1966). Their position in the volcanic sequence is identical to that of the upper manganese-rich horizon associated with the massive ore. They may thus represent an intense development of this zone. Similar deposits in Japan and Indonesia have been classified as exhalative-sedimentary, the manganese being contributed by volcanic hot springs discharging directly onto the seafloor (STANTON, 1972).

STRATIGRAPHIC CONTROL OF THE VOLCANOGENIC SULPHIDES

The mineralized pyroclastic rocks of the dacitic-rhyolitic lava, tuff and breccia formation are overlain by a tuffaceous sedimentary unit marking the division between the two major volcanic episodes in the eastern Pontids (Table 1). Occasionally the Upper Volcanic Cycle directly overlies the mineralization, the sedimentary unit being missing. This relationship has been described by CATAGAY (1977) for the Madenkoy/Cayeli deposit.

The host-rock unconformably overlies the dacite lavas of the Lower Volcanic Cycle or, because of its close spatial association with the dominant fracture system, is in fault contact with other members of the Cycle (fig. 2). The most obvious difference between the host-rock and the dacite lavas lies in the high proportion of pyroclastic rocks associated with the former, although there is also a pronounced petrological difference. The differentiation index (THORNTON & TUTTLE, 1960) is lower in the dacites than in the host-rock dacitic-rhyolitic lava, tuff and breccia formation, (Table 2). The trend is closely similar to that

Table 2.- Differentiation Indices for acid volcanic rocks from the northern Harsit river and Japan.

	Northern Harsit river area volcanics		Kosaka mine - Japan*		Tsuchihata Mining area - Japan*	
	Dacite	Dacitic-rhyolitic lava, tuff and breccia = host rock	Older volcanic rocks	Lava dome volcanic rocks = host rock	Older volcanic rocks	Lava Dome volcanic rocks = host rock
Range	66.2-87.3	75.5-97.5	78-91.8	83-92	62-88	85-90
Mean	79.17	87.25	84	87	74	88
S.d	5.56	5.34	-	-	-	-
P.	27	31	-	-	-	-

* Data from Tatsumi and Clark (1972)

S.d: Standard deviation

P : Population

shown by the Japanese acid volcanic rocks described by TATSUMI & CLARK (1972). The data imply that the host-rock formation is more differentiated than the older dacites.

Detailed studies of the Harsit-Koprubasi and Harkkoy Mine areas (EGIN, 1978) reveal that dome-shaped rhyolites are closely related to the ore-deposits. The lavas occur in the lower part of the host-rock sequence. They are of fine grain-size and contain sericitized plagioclase, orthoclase, and biotite laths, together with quartz, aligned in a fine-grained matrix. The rhyolite lavas are overlain and surrounded by breccias which contain angular to rounded lava fragments, ranging in size from a few mm to a few cm in diameter, contained in a tuffaceous matrix. The variation in thickness and lateral extent of the breccias is remarkable, although they average about 40 m in thickness. At the Harsit-Koprubasi Mine they locally reach thicknesses in excess of 100 m, grading upwards into tuffs which are also about 100 m thick. Towards the top of the host-rock the tuffs contain discontinuous, lenticular intercalations of radiolarian chert. These grade upwards into the tuffaceous sedimentary unit which consists of marls, mudstones, radiolarian cherts and some limestones and sandstones admixed with varying amounts of volcanic ash. The sedimentary unit varies in thickness from 1 m to 50 m, within short

lateral distances, and may be related to an uneven bottom topography due to development of the rhyolitic lava domes. The following species support an Upper Maestrichtian age for the sediments: *Heterohelise americana*, *Globotruncana mayaroensis*, *Globotruncana gansseri* (A.T.S. RAMSAY, pers. comm.).

The host-rock is closely associated with the dominant fault pattern and is itself extensively fractured. Within the host-rock Nb and Zr, determined on core and surface samples in the vicinity of the Harsit-Koprubasi deposit, show a 2 to 4 fold enrichment in the breccias when compared to the rhyolite lavas or the tuffs (fig. 4). The breccias show close spatial association with the lava domes and are probably derived from ascending magmas which came into contact with seawater. The explosive activity leading to their formation may also be related to sudden release of gas which occurred when gas-charged magma moved into a highly fractured zone. The distribution of Zr and Nb between the breccias and tuffs suggests a zoned magma chamber, the breccias resulting from a magma column enriched upwards in Nb and Zr by diffusional processes (MACDONALD, pers. comm.). This chamber then erupted and subsequently refilled with less evolved magma which produced the tuffs. Irrespective of the mechanism behind the enrichments, the high contents of Nb and Zr in the breccias could be useful in tracing volcanic centres. The close time and space association of these centres with mineralization may in turn determine the location of orebodies.

Volcanics both underlying and overlying the host unit are unmineralized. SAWA & ALTUN (1977) have reported that ore pebbles occur in the Upper Cretaceous to early Tertiary sedimentary rocks which underlie the Upper Basic Series, while detrital barite can be seen in mudstones overlying ore and massive barite at the Yaylabasi mine, near Macka. In the Harsit river area lenses of reworked barite are found conformable to the bedding planes of radiolarian cherts overlying massive ore at the Harsit-Koprubasi mine. The complete absence of hydrothermal alteration in the Upper Cretaceous limestones at the Israil mine (KIEFT, 1956) is further indication that the mineralization was confined to a narrow time gap.

TECTONIC CONTROL OF VOLCANOGENIC SULPHIDES

The dominant fault directions in the eastern Pontids are approximately NE-SW and NW-SE (SCHULT-

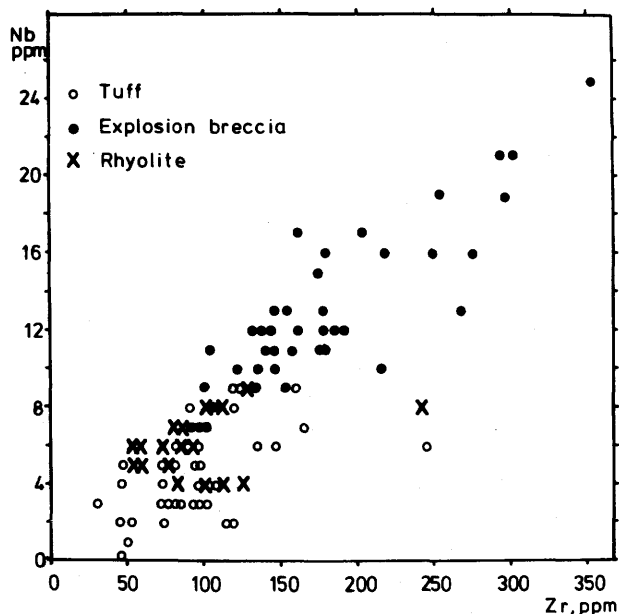


Figure 4.- Nb vs. Zr in rhyolites, explosion breccias and tuffs of the host rock.

