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THE STRATIGRAPHY, SEDIMENTOLOGY AND ORIGIN OF THE COPPER (SILVER-URANIUM) DEPOSITS FOUND IN AN AREA BETWEEN DELİCE AND YERKÖY (MIDDLE ANATOLIA)

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ABSTRACT.— The stratigraphic position, sedimentologic characteristics and origin of the copper deposits of Oligocene (—Miocene?) age are investigated in an area between Delice and Yerköy, on the northern side of Delice river. Copper mineralization is observed mainly in three different stratigraphic positions in the region. The first type is the native copper ore, found in red and gray colored continental sandstones and conglomerate which overlie marine fossiliferous (Middle Eocene) limestones. The second type is the malachite ore, found in Oligocene (—Miocene?) units of the Toprakhk tepe formation which consists of red sandstones, conglomerate and mudstones. This ore is restricted into the fine-grained, gray-colored sandstone and is rich in carbonized plant remains. The third type is the primary native copper and malachite ore found at the upper parts of the Toprakhk tepe formation. While the native copper mineralization is strictly associated with fault zones and slickensided surfaces, the malachite mineralization occurs in the form of a cement, binding mostly the aetritic volcanic material. Malachite type mineralization represents point bar and flood plain environmental condition of sedimentation. The local occurrence of malachite ore together with plant remains in gray-colored sandstone of the red-bed series indicates that this type of ore was deposited primarily (probably as a sulfide or native copper or malachite) during the deposition of the host rock material under chemically reducing conditions. On the other hand, the native copper ore is supposedly an epigenetic type and related to the tenaonal and compressional forces. Cuprite and malachite found with native copper was formed secondarily under surface conditions.

INTRODUCTION

Sedimentary rocks, the age of which are assumed generally as Oligo-Miocene, cover large areas in Central Anatolia. There are many scattered copper exposures (Fig.l) in these rocks. These exposures are mostly concen-

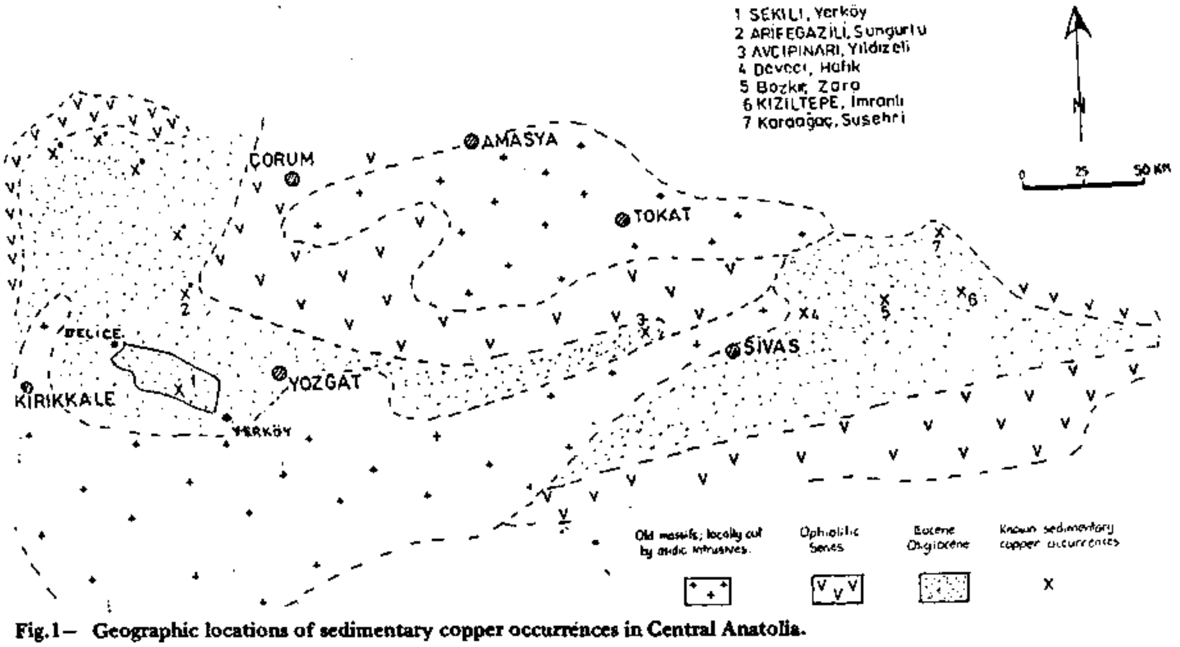


Fig.1— Geographic locations of sedimentary copper occurrences in Central Anatolia.

trated in the Çankırı-Çorum basin and in the vicinity of Sivas. These exposures (or prospects) which are known as red-bed type copper occurrences as they are found in red-colored fluvial deposits, show great lithologic, sediirientologic and some stratigraphic similarities to other red-bed type-occurrences in other parts of the world (for example, White Pine in Michigan (Hamilton, 1967), Nacimiento in New Mexico (Woodward et al., 1974) Corocoro in Bolivia (Ljungren and Meyer, 1964) and San Bartolo in Chile (Flint, 1986)).

The purpose of this article is to present information on the stratigraphic situation, sedimentologic characteristics and mechanisms of formation of the copper occurrences exposed between Delice and Yerköy (Fig.1, no.1). In this study, two 1: 25 000 scale geologic map sheets are prepared but as the mineralization is exposed over a large area, the geologic mapping is later expanded to cover a 350 km^2 area the boundaries of which are marked by Delice town in the west, Yerköy town in the southeast, Delice river in the south and Salmanlı village in the north. All the geologic information is compiled on a 1: 100 000 scale Kırşehir 1-32 sheet (Fig.2). During the field work numerous samples are taken to make petrographic, geochemical and paleontologic investigations.

