

## Geochemistry and Origin of the Oligocene Binkılıç Manganese Deposit; Thrace Basin, Turkey

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**Abstract:** Many Oligocene Manganese deposits are found in the Thrace basin, a Tertiary collisional-collapse type basin in the north-western part of Turkey. All the mineralizations are originally sedimentary type. The most economically important deposits are around Çatalca; of these, the Binkılıç manganese ore occurs conformably within the Oligocene fossiliferous formations, as a stratiform type manganese deposit.

The manganese ores at Binkılıç show a continuity along strike and consists of micro-to Cryptocrystalline pyrolusite, psilomelane, radial manganite, cryptomelane, wad, rhodochrosite and dispersed organic matter, calcite, feldspar, clay minerals, and quartz but generally only minor quantities of limonite and goethite. Mn oxides with variable carbonate admixtures constitute the predominant ores. Fine laminations, oolitic and pisolitic textures, and lithologic characteristics of the sedimentary formations suggest deposition in a restricted marine environment.

The compositional trends and geologic evidence of the Binkılıç manganese deposit indicate that Mn oxides were precipitated as chemical marine sediments in a shallow-water environment and are associated with relatively rapid marine transgressive-regressive events which caused the sea-level changes. The first source is uncertain but may have been input of Mn from runoff and fluvial-sediment loads which derived from the metamorphic rocks of the Stranjha Massif.

### Oligosen Yaşlı Binkılıç Manganez Yatağının Jeokimyasal Özellikleri ve Kökeni; Trakya Havzası, Türkiye

**Özet:** Türkiye'nin Kuzeybatısında yer alan faylanmayla gelişmiş çökme tipi Tersiyen Trakya havzasında birçok Oligosen yaşlı sedimanter manganez yatağı ortaya konmuştur. En ekonomik olanlarının Çatalca civarında olduğu bu yataklardan Binkılıç yatağı, Oligosen fosilli formasyonlar içinde uyumlu olarak oluşmuştur.

Belirli bir süreklilik gösteren Binkılıç manganez cevherleşmesi, mikro-kriptokristalin pirolusit, nadiren botryoidal dokulu psilomelan, radyal manganit, kriptomelan, vad, rodakrosit gibi mangan mineralleri yanında saçılmış organik madde, kalsit, feldspat, kuvars, kil mineralleri ve az miktarda limonit ve götit içerir. Hakim cevher minerallerini, çeşitli karbonatlarla bir arada yataklanmış olan manganez oksitler teşkil eder. Sedimanter formasyonlardaki ince laminasyon, oolitic ve pisolitik dokular ile litolojik özellikler sınırlı bir denizel ortamda yataklanmayı işaret eder.

Binkılıç manganez yatağı, sıç su ortamında kimyasal olaylarla çökelmiş bir cevherleşmedir ve deniz suyu seviyesi değişimlerine yolaçan nispetten hızlı gelişmiş transgressif ve regressif olaylarla ilişkilidir. İlk kaynak kesin olmamakla birlikte Istranca Masifinin metamorfik kayaları olduğu söylenebilir.

### Introduction

Manganese mines of the Çatalca district are located about 47 km NW of the city of Istanbul on the Thrace Peninsula in NW Turkey (Fig. 1). The Çatalca district lies within the Tertiary Thrace Basin and is roughly 30 km (west to east) by 10 km (north to south) in size and encompasses one active until 1987 and two idle mines as well as several large prospects. The Binkılıç mine is the most important manganese mineralization of the district and consists of battery-

grade Mn oxides. This deposit was the main producer of Mn in Turkey during the period 1970-1987 and furnished nearly 100 000 tons of manganese ore during the 6- year period 1975-1981.

The geology and stratigraphy of the manganese oxide-bearing sedimentary formations of the Çatalca district were first described by Akartuna (1953). Further investigations were carried out by Ülkümen (1960), Uzkut (1971) and Öztürk (1990). Ateşok (1979) presented the results of flotation studies of the low-grade

manganese ores of the Trace-Binkiliç mine. The latest geological study carried out by Öztürk and Frakes (1995).