ZE-WESTRUM, 1961), indeed these conjugate directions clearly influence the trends of the eastern Turkish, Black Sea coastline. TUGAL (1969), ONER & IWAO (1974), POPOVIC (1975) and CAGATAY (1977) have all suggested that the faults facilitated magmatic activity, while POLLAK (1968), GUMUS (1970), SNELGROVE (1971) and AKINCI (1974) have suggested that they are further responsible for localization of ore-forming solutions.

The spatial association of igneous rocks with NE-SW and NW-SE trending faults is well demonstrated in the northern Harsit river area (fig. 2). This is shown by the distribution of quartz porphyrys in the south and southwest, and of dolerite sheets and rhyodacites of the Upper Volcanic Cycle in the north. Direct control of mineralization by faulting, however, cannot be seen in the sense demonstrated by AKINCI (*loc. cit.*) at Bulancak. The host-rock, however, does show close spatial association with the conjugate fault pattern. This is well demonstrated in the Ketencukuru district, near Yalc Tepe, to the west and south of Caldagı, near Kovancik and in the vicinity of the Harsit-Koprubasi and Harkkoy mines. It is perhaps relevant that the host-rock does not occur in the relatively unfaulted district in the east and northeast of the area shown in figure 2, where the sedimentary series and/or the Upper Basic Series directly overlie barren dacites of the Lower Volcanic Cycle. Localization of the host-rock horizon would thus be facilitated by careful mapping of the conjugate fault system.

KRONBERG (1970) considers that the tectonic movements responsible for faulting began during the Lias but continued throughout the Alpine orogeny. He noticed a relatively weak development of N-S striking faults in addition to the conjugate system. Faults with this strike are well developed south of Kovancik Mah (fig. 2), the rose diagram shown in figure 5 confirming this trend. Their presence is further supported by the N-S disposition of sections of the major river valleys. The northern Harsit river forms a deep valley running approximately N-S, and is one of the major lineaments visible on air photographs. Fault control of the valley can be demonstrated 1 to 2 km south of Aslancik and north of Kuskaya, and by lithological differences across the river near Koprubasi. Although N-S faults are subordinate to the conjugate system in their relationship to the emplacement of the volcanics, including the host-rock formation, examination of figure 2 indicates that, apart from the Harsit-Koprubasi mine, mineralization at Yalc T., and manganese occurrences near Aslancik and Kemalije

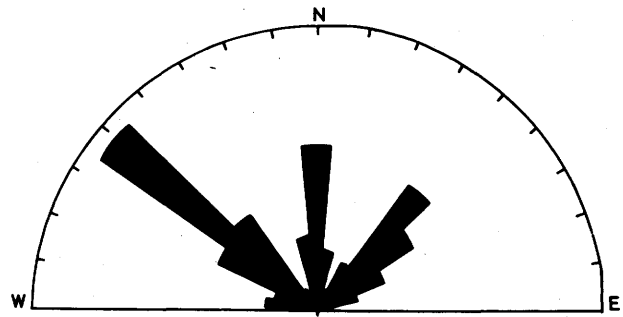


Figure 5.- Fault strike in the northern Harsit river area, 207 measurements.

are related to their intersections with the conjugate system.

WALL ROCK ALTERATION AND LITHOGEOCHEMICAL DISPERSION AT THE HARSIT-KOPRUBASI MINE

ANALYTICAL TECHNIQUES

Mineral species resulting from hydrothermal alteration were identified from characteristic X-Ray diffraction patterns using techniques outlined by THOREZ (1975, 1976), including examination after heat treatment and glycolation. Reflection intensities were used as a semi-quantitative measure of relative abundances.

Altered wall rocks, together with 115 surface samples and 17 near surface samples from borehole cores located within an area 1000 m by 800 m in the vicinity of the Harsit-Koprubasi mine, have been analysed by X-Ray fluorescence for Si, Al, total Fe, Mg, Ca, Na, K, Ti, Mn, total S, P, Ba, Mo, Nb, Zr, Y, Sr, Rb, Zn, Cu, Ni and Cr. Individual analyses are given by EGIN (1978). Although the sample distribution has been affected by the dense vegetation and overburden the samples analysed were relatively fresh. Analysed samples, including those at outcrop, still retain unaltered sulphide minerals, including pyrite.

In the lithogeochemical survey background samples were chosen, for every lithological unit, from areas remote and free from mineralization. SIEGEL (1974) has suggested that a figure of $\bar{x} + 2s.d.$ (mean + 2 standard deviations) be taken as the limit of regional and local fluctuations, the threshold. Threshold values of $\bar{x} + 2s.d.$ for each lithological unit are shown in

Table 3.- Arithmetic mean background values, threshold and anomalous concentration intervals for lithological units from the northern Harsit river area.

	S (%)				Ba (ppm)				Cu (ppm)				Zn (ppm)				Fe ₂ O ₃ (%)				Mn (ppm)			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
RYD	0.06	0.14	0.26	0.86	1227	1735	2497	6307	0	*7	**16	**61	23	75	153	543	1.74	3.26	5.54	16.94	230	370	580	1630
D	0.14	0.30	0.54	1.74	1217	1651	2302	5557	95	205	370	1195	65	101	155	425	8.55	11.93	17.00	42.35	1161	1621	2311	5761
SS	0.09	0.39	0.84	3.09	91	231	441	1491	8	32	68	248	18	64	133	478	1.63	3.47	6.23	20.03	228	684	1368	4788
R	0.05	0.09	0.15	0.45	209	481	889	2929	7	31	67	247	30	64	115	370	1.82	2.36	3.17	7.22	251	575	1061	3491
DA	0.05	0.11	0.20	0.65	559	843	1269	3399	1	7	16	61	30	50	80	230	2.59	3.83	5.69	14.99	464	924	1614	5064

* Total Fe as Fe₂O₃

** DA values used

1. Arithmetic Mean (\bar{x})

2. Arithmetic Mean + 2 standard deviations ($\bar{x} + 2s.d.$)

3. $\bar{x} + 5s.d.$

4. $\bar{x} + 20s.d.$

RYD Rhyodacite, Upper Volcanic Cycle

D Dolerite, " " "

SS Tuffaceous Sedimentary Series

R Host-rock

DA Dacite, Lower Volcanic Cycle

Table 3, together with levels of $\bar{x} + 5s.d.$ and $\bar{x} + 20s.d.$

WALL ROCK ALTERATION

Alteration seen in the northern Harsit river area can be subdivided into the following categories which bear close resemblance to those proposed by MEYER & HEMLEY (1967).

- I. Advanced argillic : Dickite + kaolinite + siderite + ferroan dolomite + sericite \pm quartz.
- II. Sericitic : Sericite + illite + quartz \pm kaolinite.
- III. Intermediate argillic : Illite + montmorillonite + chlorite \pm kaolinite \pm quartz.
- IV. "Propylitic": Montmorillonite + mordenite \pm chlorite.

The above assemblages are characteristic mineral associations but do not imply equilibrium between the

species. Kaolinite, for example, is unlikely to form in equilibrium with montmorillonite (Assemblage III). Some of the kaolinite is undoubtedly a supergene product.