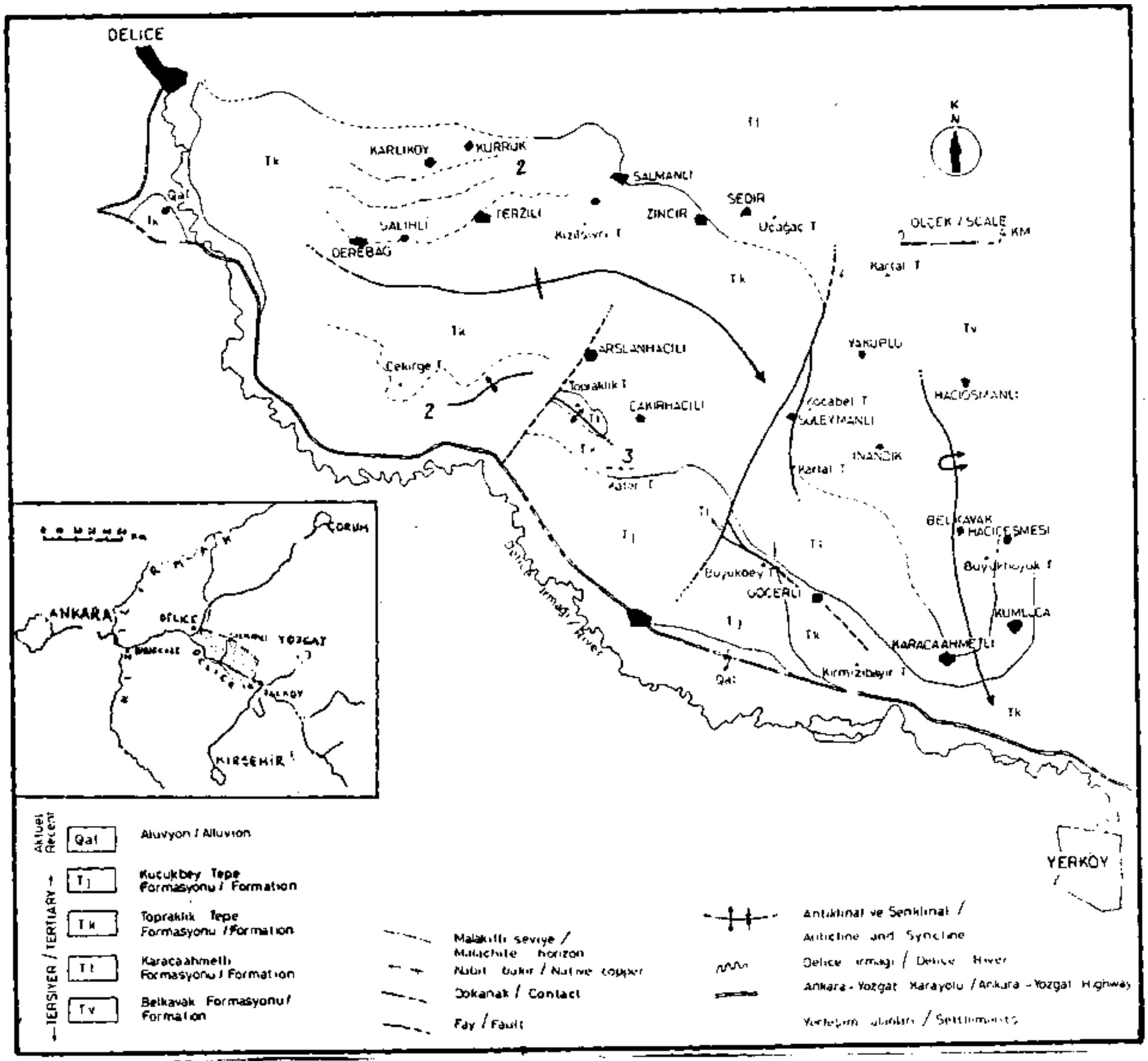


Fig.2— Geological map of the area between Delice and Yerköy (Kırşehir İ—32 sheet).
1— First ore type: Hacı Verim (Göçerli) occurrence; 2— Second ore type: Çekirge tepe and Terzili occurrences; 3— Third ore type: Cenik çayı occurrences.

RED-BED TYPE COPPER DEPOSITS

Red-bed type copper deposits are found in thick, red, purplish brown sandstones, siltstones, mudstones and sometimes in dolomitic rocks, generally located close to the evaporitic series and they are roughly concordant with their surrounding succession with a thickness varying from a few millimeters to a few meters, lateral extension reaching to several kilometers and occurring in the form of lenses and layers. The color of zones where the mineralization is found is mostly different than the underlying and overlying red deposits and is usually gray or greenish-gray. The mineralized zones almost always contain carbonized plant remains. The mineralized gray sandstones which do not contain carbonized material is generally associated with shales rich in organic matter.

The red arenitic, arkosic material and shale are derived from the surroundings. The red color of the sedimentary rocks is the result of the oxidation of ferrous iron to ferric iron leading to the formation of hematite as coatings around the grains or as a cement between them.

The most important minerals of the red-bed type deposits are copper sulfide and copper-iron sulfide minerals. The major primary minerals are chalcocite and pyrite. These deposits contain varying amounts ofchalcopyrite, bornite, native copper, covellite, digenite, native silver and uraninite. Gangue minerals are quartz, feldspar, chlorite, illite, barite, gypsum, anhydrite and dolomite which are contributed mostly from the host rock.

Bastin (1933) gives Greta and Magnum (Oklahoma) and Nacimiento (New Mexico) as examples of such deposits. More recent investigations (Rose, 1976; Gustafson and Williams, 1981; Haynes, 1986 a) classified some of the famous deposits such as Kupferschiefer of Germany and Poland, Roan in Zambia and Zaire, Dzhezkazgan in the USSR and White Pine in the USA, as stratiform, red-bed type copper deposits. Haynes (1986 6) listed the various characteristics of the host rock which contain this type of deposit in a table (Haynes, 1986 *b*, Table 1) claimed that the depositional environment was one between shallow lacustrine and sabkha (Fig.3).

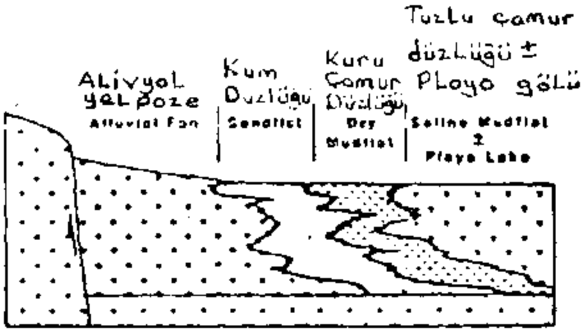


Fig.3— Section showing closed basin environment where sedimentary copper ores are deposited (taken from Haynes, 1986).

Flint (1986) suggested that the depositional environment was not only a low-energy environment but also the late orogenic molasse basins giving as examples the famous Coracora deposit in Bolivia, the Coloso deposit which is found in conglomerates in Northern Chile and the San Bartolo deposit in Chile. Among these, for example, the San Bartolo deposit is found in continental Tertiary sediments representing a deposition into a closed basin in an arid climate, an alluvial fan, playa environment and lacustrine facies conditions. The mineralization which is in the form of native copper, cuprite and atacamite is in sandstone and constitutes thin layers. It is deposited in a high-energy playa marginal sandflat environment (Flint, 1986). The ore minerals constitute the matrix of lithic arkose and replaces the carbonate/sulfate cement of the rock. Native copper is found as sheets, filling the tectonic fractures as in Corocoro (Flint, 1986).

There are different opinions on the formation of red-bed type copper deposits. These opinions can be grouped in two major catagories: epigenetic and syngenetic. Epigenetic opinion defends that mineralization forms following the completion of sedimentation as a result of diagenetic compaction. Some of the supporters of the epigenetic opinion claim that copper deposits are formed during bacterial sulfate reduction (Haynes, 1986 a) whereas some others propose a formation similar to the formation of "roll-type" uranium deposits (Shockey et ah, 1974) and still some others suggest a mechanism where copper-rich solutions replace previously formed biogenie pyrite and anhydrite (Haynes, 1986 a). According to Rose (1976) a substantial amount of salty and chloride-rich connate water was mobilized from the sediments during the diagenetic compaction which dissolved the copper existing in the rea-bed series and deposited them where the oxidation potential was low. The investigations of Haynes (1986 a) showed that chalcocite was deposited at the uppermost part (a zone of maximum 50 cm) of the depositional surface as a result of sulfate reduction by bacteria. The information on porosity and permeability behaviour of shales and sandstones under compression shows that the copper transporting solutions migrated along the stratification, not across it. The syngenetic opinion finds its support from the stratiform nature and concordant appearance of the ore with the walls of the host rock. In literature, the formation of syngenetic ore is explained by the influx of metal-rich fresh water into a chloride-rich lake or lagoon where the metals are deposited when they come into contact with a reducing environment (Dunham, 1964; Haranczyk, 1970; Garlick, 1974).