The Binkiliç deposits are similar to the Oligocene stratiform manganese deposits at Chiatura in Georgia and Nikopol in the south Ukraine containing up to 80 % of the World's present onshore reserves of manganese (Frakes and Bolton 1992). In general, the mineralization of this type was formed as stratiform manganese oxides along paleoshorelines, probably adjacent to an anoxic basin.

The main purpose of this paper is to summarize some of the geological, mineralogical and geochemical results of two separate investigations, one by the Mineral Research and Exploration Institute of Turkey and the other by a working group, which participated in a research project titled "sedimentary Manganese Deposits of the Trace Region" and to present a depositional model including the source of dissolved man-

ganese, precipitation factors and chemical relation between the occurrence of manganese and the host rock. Further, on the basis of trace element concentration, possible element input to the anoxic zone from sea bottom was investigated by means of some diagnostic diagrams.

**Analytical Methods**

Sample material was taken by the author from open-pit locations for a petrographic and geochemical study throughout the district. Approximately 1-2 kg material were sampled in each location. In the laboratory, massive and hard materials were broken into small chips with a jaw breaker. Then, soft ores and crushed chips were ground to a fine powder in a tungsten carbide mill. A 200 g of split was used for geochemical analyses. Petrographic investigation was carried out by transmitted and reflected light microscopy. Chemical analyses were done by X-ray Fluorescence Spectrometry and Atomic Absorption spectrometry. Rare earth elements were determined by