Figure 6 shows the surface expression of the wallrock alteration in the Harsit-Koprubasi mine area. The inner zone, in the immediate vicinity of the orebody, is dominated by sericite and quartz. It is succeeded outwards by a zone in which illite is dominant, usually accompanied by montmorillonite, chlorite, quartz and kaolinite. Montmorillonite and mordenite characterize the inner and outer parts of assemblage IV respectively, together constituting the outer zone of the halo. Mordenite, in particular, extends to about 500 m south southwest of the orebody.

Vertical expression of the alteration halo is shown in figure 7, based on borehole core data and available surface samples. The borehole cores are from the

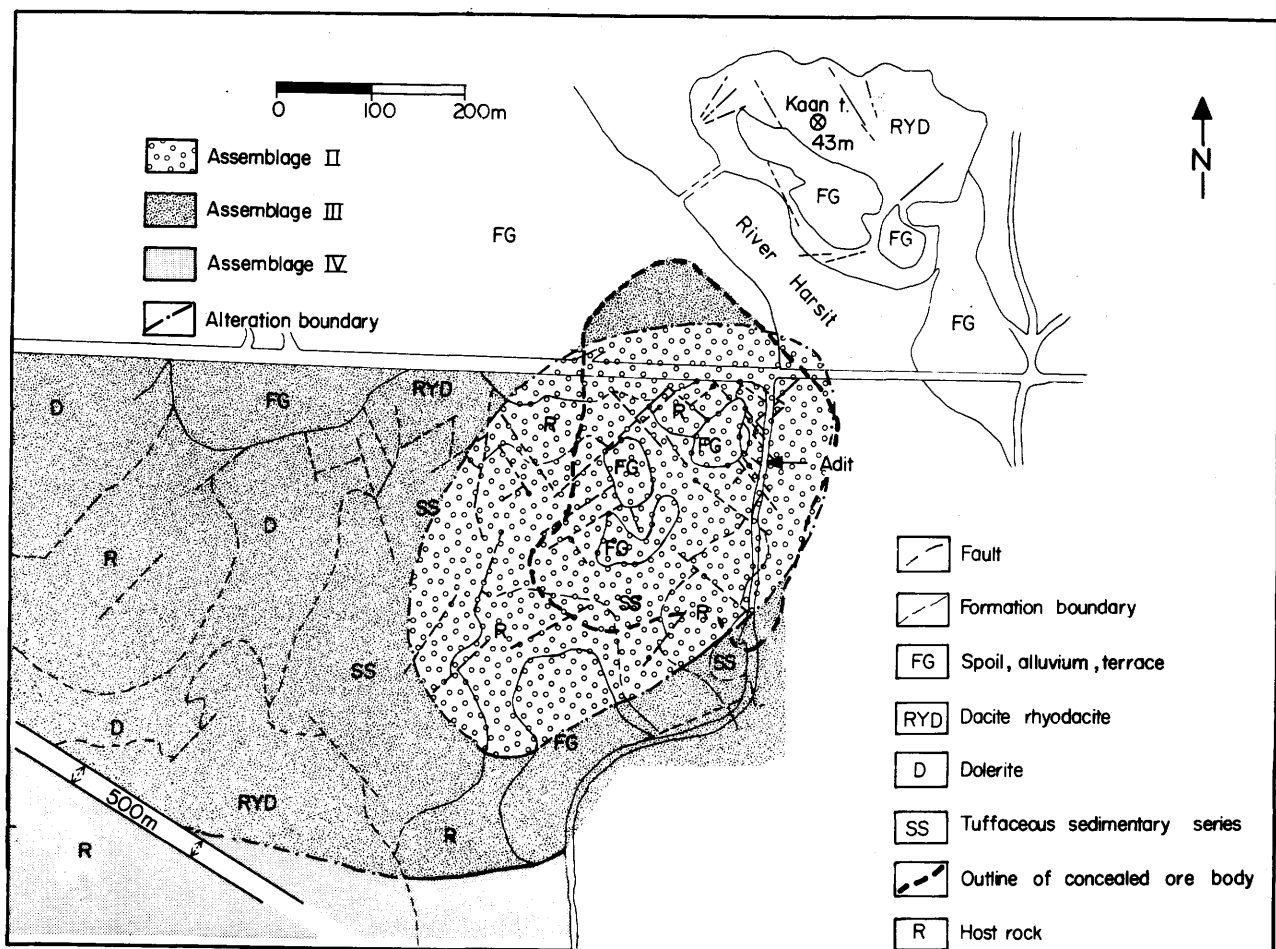


Figure 6.- Surface expression of the alteration halo in the Harsit-Koprubasi mine area. I, advanced argillic; II, sericitic; III, intermediate argillic; IV, propylitic.