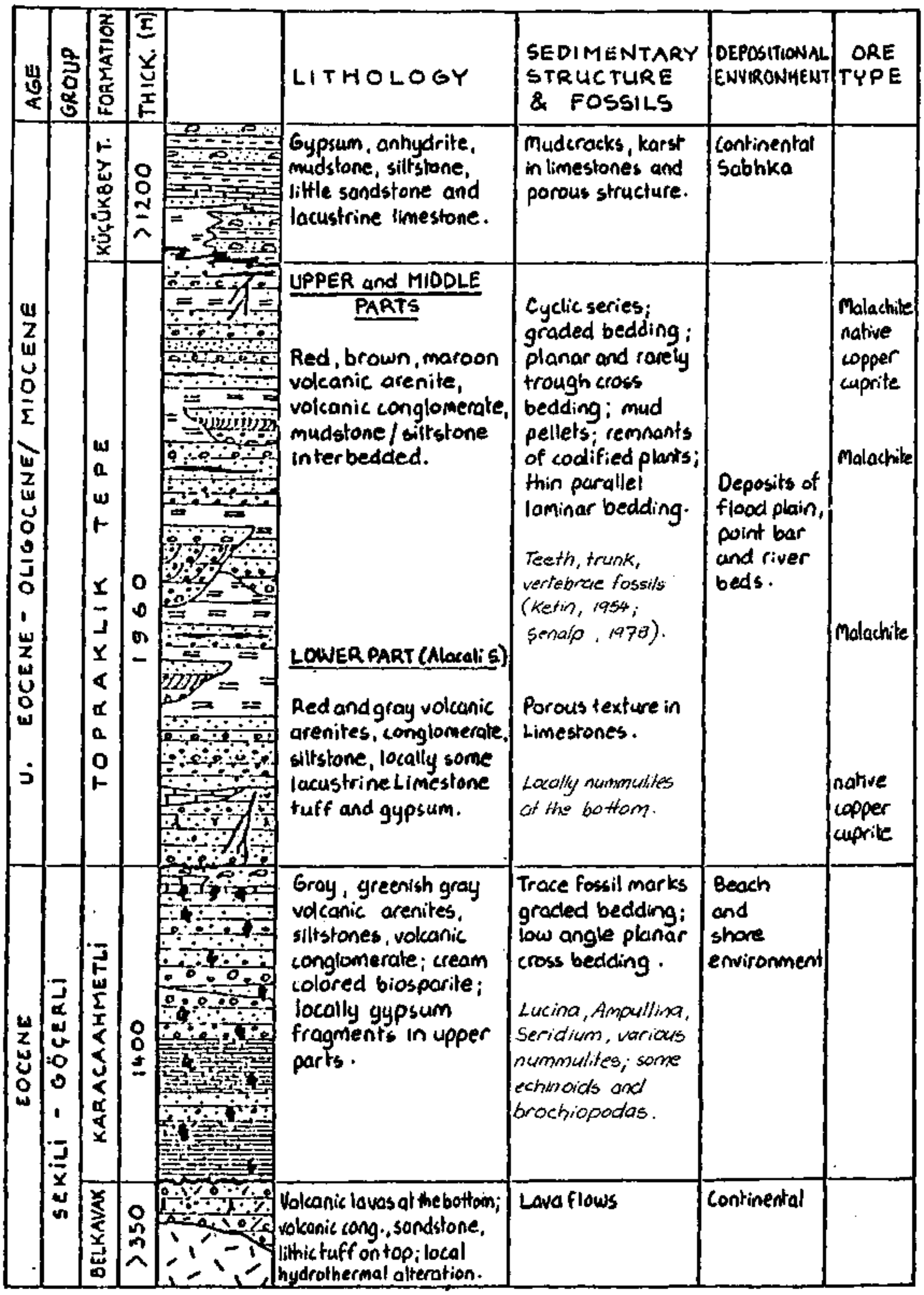
PREVIOUS WORK

There is no publication in the literature on the geology and formation of copper occurrences found in the study area. Some of these occurrences were pointed out to the author by Mr. Güner Aytuğ during a one day field trip in 1975 who worked for the Turkish Iron and Steel Works. Other than this unpublished investigation, the only other two unpublished reports are Teşrekli and Pehlivanoğlu's (1982) short notes on the occurrence of copper in the region and Ketin's (1954) report on the regional geology. A firm (the name of which is probably İZBAK Mining and Smelting Limited Corporation) operated some of the copper-carbonate zones in the early 1970's for a short time and constructed some leaching ponds on the Terzili road. The crushing and sieving machinery is dismantled and the leaching ponds are now left in ruin.

GEOLOGY-STRATIGRAPHY

The Middle Eocene Sekili-Göçerli group forms the base of the stratification (Fig.4) in the study area. This group consists of Belkavak and Karacaahmetli formations and is exposed in the northern and eastern parts. The Sekili-Göçerligroup represents the northern flank of an approximately EW trending syncline between Delice-Salmanh-Sedir and underlies the red Topraklık tepe formation further south. The Belkavak formation consists of volcanic lavas (mainly andesite and to a lesser extent rhyolite and basalt), volcanic conglomerate and volcanic sandstone. This formation is interbedded with agglomerate, breccia and tuff layers further east between Yerköy and Yozgat. Various sandstones and limestones of fossil-rich marine Karacaahmetli formation overlies the Belkavak formation partly with an unconformity. The uppermost parts of the Karacaahmetli formation is characterized by beach sands with trace fossils and fossiliferous shallow sea limestones, and underlies the Topraklık tepe formation with a low-angle (15 degree) unconformity.

At the end of Middle Eocene the sea covering the study area completely retreated and to Late Oligocene (or Miocene) only the fluvial deposits of the Topraklık Tepe formation and lacustrine evaporites, limestones and



AGE	GROUP	FORMATION	THICK. (m)	LITHOLOGY	SEDIMENTARY STRUCTURE & FOSSILS	DEPOSITIONAL ENVIRONMENT	ORE TYPE
U. EOCENE - OLIGOCENE/ MIOCENE		KÜÇÜKBEY T.	>1200	Gypsum, anhydrite, mudstone, siltstone, little sandstone and lacustrine limestone.	Mudcracks, karst in limestones and porous structure.	Continental Sabhka	
		TOPRAKLIK TEPE	1960	UPPER and MIDDLE PARTS Red, brown, maroon volcanic arenite, volcanic conglomerate, mudstone / siltstone interbedded. LOWER PART (Alacali S) Red and gray volcanic arenites, conglomerate, siltstone, locally some lacustrine Limestone tuff and gypsum.	Cyclic series; graded bedding; planar and rarely trough cross bedding; mud pellets; remnants of codified plants; thin parallel laminar bedding. *Teeth, trunk, vertebrae fossils (Ketin, 1954; Şenalp, 1978).* Porous texture in Limestones. *Locally nummulites at the bottom.*	Deposits of flood plain, point bar and river beds.	Malachite native copper cuprite Malachite Malachite native copper cuprite
EOCENE	SEKİLİ - GÖÇERLİ	KARACAAHMETLİ	1400	Gray, greenish gray volcanic arenites, siltstones, volcanic conglomerate; cream colored biosparite; locally gypsum fragments in upper parts.	Trace fossil marks graded bedding; low angle planar cross bedding. *Lucina, Ampullina, Seridium, various nummulites; some echinoids and brochiopodas.*	Beach and shore environment	
		BELKAVAK	>350	Volcanic lavas at the bottom; volcanic cong., sandstone, lithic tuff on top; local hydrothermal alteration.	Lava flows	Continental	

Fig.4— Stratigraphic column of the Delice-Yerköy area.

clastic sediments ofKüçükbeyTepeformation were deposited. All these units were later folded, steepened (Fi-g.5), overturned on the southeastern flank (Fig.2) and faulted in the.eastern part of the study area.

The copper deposits which this article deals with are all confined to the Topraklık tepe formation.

Fig.5— (a) Steepining and (b) overturning of the interbedding of the red and gray colored series located at the lower parts of the Topraklık tepe formation.