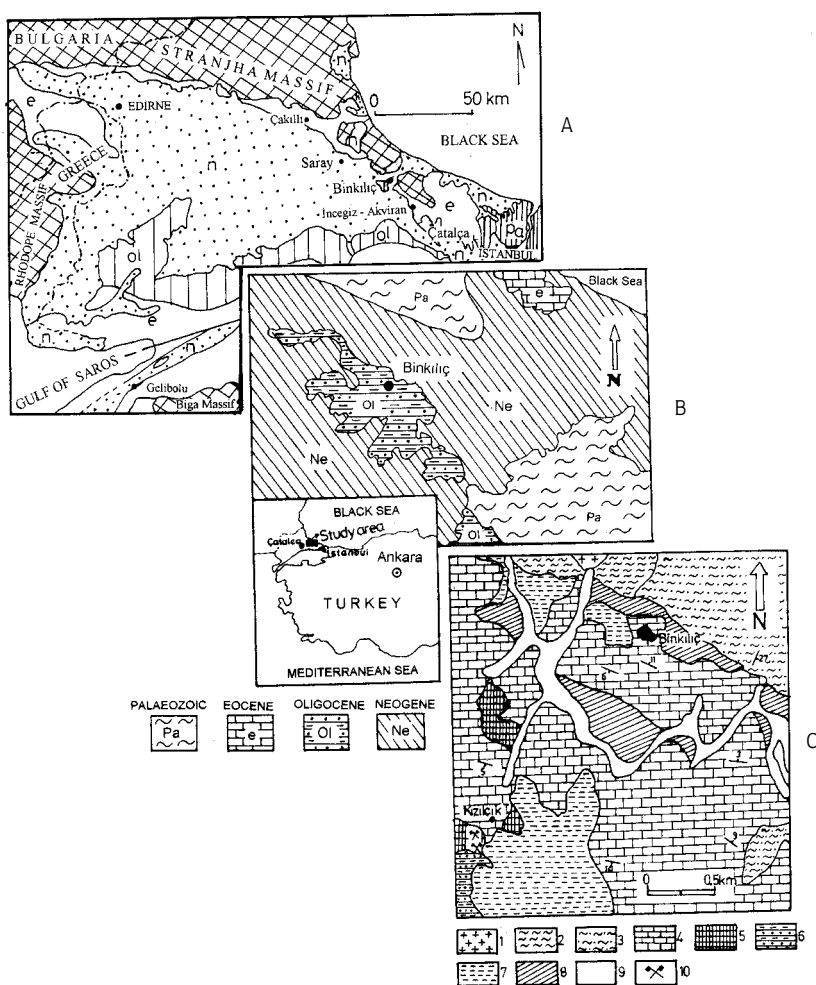


Figure 1. A: Generalized geological map of the Thrace basin showing the Binkiliç and other Oligocene manganese deposits. NAF: North Anatolian Fault, Ol: Oligocene, e: Eocene, n: Neogene, Pa: Paleozoic, hatched areas: crystalline basement (After Öztürk and Frakes, 1995). B: Detailed geological map of the Binkiliç area (for lithology see Figure 2 and text). C: Detailed Geological map of the Binkiliç manganese deposits. 1- Granite, 2- Gneiss 3- Schist, 4- Lime Stone, 5- Congerian limestone, 6- Fish series, 7- Sandstone, marl and sand, 8- Gravely sand and clay, 9- Alluvium, 10- Manganese deposits.

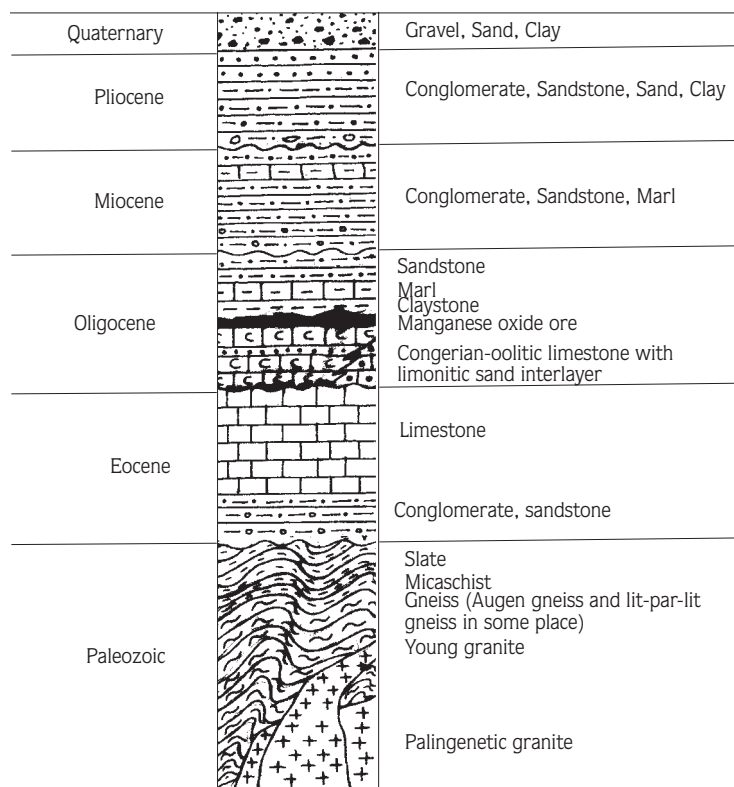


Figure 2. Stratigraphic section of the Çatalca district.

inductively coupled plasma (ICP) analysis. The mineralogy of the ore was determined by XRD analyses. The average analytical results are shown in Table 1.

### Geology

The Çatalca district contains igneous, volcanic, metamorphic, and sedimentary rocks of Paleozoic, Mesozoic, Tertiary and Quaternary age. Figure 1A is geologic sketch map of the Thrace basin showing major tectonostratigraphic units, and Figure 1B and C are simplified and detailed geologic map of the Binkılıç manganese deposit, respectively. A stratigraphic section showing the age and spatial relations of the major units is given in Figure 2.

A crystalline basement of Paleozoic age is the oldest lithostratigraphic unit in the Çatalca district. It is composed of intensively folded metamorphic rocks intruded by a younger granite (probably middle Devonian aged, Akartuna 1953). Petrographically, the metamorphic rocks are divided into lower and upper units. The lower is a yellowish white quartz-feldspar gneiss and palingenetic granite containing pink colored K-feldspar that sporadically crop out in deep valleys. The quartz-feldspar gneiss consists mainly of quartz and feldspar with variable amounts of biotite, mus-

covite, amphibole and secondary chlorite after biotite. Lepidoblastic texture is common. This gneiss commonly alters with feldspar-rich schist and quartzite at the upper level and is migmatized along its contact with the middle Devonian granite intrusion. In some places it exhibits augen texture due to large K-feldspar and rare pink and white plagioclase crystals. The upper unit can be divided into two formational groups as gray micaschists containing lensoidal quartzite and slates. They have mainly schistose textures and less commonly granoblastic textures. The lower parts of the micaschists contain lit-par-lit gneiss, especially conformably to schistosity.