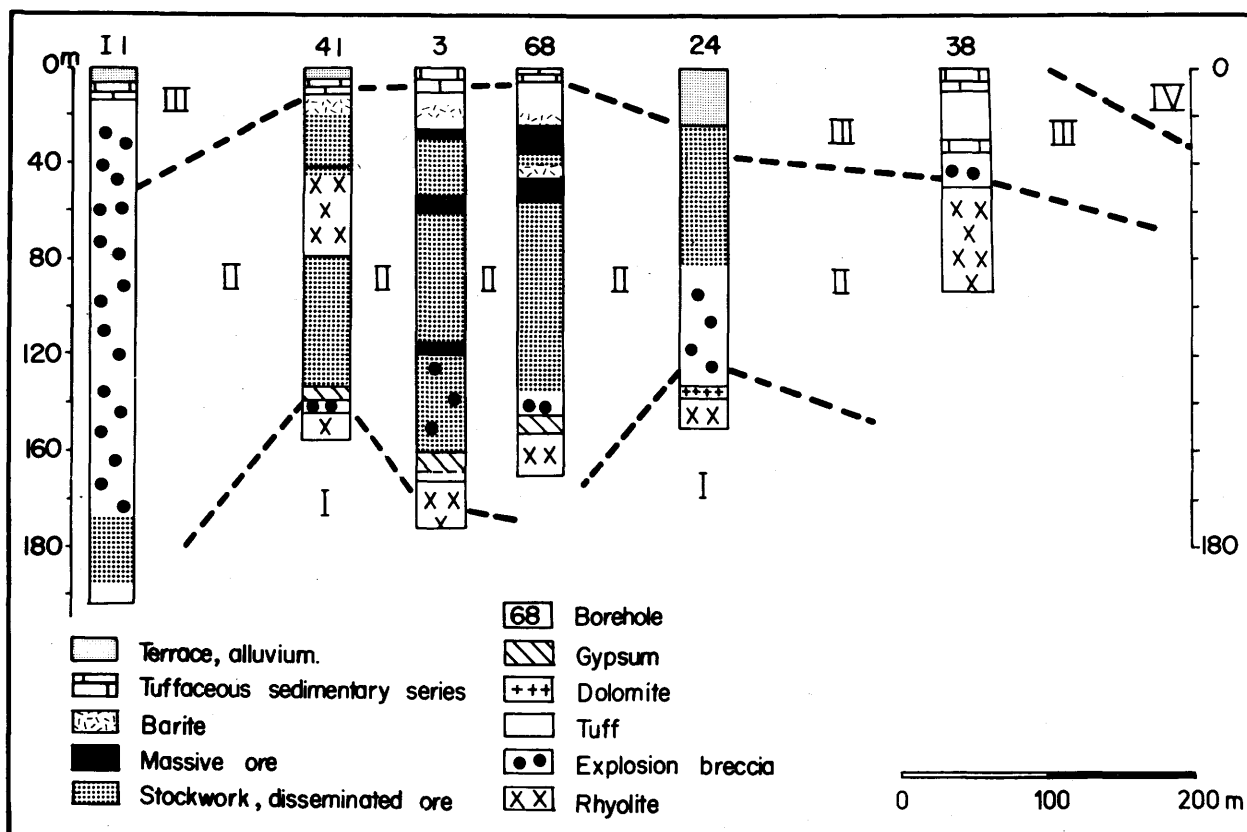


Figure 7.- Vertical expression of the alteration mineral assemblages in the Harsit-Koprubasi mine. I, II, III and IV as in figure 6.

extensive, vertical hole, diamond drilling undertaken at Koprubasi by M.T.A. Assemblages II and III are those seen in surface samples and shown on figure 6. Assemblage I is intercepted in some of the deeper levels of the borehole cores. It is characterized by the presence of substantial dickite, ferroan dolomite and siderite. Assemblage IV, as shown in figure 7, is only represented by the montmorillonite-rich inner part.

Only assemblages I, II and III are present at Harkkoy and Ketencukuru. The absence of assemblage IV may be due to limited surface outcrop.

LITHOGEOCHEMISTRY

Average data presented in Table 4 show that in the alteration halo Al, Mg and K are enriched relative to surrounding rocks of similar bulk petrography, while Ca and Na are depleted. Iron is also depleted in the halo except in Zone I. Aluminium is notably enriched in Zones I and II while K shows its greatest enrichment in Zone II. Magnesium is enriched in assemblages II, III and the inner part of IV. The outermost zones

also show relative enrichment in Ca and Na compared to Zones I and II. The halo is thus characterized by an outwards increase in Mg, Ca and Na and a decrease in Al, Fe and K. The bulk chemistry clearly reflects the development of hypogene alteration products, such as kaolinite, illite, montmorillonite and mordenite, in the alteration halo.

The distributions of S, Ba, Cu and Zn and of Fe and Mn in the vicinity of the Harsit-Koprubasi mine are shown in figures 8 to 13 inclusive. Fe, S, Ba, Cu and Zn are the most abundant elements in the polymetallic ores while further Fe, together with Mn, are representative of the exhalative phase of the volcanogenic mineralization. Two conspicuously anomalous areas are evident. Anomaly A occurs over the known Harsit-Koprubasi orebodies while a second anomaly, anomaly B, is present for all elements 400 m southwest of the adit and beyond the known limits of the concealed orebodies. Both anomalies occur in the same lithological unit but appear to be separate and discrete. Younger volcanic units, such as the intru-

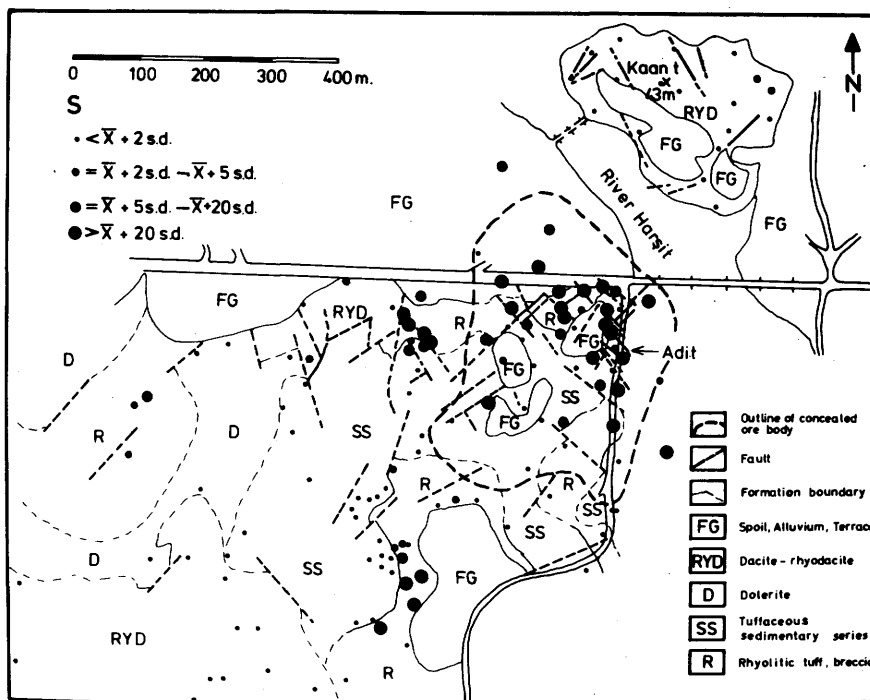


Figure 8.- Lithochemical distribution of S in the Harsit-Koprubasi mine area.

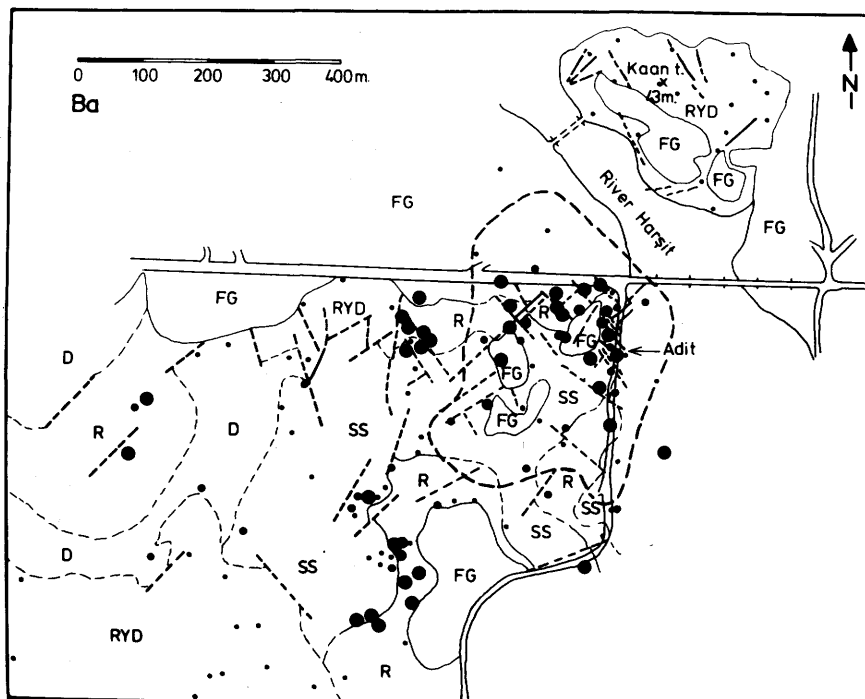


Figure 9.- Lithochemical distribution of Ba in the Harsit-Koprubasi mine area, Legend as shown in figure 8.