ORE TYPES

Three different ore types are recognized based on their stratigraphio location These are:

1-The epigenetic native copper (f

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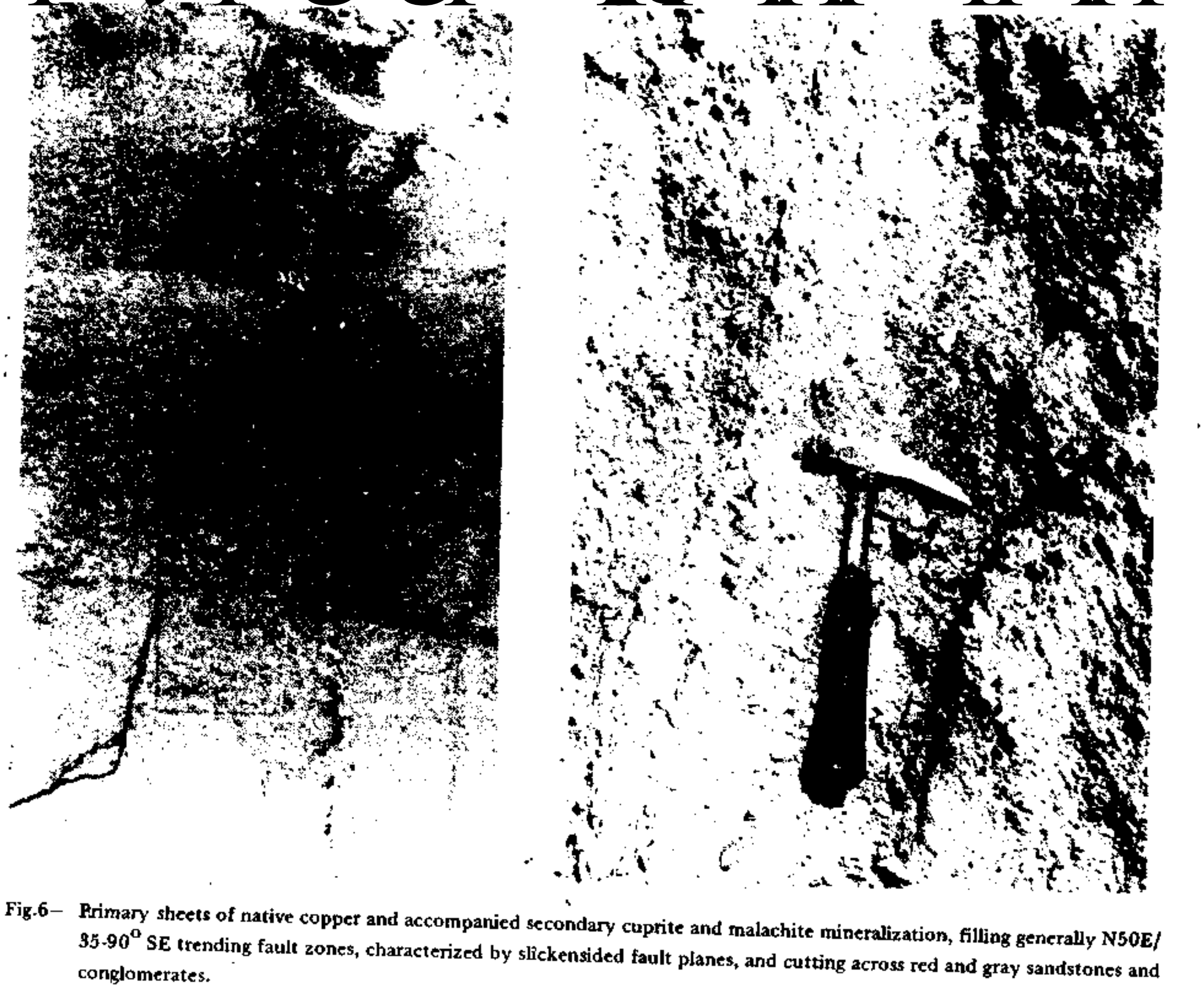


Fig.6— Primary sheets of native copper and accompanied secondary cuprite and malachite mineralization, filling generally N50E/ 35-90° SE trending fault zones, characterized by slickensided fault planes, and cutting across red and gray sandstones and conglomerates.

Fig.7 — The separate malachite horizons, the thickness of which hardly exceed a few centimeters. They are concordant with the bedding of the host rocks.

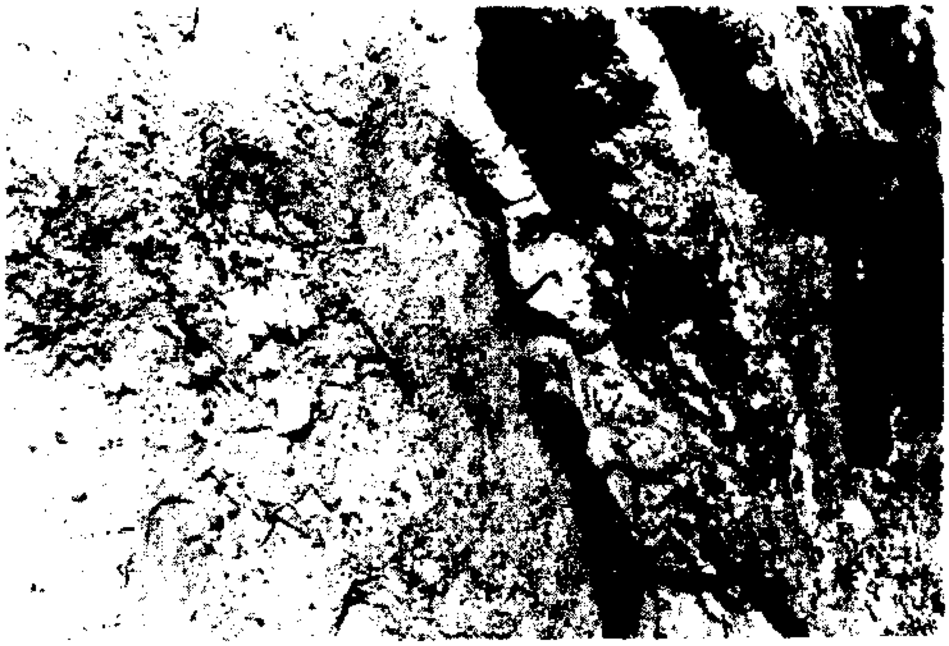


Fig.8 — The appearance of malachite as cement and concretions in sandstones found at the base of red conglomerates (Göçerli occurrence).

Fig.9— Slickensided fault planes containing native copper mineralization and their close-up view.

Sandstones and conglomerates which host the first ore type show graded bedding (Fig. 10). They are overturned and dip nearly vertical (Fig.5). Sandstones at the bottom of this formation contain gypsum fragments up to 2 x 5 cm in size.

Native copper (Fig.11) is the most important primary mineral in this tectonically controlled ore type. Investigations under the microscope show the presence of small amounts of chalcocite inclusions in the native

Fig.10—Graded bedding in sandstones and conglomerates, host for the native copper mineralization.

copper. Cuprite and malachite which widely associate with native copper are formed secondarily as a result of oxidation at the surface. Some of the malachites which are locally found as concretions in sandstone are probably primary occurrences.

The presence of wedges and lenses of conglomerate in gray-colored sandstones, the cyclic and gradual transition from coarse to fine grain in the host rock, the presence of dark-colored heavy mineral lamination in sandstones, the occurrence of cross-bedding, absence of fossils and interbedding of fine grained red horizons with gray colored sandstones all indicate a fluvial depositional environment.

The second ore type is found in the gray-colored, fine-grained sandstones rich in plant residue. Earthy malachite and insignificant amounts of azurite are the major minerals. Mineralization is either in the form of cement binding the fine/medium sized grains of sandstones which contain a high percentage (up to 85 percent) of volcanic rock fragments or in the form of replacements around the carbonized plant residue (Fig. 12).