The Eocene rocks in the Çatalca district are basal conglomerate and sandstone lying directly upon the basement, and fossil-rich micritic limestones and are separated by a marked angular unconformity from the metamorphic basement. The conglomerates and sandstones with claystone interlayer were made up of the material from the basement rocks which were worked by longshore currents and waves in a tidal flat during the middle-upper Eocene. This unit is locally several ten meters or at least several centimeters thick and is characterized by a fining-upward grain-size. The micritic limestones are represented by sedimentation as-

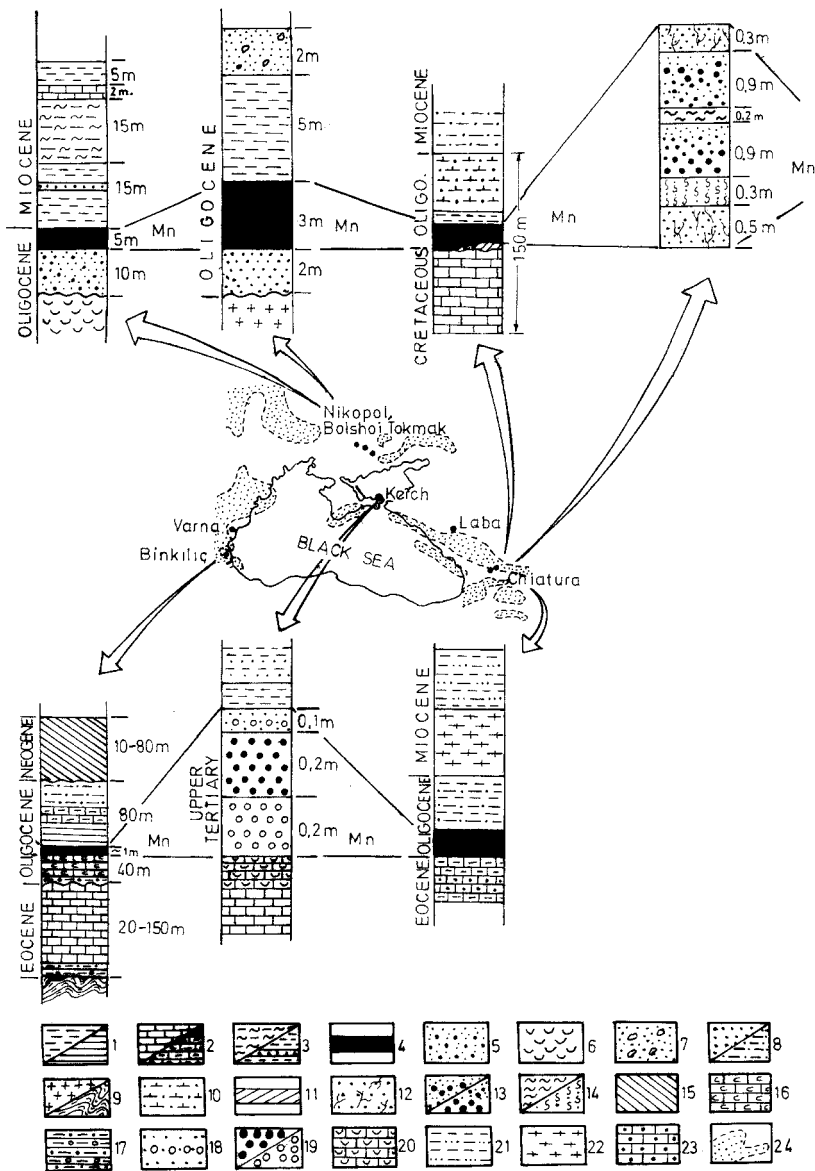


Figure 3. Correlation of selected Tertiary stratigraphies with sedimentary manganese deposits around Black Sea. All deposits are Oligocene age and are in associated with shallow water sediments. 1- Clay/calystone, 2- Limestone/Marl, 3- Bedded clay/sandy bedded clay, 4- Mn oxide ore, 5- Glauconitic sand, 6- Primary kaoline, 7- Sand with quartz fragments, 8- Sand/sandstone, 9- Magmatic/metamorphic basement, 10- Shaly sandstone, 11- Mn carbonate ore, 12- Manganeous sandstone, 13- Granular oxide ore, 14- "Belta" and "Mtsuri" oxide ore, 15- Conglomerate, sandstone and marl, 16- Congerian oolitic limestone, 17- Conglomerate and sandstone, 18- Sandy ore, 19- Detrital pisolitic and oolitic ore, 20- Argillaceous and sandy coquiha, 21- Clay and sandy marl, 22- Limestone, marl and sandstone, 23- Calcareous sandstone, 24- Early Oligocene continental area (island and archipelagos, after Sapozhnikov 1970).

sociated with transgressive marine conditions, which returned to the district during Lutetian and are mostly overlain by a marine sequence of Congeria-bearing limestones of Oligocene age.

The Oligocene sequence is separated by an unconformity from the Eocene rocks. Manganese oxide orebodies always appear to be associated with this sequence. Its thickness varies from 50 to 150 meters. The lower part of the sequence, that is about 100 meters thick, is composed of the sandstones and the fossiliferous limestones (Congerian series); the upper part, which is 50-60 meter thick is composed of silty