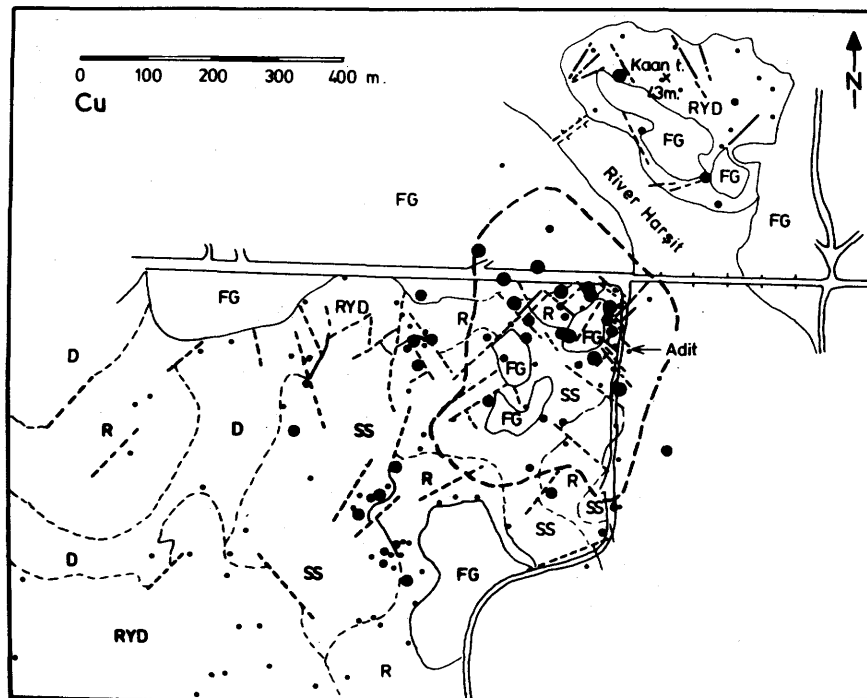


Figure 10.- Lithogeochemical distribution of Cu in the Harsit-Koprubasi mine area, Legend as shown in figure 8.

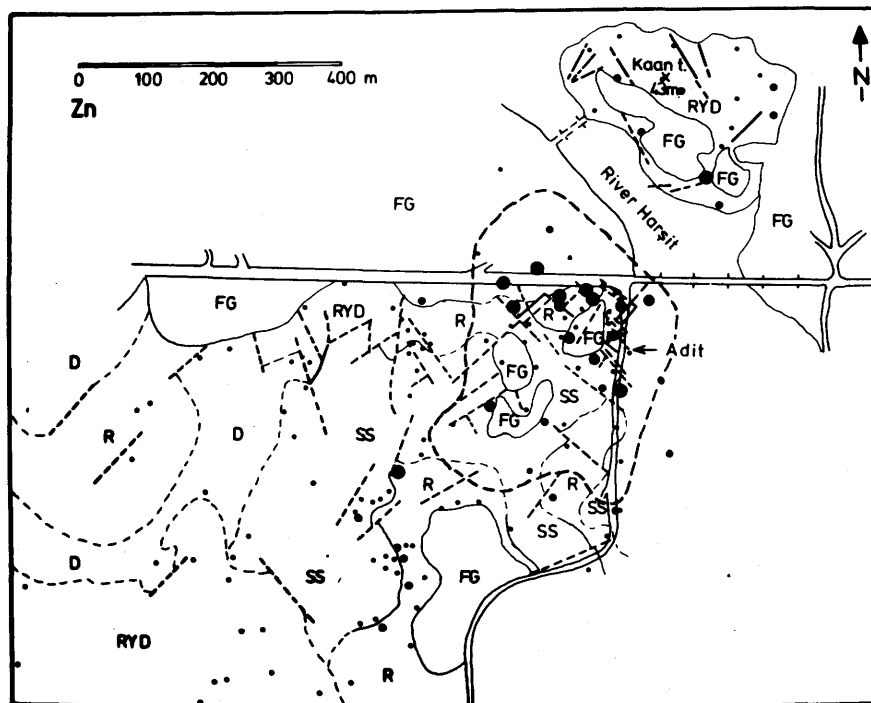


Figure 11.- Lithogeochemical distribution of Zn in the Harsit-Koprubasi mine area, Legend as shown in figure 8.

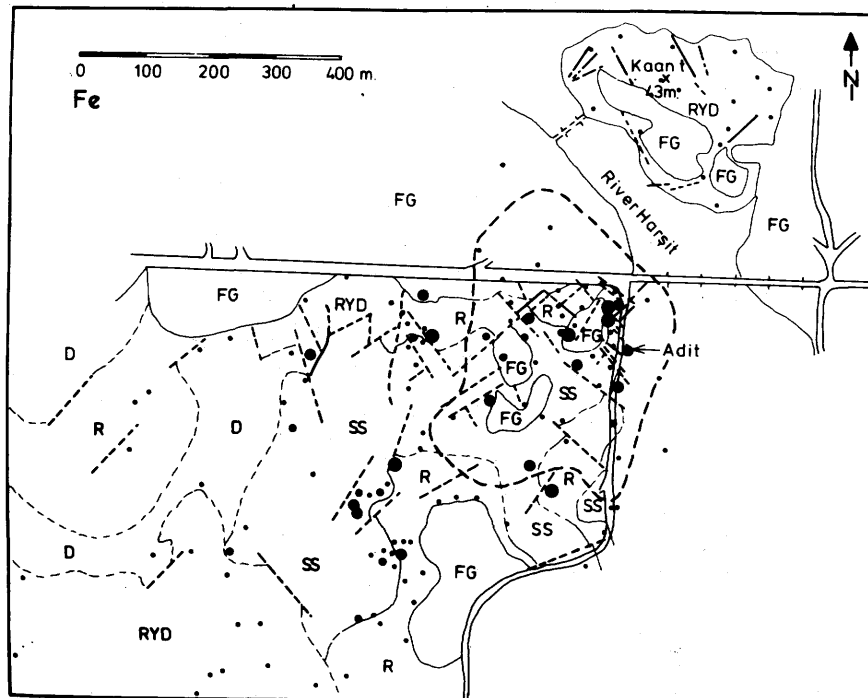


Figure 12.- Lithogeochemical distribution of Fe in the Harsit-Koprubasi mine area, Legend as shown in figure 8.