The second ore type is exposed west of the study area and constitutes three separate layers on the southern flank of the roughly E—W trending syncline (Fig.4), The thickness of the mineralized sandstone layers vary from 10 to 200 cm and extends intermittently several kilometers along the strike.

The presence of cyclic graded bedding, cross-bedding (sometimes trough-bedding) (Fig.13), mud pellets (Fig.14), thin parallel laminations (Fig.14 and 15), carbonized plant remains and the absence of marine fossils suggest that the mineralization is related with fluvial deposition and took place in point bar and flood plain environments.

The occurrence of mineralization in gray-colored sandstones enclosed in red series and the presence of organic remains only in the gray-colored horizons indicates the prevalance of temporary reducing conditions in .•!

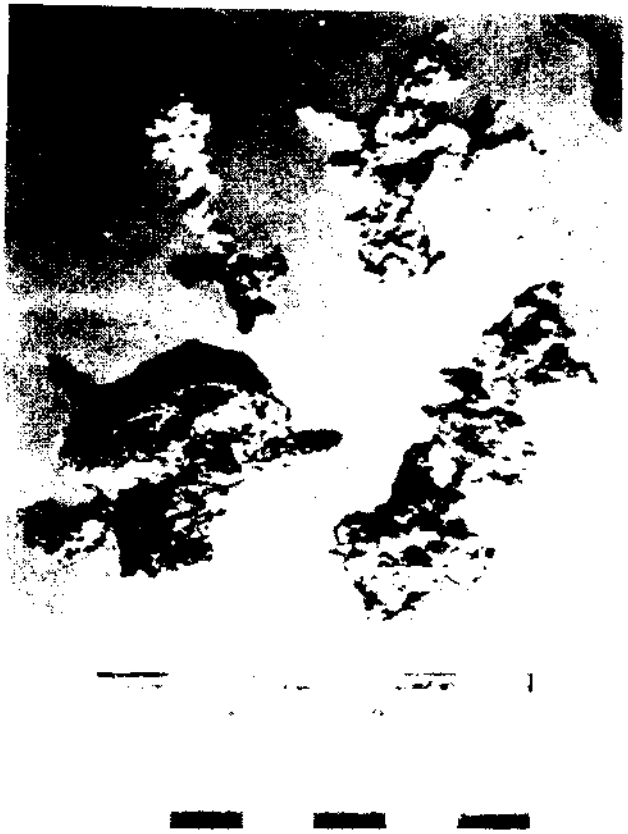


Fig.11 – Sheets of native copper; their thickness varies from 1 to 10 mm.

Fig.12 – Coalified plant remains which played an important role in the precipitation of second ore type. Mineralization replaces the plant residue from outside to inside and cements between the grains of enveloping sandstone.

Fig.13– Facies changes and sedimentary structures in mineralized host rock; bottom laminated fine-grained sandstones are overlain by sandstones with planar cross-bedding and top conglomerate layer.

Fig.14– Holes of mud pellets in cross bedded thin parallel laminated sandstones.

Fig. 15— Fine grained sandstones characterized by heavy mineral (magnetite) laminations.

Continental oxidizing environment. The evidence gathered so far suggests that malachite has a primary origin, however, in the absence of bore hole samples it is still not impossible to claim that malachite is formed after the surficial alteration of other copper (oxide, sulfide or native) minerals.

The third ore type found where the Cenik stream cuts across the Çakırhacılı village road is exposedin roughly E—W trending, 70° S dipping, 6 m thick and 10-15 m long sandstones and conglomerates (Fig.8). Mineralization, the thickness of which is 75 cm, is in the form of malachite filling between the coarse grains of red sandstone. Under this horizon the fine-grained, laminated red sandstones contain sheets of native copper (Fig.16) along the fault planes trending parallel to the bedding. There are mine dumps and collapsed declines indicating that the native copper was previously mined.

Gypsum-anhydrite layers of the Küçükbey Tepe formation come over the mineralized zone eleven meters south. The spring water in the vicinity is not potable as it is bitter and salty. The Küçükbey tepe formation contains a rock salt deposit which is operated by the Monopoly Administration 2.5 km south of Sekili.

CHEMICAL ANALYSES

Several rock (grab) and stream sediment samples are taken and analysed for Cu, Ag, An, Zn, Co, Ni and Mo and four of them for uranium. Only the results of Cu, Ag and U3O8 are given here and shown on geologic and stratigraphic sections in Figures 17, 18 and 19. The present data indicates the existence of *A* significant positive correlation among copper, silver and uranium.

Analytical results of stream sediment samples collected from the dry streams of the Hacı Verim (Göçerli) occurrence are shown in Figure 20. All the analyses except uranium were made by Perkin-Elmer's atomic absorption spectrophptometer in the Rock Chemistry Laboratory of the Geological Engineering Department of Hacettepe University. The detection limits of copper and silver are 5 and 1 ppm respectively. All the uranium analysis and some of the silver and gold analyses are done in the General Directorate of Mineral Research and Exploration (MTA).

Fig. 16—Sheets of native copper collected from fault planes cutting across red colored fine grained sandstones; outer parts of some of the native coppers are partly altered to cuprite and malachite.

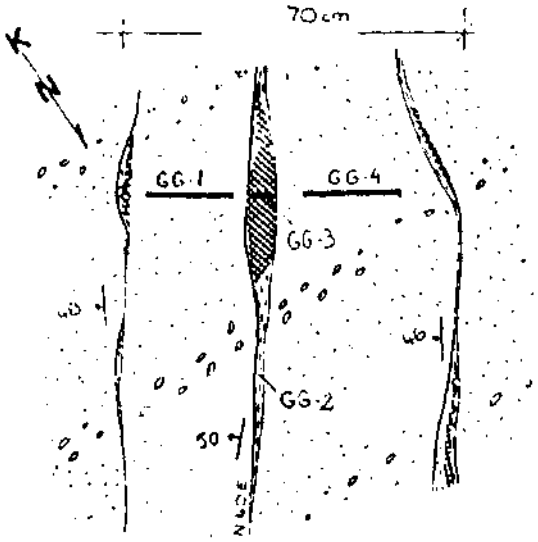


Fig. 17—Distribution of copper and silver (ppm) in channel samples collected from the traverses laid perpendicular to the mineralized veins in the Hacı Verim (Göçerli) occurrence.

GG-1: Cu 117, Ag 1; GG-2: Cu 8461, Ag not analysed; GG-3: 447000, Ag 23; GG-4' Cu 253, Ag1.