claystones, organic material-rich marl, and finely laminated sandstone (Fish series). The Congerian series are characterized by an abundance of the pelecypod genus *Congerina*, gastropods, foraminifera and ostracods (Öztürk and Frakes 1995), and by primary carbonate pisoliths and laterally pass to black-gray colored marl and shale precipitated in a prodeltaic environment. The lower part of the Oligocene sequence was deposited under shallow-water conditions, possibly in a lagoon environment linked with the open sea because of absence of chemical sediments such as evaporites. The fish series also called as Karton series and reflect various facies of a delta. The manganese

oxide mineralization occurs at the basis of the Fish series. According to the results of exploration drilling in the Binkılıç mine, the average thickness of Mn oxide ore is approximately one meter.

In the Çatalca district, the Neogene unit is represented by conglomerate, sandstone and marl of miocene age, and gray-yellow weakly cemented conglomerate, sandstone, sand and clay of Pliocene age. The sandstone and marl subunit is several tens of meter thick and locally contain lenses of gray clay. The Pliocene sediments are continental in origin. All the units, like Oligocene sequence, are essentially undeformed, although Eocene and pre-Eocene fault block movements have occurred in the region. The Quaternary sediments, which are composed of clay, sand, and gravel are the youngest lithostratigraphic unit in the Çatalca district.

#### Description of the Manganese Deposits

Regionally, sedimentary manganese has been noted in many mines and surface occurrences for a distance of about 100 km east-west, and over a width of 10 km within the Tertiary Thrace Basin, an extension of the Paratethys. Development for manganese has been carried out on at least four deposits within this basin; Binkılıç, İncegiz-Akviran, Çakıllı, and Saray. They consist essentially of flat-lying strata of primary sedimentary manganese oxides and secondary manganese carbonates, but the manganese carbonata are very rare and do not show any economic importance.

The Oligocene manganese deposits at Çatalca are present at the same stratigraphic horizon throughout district, which has led to the belief that they are associated with a single episode of mineralization. This stratigraphic horizon is characterized by variable composition and thickness and is represented by primary, high-grade manganese oxide ores at Binkılıç.