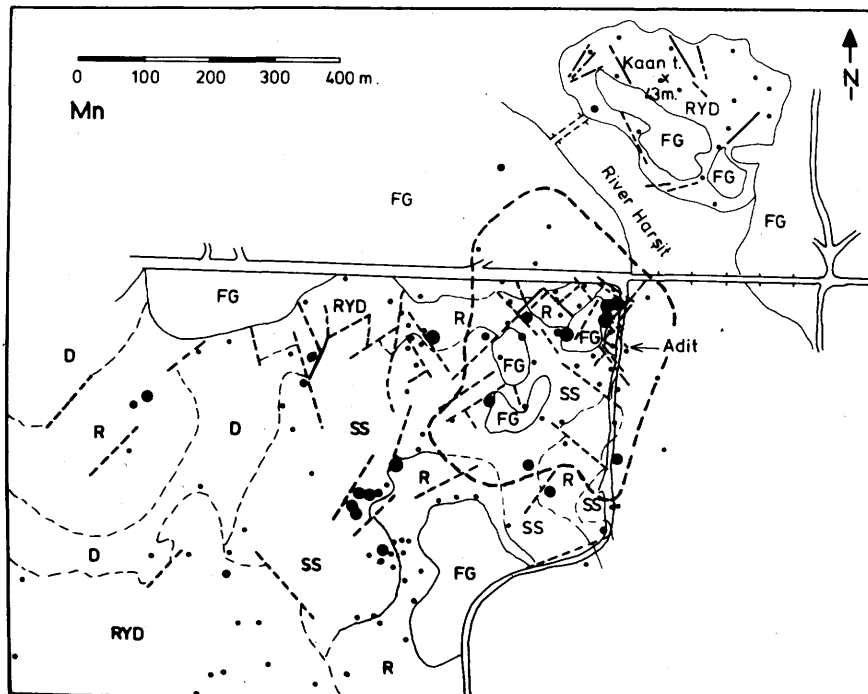


Figure 13.- Lithogeochemical distribution of Mn in the Harsit-Koprubasi mine area, Legend as shown in figure 8.

Table 4.- Analyses of unaltered acid volcanic rocks from the northern Harsit river area together with representative analyses of rocks from the hydrothermal alteration halo of the Harsit-Koprubasi ore deposit.

	1	2	3	4	5	6	7	8
SiO ₂	70.62	69.61	77.65	52.51	54.10	57.77	70.26	71.43
Al ₂ O ₃	14.81	15.07	12.12	36.05	29.50	26.54	15.31	11.69
Fe ₂ O ₃	2.59	2.97	1.44	4.81	1.06	1.05	1.52	0.96
MgO	0.52	0.33	0.51	0.07	1.89	2.72	2.45	0.35
CaO	2.22	3.00	1.61	0.00	0.06	0.30	1.58	1.97
Na ₂ O	2.62	3.96	1.69	0.00	0.19	1.34	1.27	1.29
K ₂ O	3.58	1.22	3.30	0.00	6.98	6.42	2.04	1.99
TiO ₂	0.32	0.12	0.24	0.42	0.38	0.29	0.31	0.20
MnO	0.06	0.11	0.03	0.10	0.02	0.08	0.07	0.02
S	0.05	0.03	0.03	0.08	0.60	0.44	0.05	0.13
P ₂ O ₅	0.10	0.22	0.09	0.00	0.03	0.04	0.01	0.03

1. Average dacite-rhyodacite (Egin *et al.*, in press).
2. Unaltered rhyolite, 53, (Egin, 1978).
3. Unaltered rhyolite, 59, (Egin, 1978).
4. Kaolinized tuff, H47-27m, assemblage I.
5. Sericitized tuff, H31-138m, assemblage II.
6. Illitic tuff, HI-66m, assemblage III.
7. Montmorillonitic tuff, 169, assemblage IV.
8. Mordenite-bearing tuff, 183, assemblage IV.

sive dolerites and the rhyodacites of the Upper Volcanic Cycle, contain no significant dispersion patterns. This further emphasises the co-eval nature of the mineralization and host rock. Localities which show anomalous values for one, or a restricted number of elements, may reflect contamination. This is exemplified near Kaan Tepe where Upper Volcanic Cycle rhyodacites show anomalous Cu and Zn levels. These are undoubtedly related to secondary dispersion from neighbouring spoil heaps (figs. 10 and 11). It is perhaps significant that these samples do not have anomalous S levels.

There is no reliable method to relate anomaly intensity to tenor of mineralization although BEUS & GRIGORIAN (1977) have shown that wider and more intense halos form around thick orebodies. Characteristics of the concealed massive ore, such as thickness

and depth to ore body are shown in figures 14a and 14b. Some relationship clearly exists between halo intensity and ore-thickness to the northwest of the adit. The absence or weakness of the anomaly southwest of the adit, however, suggests that overburden thickness also influences the anomaly. Figure 15 shows the thickness of the tuffaceous sedimentary series and figures 8 to 13 indicate that to the west of the adit, normal or weakly anomalous samples occur where this unit is thickest.

In the host rock the width of dispersion is such that Ba, S > CU > Zn > Fe > Mn. The relative abundances however differ markedly between the host rock and the hanging wall tuffaceous sedimentary series. Ba, S, Zn and, to a lesser extent, Cu occur in the host rock unit while Fe and Mn concentrate in the hanging wall, thus giving vertical zonation. Figure 16

shows that, from topographically controlled sampling in the flat-lying lithological units involved in anomaly B, Mn and Fe occur at higher levels than Ba. Co-variance of Ba and S (in barite), rather than between Fe and S, suggest that the Fe is not in a sulphide phase but is more likely occurring as an oxide together with Mn.

Dispersion is directly related to changes in the internal equilibrium of the ore-forming solutions, the mobility in a fluid transporting medium following the

sequence $Ba > Cu > Zn > Fe > Mn$ (BEUS & GRI-GORIAN, 1977). This is closely similar to the order of stabilities of these elements in the complexes described by BARNES & CZAMANSKE (1967). Lateral dispersion of Ba would thus be more extensive than Mn, which yields the smallest halo. In the vertical sense, however, the presence of Mn, with Fe, at higher stratigraphical levels than Ba, Cu or Zn is believed to be due to changes in temperature, pH and oxidation state of the ascending ore-fluids. In the immediate vicinity of sulphide deposition, in the high temperature reducing environment, the pH is low, while away from the sulphide zone conditions become more oxidising, weakly acid to alkaline, and temperatures are lower, enhancing precipitation of Fe and Mn. EGIN (1978) has determined homogenization temperatures from fluid inclusions present in the minerals sphalerite, barite and quartz. Temperatures from the lowermost stockwork ore, composed of quartz-pyrite veins, fall within a narrow range, between 260°C and 298°C, with a mean value of 285°C. They are the highest temperatures found within the deposits. Stockwork sphalerite occurring beneath massive, black ore has a mean temperature of 247°C with a range from 230°C to 272°C. Sphalerite from the massive ore yields a mean temperature of 228°C, although barite from the same part of the deposit averages 249°C. The baritic zone, overlying the massive, black ore, has yielded the lowest temperatures in the deposits. Barite from this zone averages 175°C. The data indicate a steep temperature gradient from the lower, quartz-rich stockwork ore to the upper baritic zone. The gradient is approximately 12°C/10 m. The solubility of barite is temperature dependent, precipitation taking place on cooling from any temperature. This is achieved as solutions move from the lower stockwork ore to the upper massive and baritic ores, barite thus being found close to the main orebody.