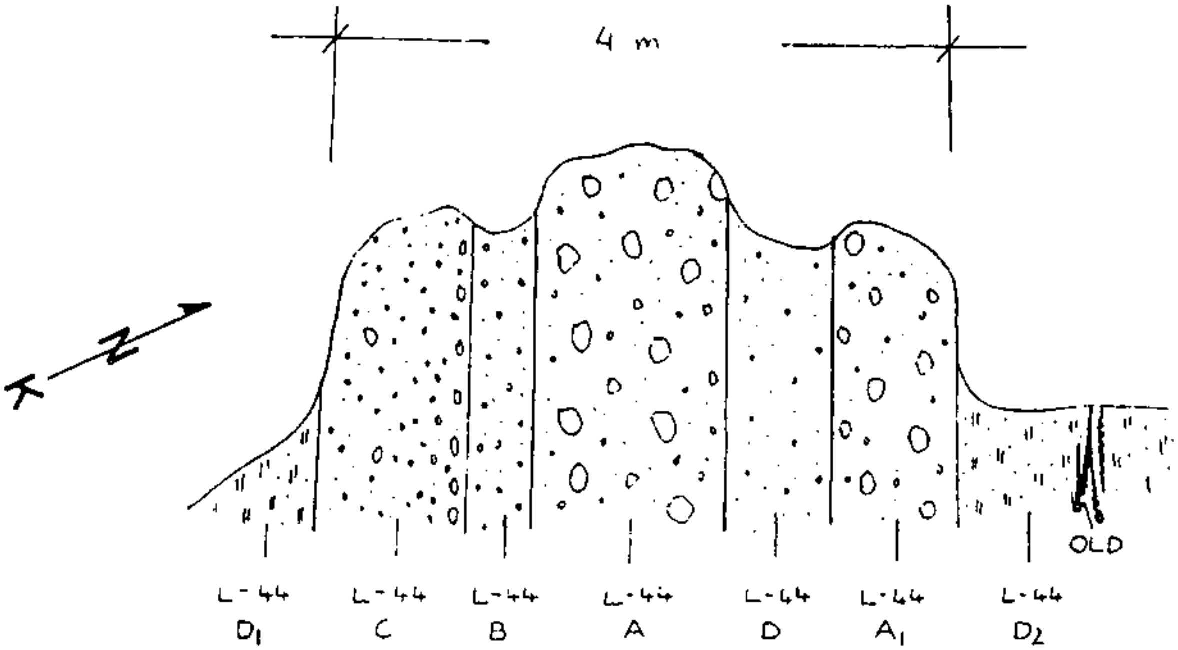


Fig.18—Distribution of copper, silver and uranium (ppm) in various sandstones and conglomerate layers in the Cenik çayı occurrence. L—44 A: Cu 972, Ag 3, U_3O_8 13; L—44B: Cu not analysed, Ag 1; L—44 C: Cu 11000, Ag 1; L—44d_1: Cu 5, Ag 1; L—44d_2: Cu 45000, Ag 9; OLD: Cu 33000, Ag 10.

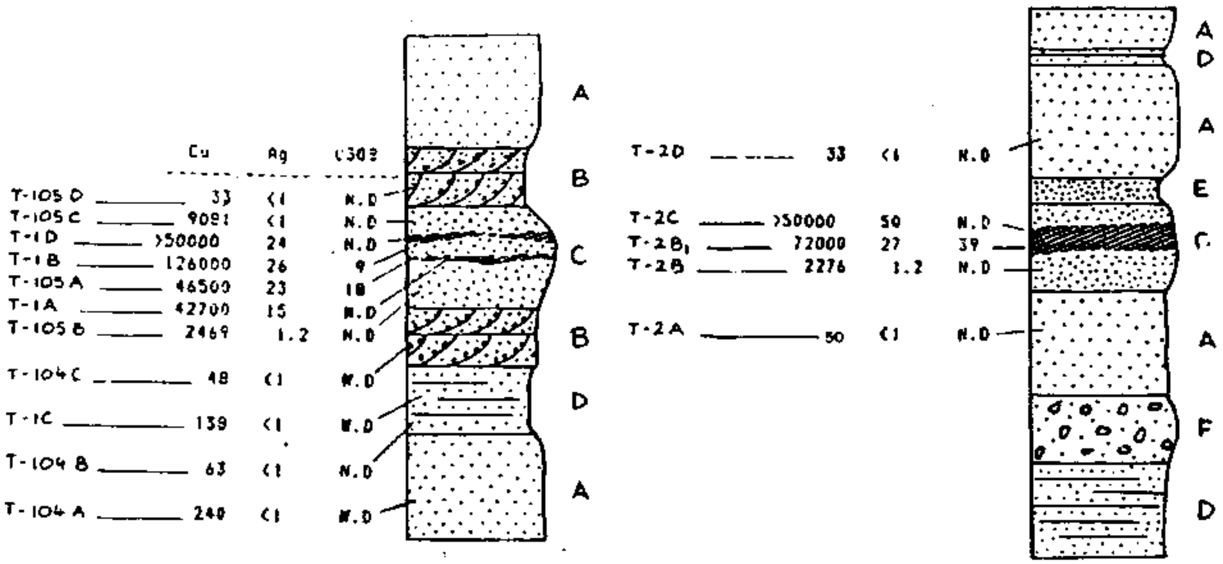
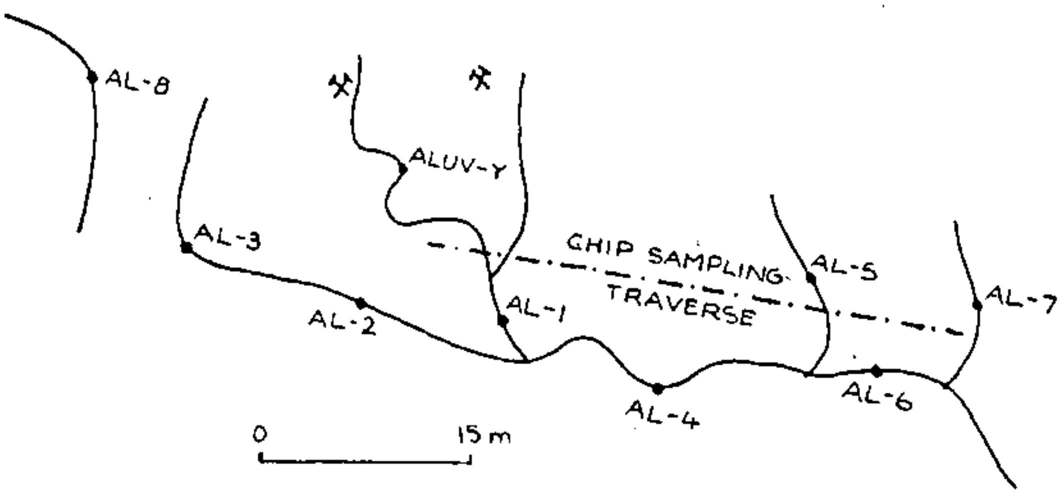


Fig. 19—Distribution of copper, silver and uranium (ppm) in samples collected from mineralized and barren horizons in Çekirge tepe and Terzili. N.D—not determined. A— red cdmpact sandstone; B— cross bedded red sandstone with mud pellets; C— cream colored mineralized sandstone with carbonized plant residue; D— thin bedded, magnetite laminated sandstone; E— red sandstone with mud pellets; F— red conglomerate with clay pellets.

The results obtained for gold by the M.İ.B.K. method at Hacettepe University are not verified by the cupulation method used by MTA Uranium analyses are done on second and third ore types and 22 gr/ton U_3O_8 (average of three samples) and 13 gr/ton U_3O_8 are found, respectively.



Example	Ag	Cu	Zn	Co	Ni
CHIP	–	681	56	12	22
ALUV–Y	5.5	% 9.1	35	10	23
AL–1	17	107	34	17	26
AL–2	–	42	36	17	26
AL–3	–	37	34	14	27
AL–4	–	91	27	14	27
AL–5	–	75	40	14	25
AL–6	–	81	37	14	25
AL–7	–	36	18	11	16
AL–8	–	33	31	10	20

Fig.20– Distribution of Cu, Ag, Zn, Co and Ni in stream sediment samples (ppm) from the streams draining the Hacı Verim occurrence.

Analyses of samples collected from the mineralized host rock and its walls did not indicate any distinct anomalous values for Co, Au, Mo, Ni and Zn. The reason for this is probably the difference among the solubility, transportation and depositional parameters of these elements and those of copper, silver and uranium.

GENESIS

Copper is supplied by leaching from the Middle Eocene volcanics which now cover north and east of the study area. There is enough copper (and silver and uranium) in the volcanics to be the source for the mineralization in the field. For example, a rough estimate indicates that to have an ore deposit with a 2500 x 20 m area, 10 cm thickness, containing 1 % Cu and 25 ppm Ag, there must be a source rock with a 2500 x 100 m area, 10 m thickness containing 20 ppm Cu and 0.05 ppm Ag. The Middle Eocene volcanic rocks of the area contain sufficient amounts of these metals (e.g., 125 ppm Cu and 0.12 ppm Ag in andesites). Additionally, petrographic and sedimentological evidences are also in support of a volcanic source. The sandstone and conglomerate which host the mineralization contain up to 80 - 85 % volcanic rock fragments indicating that the source region was dominated by volcanic rocks.

The leaching process was accentuated by the hydrothermal activities which took place at the closing phase of the volcanism and such metal-rich solutions found their way to the streams following ephemeral rains. The

$$Cu^{+} + 2Cl^{-} = CuCl_2^{-} \qquad K = 10^{+5.4}$$

$$Cu^{+} + 3Cl^{-} = CuCl_3^{--} \qquad K = 10^{+4.94}$$

It is known that Cu + + also forms a complex with Cl (CuCl^{+}, K= $10^{+2.8}$), but this complex is not stable and decomposes quickly under surficial environmental conditions (Rose, 1976). Furthermore, at 1 atm. pressure and

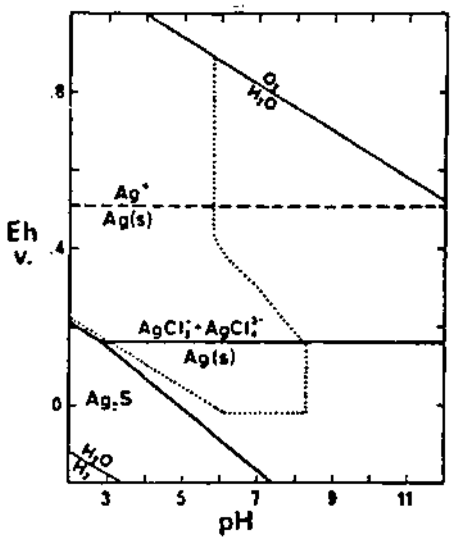


Fig.22— Eh—pH diagram of silver and comparison of its stability in the absence and presence of Cl . Dashed line shows the absence of Cl heavy lines show 0.5 m Cl and 10 m Ag, dotted line indicates the 10 m Cu area (taken from Rose, 1976).

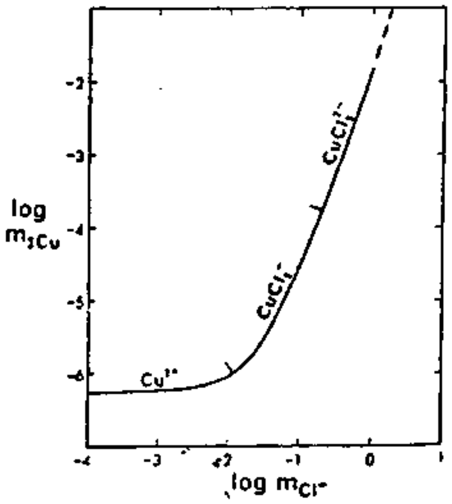


Fig.23—Maximum solubility of Cu in relation to Cl $^{-}$ content at pH 7 in the Cu-O-H-Cl system (taken from Rose, 1976).

strong argillization of the feldspars in the volcanic rock fragments is in support of the prevalance of such a hydrothermal phase. Further evidence for hydrothermal activities are the argillization of the volcanics (Fig.21) along the road between Yerköy and Yozgat, and the presence of widespread crystal quartz, amethyst and opal veins distributed irregularly in the volcanics in the vicinity of Belkavak village.

From the geochemical point of view, however, it is not possible to mobilize substantial amounts of copper with surface waters (Rose, 1976). Such a mobilization is possible only at moderate oxidation conditions with chloride-rich waters, as such waters would combine with copper and silver to form chloro-metal complexes (Rose, 1976).

Fig.21–Hydrothermal veins characterized by argillization, hematitization, limonitization and zeolitization cutting the volcanic rocks of Belkavak formation with a steep angle. Sample from an argillic zone containing 438 ppm copper.

Silver is a by-product commonly seen in red-bed type copper deposits. For example, the Creta ore (Oklahoma) contains 2 % Cu, 30 gr/ton Ag; the White Pine (Michigan) ore contains 1 % Cu, 30 gr/ton Ag; the high-grade Corocoro ore (Bolivia) contains 40 gr/ton Ag, and Nacimiento (New Mexico) 175-250 gr/ton Ag (Rose, 1976). The association of silver with copper is explained by the ease of silver ions to form complexes with Cl as Cu+ ions. While native silver quickly precipitates under mildly reducing (-1-0.5 v) conditions in a Ag-O-H system, its solubility increases rapidly in a 0.5 m NaCl solution and the area showing the solubility of silver in this system shows close similarity to the area of the $CuCl_2^-$ - $CuClg^-$ in the Cu-O-H system (Fig.22). The formation of copper complexes in relation to the Cl^- concentration and the increase in the solubility of copper at pH:7 are shown in the Cu-O-H-Cl^- system (Fig.23).

According to Rose (1976), water that contains 350 ppm Cl^- easily transports copper at a moderate oxidation potential in 25°C. In general, it is difficult to find surface or underground waters containing 350 ppm Cl^-. Such high Cl^- concentration can be obtained when seasonal surface and underground waters wash the sand flats having a continental or marine origin. The following complexes are formed (Rose, 1976) when Cl is combined with Cu+ at the surface at 25°C

25°C, relatively mobile copper carbonate ions such as $Cu(CO_3)_2^-$ and $CuC0_3(OH)_2$ are formed under $P_{CO2} > 10^{-3.5}$ and $P_{CO2} < 10^{-5}$, respectively (Garrels and Christ, 1965) (Fig.24).

It is not clearly established yet whether the second type stratiform malachite deposits are an epigenetic or a syngenetic type; while the occurrence of the mineralization in sandstones and conglomerates as a cement and concretions suggest a syngenetic origin, the replacement of carbonized plant residue by the mineralization and the occurrence of the mineralization in the fault zones support an epigenetic origin.

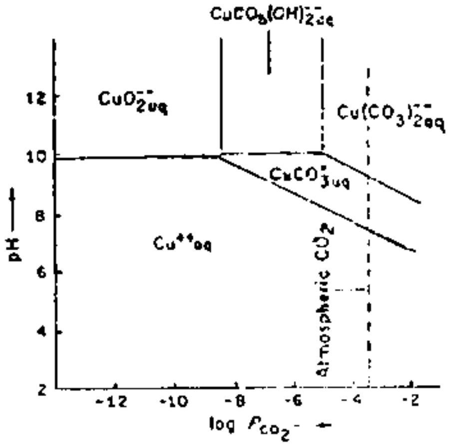


Fig.24—Distribution of dissolved copper ions as a function of pH and P_{CO_2} (atmospheric) at 25°C and 1 atm. total pressure (taken from Garrels and Christ, 1965).