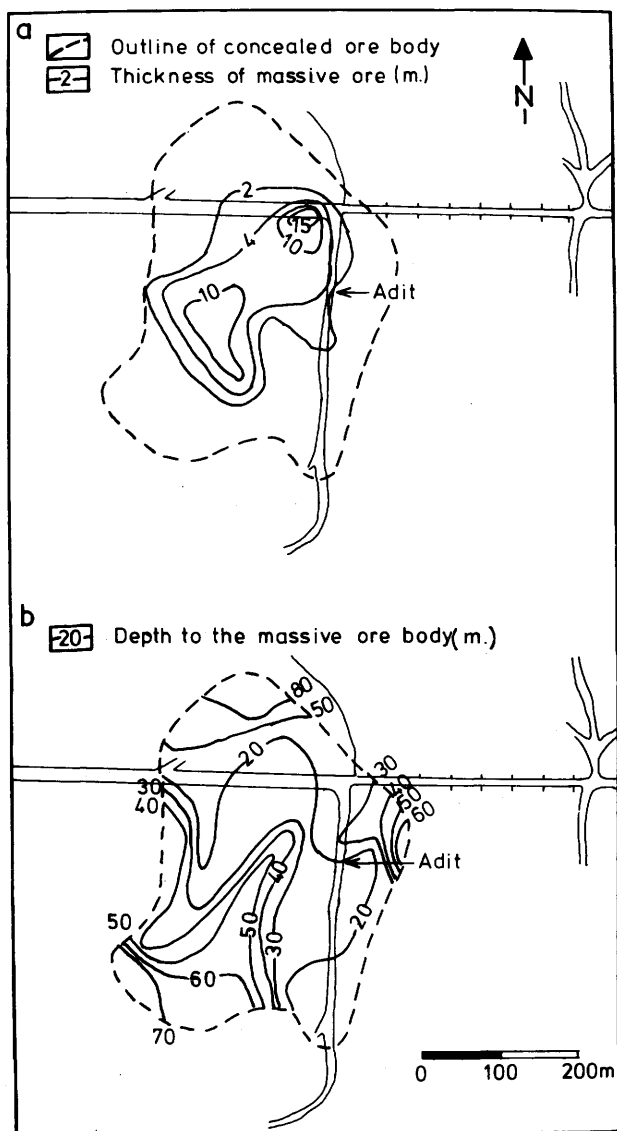


Figure 14

- a. Thickness of massive ore in the Harsit-Koprubasi mine
 b. Depth to massive ore in the Harsit-Koprubasi mine.

DISCUSSION

Wall rock alteration associated with massive, volcanogenic sulphides shows common characteristics. The hanging wall is relatively unaffected whereas the host-rock is extensively altered, usually forming distinctive halos. These may extend to 1200 m laterally and 450 m below the massive ore as observed by GOOD-FELLOW (1975) at the Brunswick n° 12 deposit. UTADA *et al.* (1974) have reported similar results from Japanese Kuroko deposits. Data presented by TUGAL (1969) for Lahanos, and by CAGATAY & BOYLE (1977) for Madenkoy/Cayeli indicate some-

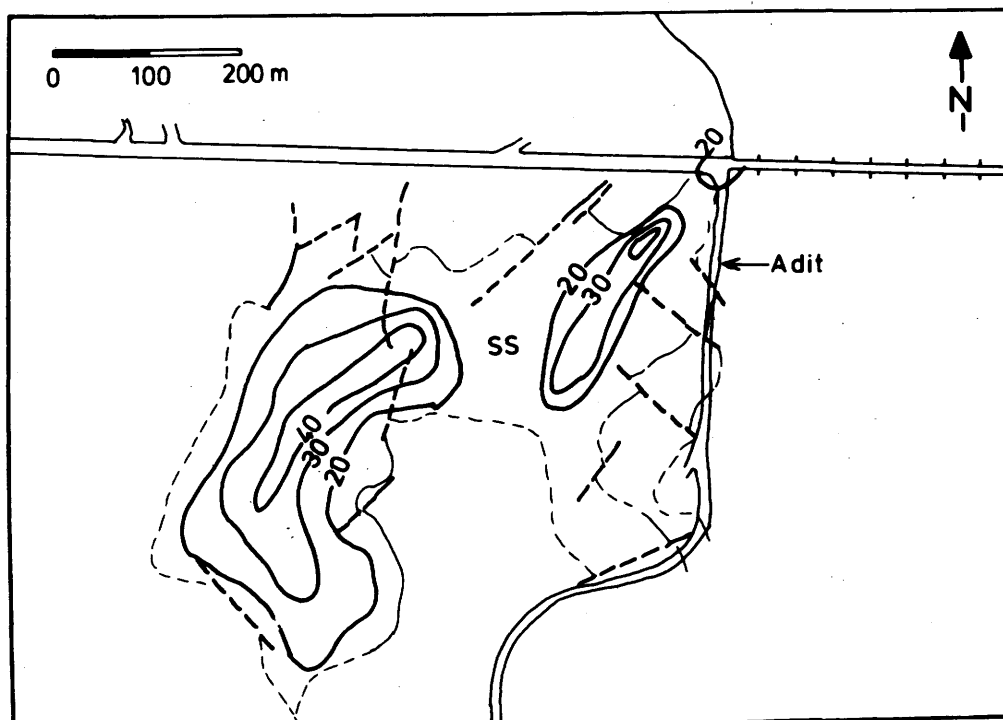


Figure 15.- Thickness, in metres, of the tuffaceous sedimentary series (SS) in the Harsit-Koprubasi mine area.