The present evidence indicate that a dry climate prevailed in the study area from time to time developing salt flats and promoting an increase in the concentrations of Cl^-, SO_4- and carbonate ions in the environment. The rain which follows a dry season quickly ascends the water table and leads to the formation of complex metal ions as copper and silver combine with chloride and sulfate ions. Repetition of this process over a few seasons or the circulation of the rain water through some subsurface evaporitic layers increases the salinity and the metal-salt concentration. The other possible mechanisms of ore formation are a) salty (brine) and metal rich waters that were trapped in a closed basin and formed a syngenetic deposit there as the water is lost by evaporation, b) such waters were transported as underground waters and formed epigenetic ore deposits when they met a reducing environment created by decaying plant residue, c) the flush of oxygen-rich rain water after a dry season into such closed basins may have caused the precipitation of copper and other associated metals, and d) waters rich in copper, other metals, chloride, sulfates and carbonates precipitate their metal load in the low-energy environments such as point bars and flood plains where such waters come in contact with decaying plants and decomposing organic matter. One or more than one of these mechanisms were probably effective in the Delice-Yerköy area.

Copper complexes precipitate in alkaline environments (pH >7) as a result of the increase in the levels of $P_{CO}2$ and f_{H2S} According to the theoretical mddelling of Haynes and Bloom (1987 a,b), native silver, native copper and copper sulfide minerals such as chalcocite,bornite and covellite precipitate in an orderly manner in response to the increase in the H_2S fugacity. Native silver saturates from waters saturated with calcite,quartz,gypsum hematite containing 3 molal Cl^-, 0.11 molal HCO3, 800 ppm Cu and 1 ppm Ag at a pH=7,6 and fH2S = 10 ;^{52} bars. Native silver precipitation is complete prior to native copper saturation at f_{H2S} = 10^{-28} ' The deposit contains only native copper and native silver as long as the H_2S fugacify does not exceed 10 bars and under such circumstances 96 % of copper and all the silver precipitate. If the water contains Pb, Zn, Co, Fe ions and the H_2S fugacity reaches to 10 bars level, based on the conditions of transportation, varying amounts of sulfides of Zn, Co, Pb, Fe and Cu are precipitated. The presence of chalcocite in native copper only in minor amounts may suggest that in the study area the H_2S fugacity hardly reached 10^{-18} bars.

The stability of some copper species are shown on a Eh-pH diagram (after Garrels and Christ, 1976) for the Cu-0_2-S-$C0_2$ system at 25°C, 1 atm. total pressure, $C0_2$ partial pressure of $10^{-3.5}$, and total dissolved sulphur content of 0.1 (Fig.25). This diagram indicates that under surface conditions malachite crystallizes at a pH range

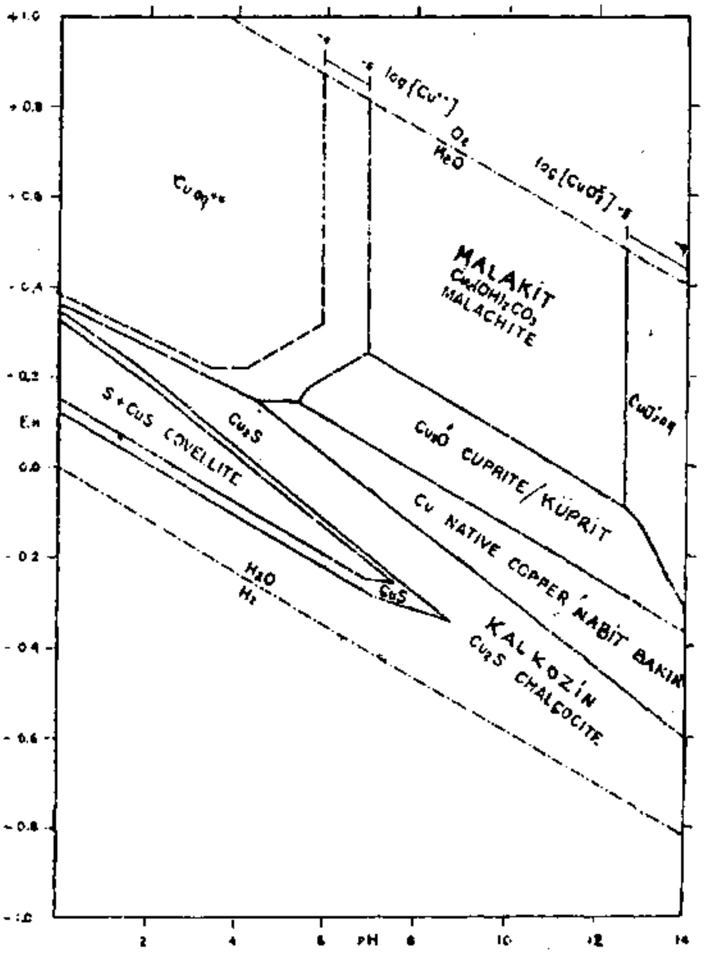


Fig.25—Stability relations among some copper compounds under 1 atm. total pressure, P_{CO_2} $10^{-3.5}$, total dissolved sulfur 10^{-2} conditions in Cu-H_2-O_2-S-CO_2 system (taken from Garrels and Christ, 1965).

of 7 to 12. According to Garrels and Christ (1965), as the $C0_2$ partial pressure is increased the stability field of malachite expands into the field of cuprite. In dry climatic conditions malachite is more stable than azurite as not enough moisture is available in the air for the stability of azurite. It is also seen from this diagram that the field of the native copper remains unaffected at atmospheric and higher PCO2 conditions. Under the given conditions a reducing environment is required for the precipitation of sulfides. The general absence of sulfides in the study area indicates either the geochemical conditions for the formation of such minerals have never been attained or previously formed sulfides were altered to malachite under a bicarbonate rich environment. Microscopic investigations to answer this problem are still in progress.

The native copper seen in the fault zones is most probably a product of remobilization. In other words, copper was leached from previously deposited cupriferous layers and filled the tensional fractures. The areal closeness of mineralized zones to the evaporitic series dictated that the metals could have been transported as chloride complexes. The high permeability of the host sandstones prevented the reduction of sulfates to sulfide by bacterial action (Haynes and Bloom, 1987 *b)* so that the environmental condition of low H2S fugacity is created for the precipitation of native copper. The compressional phase following the general tensional movements caused small displacements along the mineralized fractures and led to the formation of native copper sheets filling irregularly the slickensided fault zones. The presence of pressure twinnings in native copper seen under the ore microscope also support this.

RESULT

As a result, the depositional basin where red-bed type thick sediments (Topraklık Tepe formation) are deposited is a stream system flowing in a plain surrounded by steep mountains. This plain is cut by a few meandering rivers. Fine and sometimes coarse grained sediments brought by floods fill between these rivers and the low plains. Some plant and wood trash are deposited as a result of the loss in the stream energy in places like point bars and flood plains. The decay and coalification of this material created the environment suitable for the precipitation of copper (silver and uranium).

The constitution of the fluvial sediments in large (80-85 %) by volcanic rock fragments shows that the basin was fed by the surrounding volcanic mountains. The volcanic rocks evidently contain sufficient amounts of copper, silver and uranium.

The salinity of the basin is increased in response to seasonal aridness and metals formed complexes with Cl-, sulfate and carbonate anions. Metals of such solutions are then either deposited as independent layers where decaying organic matter is found or as material cementing between grains of sandstone and conglomerate. This type of stratiform malachite occurrences are seen in the middle parts of the Topraklık tepe formation.

Underground waters which circulate through the evaporitic series partly remobilized the stratiform ores and copper dissolved in this way is deposited as native copper in local fault zones in the lower and upper parts of the Topraklık tepe formation. The ages of the faults and the mineralization are not known definitely. Low H_2S fugacity needed for the deposition of native copper instead of sulfide minerals is provided by the high permeability of the host sandstones and high chloride activity by the evaporates in the close vicinity.

The probable metallic copper and silver reserves of the study area are 2500 tons and 3.5 tons, respectively. The contribution of the these occurrences to the country's economy will be about 11-12 billion TL at 1989 prices. The possible potential (geologic potential) is about ten times these figures.

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