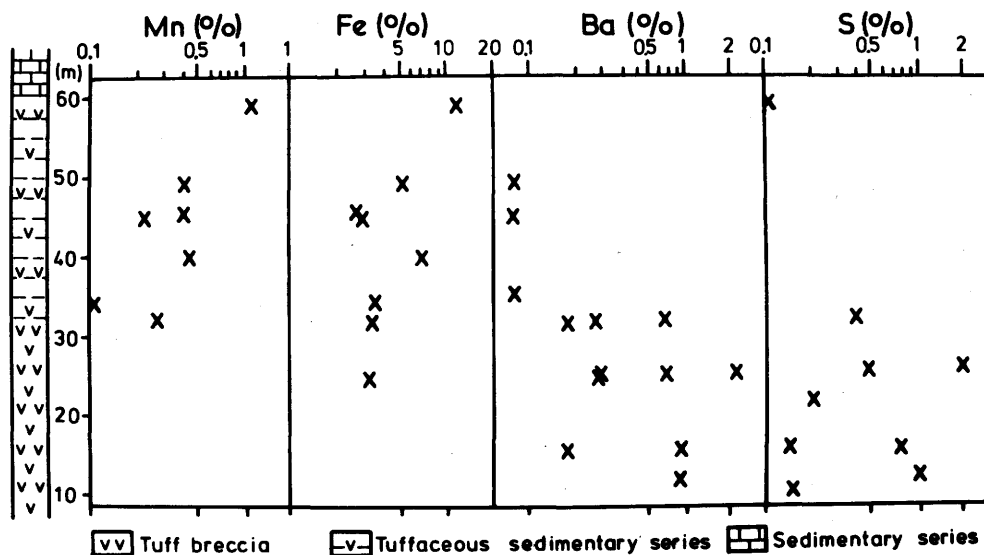


Figure 16.- Distribution of anomalous Mn, Fe, Ba and S within a vertical section of the host-rock (R) and tuffaceous sedimentary series (SS) from the Harsit-Koprubasi mine area.

what smaller halos of approximately 800 m by 800 m by 200 m.

Recently a number of studies have utilised litho-geochemistry in the search for massive volcanogenic sulphide ore-deposits. GOODFELLOW (*loc. cit.*) demonstrated that Mg, Mn and Fe increase while Ca and Na decrease in the intensely altered zone adjacent to mineralization at the Brunswick deposit, while OVCHINNIKOV & BARANOV (1971) have shown that Zn, Pb, Ag and Ba are enriched in the hanging wall, and Co, Mo and Bi in the footwall of the Rudnyy Altay and northern Armenia deposits. ISHIKAWA *et al.* (1962) concluded that Ag, Cu, Ni, Ba, Cr, V, Co and Pb contents decrease regularly with distance from Japanese Kuroko deposits and may be used as indicators of mineralization. SHIIKAWA *et al.* (1975), in a study of the Matsumine and Fukazawa mines in Akita prefecture, Japan, have revealed that Ag and Mo decrease gradually with distance from the ore while Ba, high in the main ore zone, is also enriched in the overlying lithic tuffs, where it is accompanied by Fe.

In a geobotanical survey POLLAK (1962) was able to demonstrate a Cu anomaly over the Lahanos orebody. TUGAL (1969) considered the dispersion of 25 elements at Lahanos but concluded that primary geochemical dispersion patterns were of doubtful value. At Cayeli, CAGATAY & BOYLE (1977) showed that F, As, Pb, Zn and Cu have primary halos with high anomaly contrasts in the host rock, they suggested these elements could be used as directional vectors during drilling programmes. They further showed that some, or all, of the elements As, F, Cu, Pb, Zn, Cd, Ag and Ba produced significant halos in lithic tuffs overlying the ore-deposit, and even in the succeeding Upper Basic Series. Our evidence, given above, also indicates that hanging-wall alteration is evident, as at Cayeli, and therefore may be present more widely in the eastern Pontids.

Exhalative Mn mineralization is common in the eastern Pontids. With limited exceptions, however, such as the Peronit deposits, this type of mineralization is not shown to be associated with sulphide ores. Further investigation of the Mn occurrences, together with ferruginous cherts and hematitic tuffs, may prove their association with underlying, concealed, sulphide deposits. Detection of litho-geochemical Mn and Fe anomalies may provide further localities worthy of detailed investigation.

CONCLUSIONS

Investigations of massive, polymetallic sulphide ore-deposits in the northern Harsit river area, indicate that an effective exploration programme for buried or "blind" massive sulphides should incorporate a combination of stratigraphic, structural, mineralogical and litho-geochemical considerations.

The following conclusions may be made :

1. The morphological and mineralogical zonation of massive polymetallic orebodies, such as Harsit-Koprubasi, indicate that careful re-evaluation of deposits previously classified as vein type or as exhalative manganese mineralization may lead to discovery of associated massive ore.
2. Massive sulphide deposits of the northern Harsit river area and of the eastern Pontids in general are closely related to the terminal phase of the Upper Cretaceous, tholeiitic, Lower Volcanic Cycle. The host rock is the dacitic-rhyolitic lava, tuff and breccia formation characterized by a high proportion of pyroclastic rocks. The distribution of Zr and Nb within this unit provides a possible means of locating explosive centres which may, in turn, be related to mineralization.
3. Both the host rock and its contained mineralization show a strong spatial association with the predominant fault directions which are orientated NW-SE and NE-SW. Although direct control of mineralization, in the sense shown by AKINCI (1974) at Bulancek, cannot be proved, the spatial association suggests that the faults provided channelways for magmatic activity and mineralization. A third direction of faulting, N-S in strike, may also have importance in localizing ore-deposits, intersections of two or more fault trends providing ideal loci for magmatism and mineralization.
4. Wall rock alteration is widespread in the host-rock associated with massive ore-deposits and is also evident although less strongly developed, in the hanging wall. Four alteration assemblages have been recognized. They are an inner advanced argillic zone, followed outwards by sericitic, intermediate argillic and propylitic zones. The propylitic zone can be subdivided into an inner montmorillonite-rich assemblage and an outer assemblage characterized by the presence of the zeolite mordenite.

5. Host rock horizons, and the hanging wall tuffs and tuffaceous sediments, require detailed litho-geochemical analyses for Al, Mg, Na, K, Ca, S, Ba, Zn, Cu, Fe, and Mn. The small size of the orebodies, together with their frequency in a given area, suggest that the surveys must be made on a local scale. Reconnaissance surveys, either stream sediment, soil or litho-geochemical in nature, may well overlook such small targets, or be insufficiently discriminating.
6. Within the host rock Mg, Ca and Na increase, while Al and K decrease outwards from the orebody. The lateral dispersion of other elements is such that $S, Ba > Cu, Zn > Mn, Fe$.
7. Anomalous levels of S, Ba, Zn, and to a lesser extent Cu are confined to the host rock while anomalous levels of Mn and Fe occur in the hanging wall tuffaceous sedimentary series, thus giving a vertical zonation. Investigations in the vicinity of the Harsit-Koprubasi mine have revealed a distinctly anomalous area beyond the limits of the known orebodies. This anomaly may well represent a further discrete massive sulphide lens.

ACKNOWLEDGEMENTS

The authors wish to thank the Mineral Research and Exploration Institute (M.T.A.), Ankara, for providing facilities in the field, Dr. Ömer AKINCI and Mr. Mithat KAYAALP were particularly helpful. DMH wishes to thank Dr. Sadrettin ALPAN, former General Director, M.T.A., for arranging and financing a visit to the area, and for his general interest in the project. DE acknowledges a Research Studentship provided by the Turkish Ministry of Education and M.T.A. We are indebted to Mr. R. PHILLIPS for many discussions of the Pontid mineralization and to Professor C.C. BRISTOL and Dr. N. FUJII for discussions of massive, volcanogenic sulphide deposits and for critical reading of the manuscript.

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