The most important sedimentary deposits of the world are along the Black Sea shoreline of Georgia and Ukraine. Current research suggests that these deposits are associated with relatively rapid marine transgressions and regressions across older basement rocks. The Chiatura (Georgia), Nikopol and Bolshoi Tokmak (Ukraine) deposits occur in petrologically simple terrigenous formation, interpreted as paleo-shoreline sediments and are called as the shallow-marine basin-margin deposits. The Kerch deposit, another sedimentary manganese deposit in Ukraine, is similar to these deposits. Geological research on all the deposits suggest that the deposition of manganese ore

was formed when reducing waters enriched in  $Mn^{+2}$  was welled up on the shallow-water region and mixed with oxygenated surface waters. To determine the similarities, at least in part, on the basis of associated rock and precipitation environment, the Binkılıç manganese deposit was correlated to these deposits. The stratigraphic sections illustrated are given in Figure 3. The Binkılıç sedimentary manganese formations, like these deposits, are in associated with shallow water sediments and are of Oligocene age. Further, transgression and regression events played an important role in the accumulation of terrigenous sediments. The presence of the terrigenous formations having fine laminations and graded oolitic and pisolitic texture of the ore show that the deposits were formed near to shoreline of Oligocene continental area. Therefore, it can be said that there is a similarity between the Binkılıç and these deposits.

#### Ore types

In the study area, three different ore types have been recognized. These are oolitic and pisolitic, detritus-rich and massive manganese ores. In addition to these ore types, nodules composed mostly of pyrolusite have been observed in massive type ore in places. Oolitic and pisolitic ore is generally high grade, hard ore including gray clay balls or calcite infillings, and spicules and voids representing dissolved pisoliths. Petrographically this type ore is sedimentary oxidic ore that account for approximately 95 % of the total reserves of the deposit. In some places, it also contains unsorted and generally inversely graded Mn concretions in Mn oxide cement (Figure 4). The grain size of oolites and pisolites ranges from 1 mm to 25 mm. The external bonding surfaces of ooliths and pisoliths are typically smooth, relatively dense and rare comprise tightly interlocking Mn oxide microcrystals. However, the outer surfaces show a variety of textures and largely controlled by the size and attitude of constituent crystals. Some pisoliths grains cemented to one another by Mn oxides and contain dissolution pores. Under microscope, a careful search of the grain surfaces exposed fine cortical laminae in fractured pisolith and shallow surface depressions. Some dark colored material observed are probably clay crystals filling fractures within fractured pisoliths. The detritus-rich ore consists of fine-to medium-grained clastic material weakly cemented by Mn oxides. This type ore mostly developed in the lower and upper levels of manganese oxide strata. The clastic material mostly composed of quartz, feldspar, and clay mineral in minor amounts. The thickness of this type ore is maxi-

mum up to 20 cm. The massive ore contain very fine beds and consists mostly of psilomelane, and manganite but other Mn oxides occur as well. It is generally a high grade, sometimes soft ore that include yellowish-brownish clay balls in minor amount. On the other hand, all ore types contain carbonate ore, as an other petrographic ore which chiefly composed of disseminated crystals of rhodochrosite and calcite in different amounts

### The Binkılıç Mineral Assemblage

Mineralogy as a tool in recognizing the genetic origin of manganese deposits has been used by various investigators for a long period. In most case, however, diagnostic mineral assemblage has been hampered by the weathering and metamorphism of primary ore deposit, and mineralogical variations between two or more deposits formed in similar environments (Rona 1978, Nicholson 1992, Ostwald 1992).

The mineral assemblage of the Binkılıç manganese oxide deposit is associated with shallow-marine sediments. The present minerals are pyrolusite, psilomelane, manganite, cryptomelane, wad (a soft black earthy mass of hydrated Mn oxide), rhodochrosite, calcite, quartz, feldspar, limonite, and clay minerals. Manganese oxides are common ore minerals. This mineral assemblage is relatively similar to oxidic manganese assemblage formed within clays, sands and carbonates, and rarely shale in marine environments. Interestingly, some oxide phases such as braunite, lithiophorite and todorokite, which are the major ore minerals in oxide deposits associated with the marine sediments, have never been found in the Binkılıç deposit. In other words, the diagnostic minerals using in recognizing the genetic origin of manganese deposits have not been established. The present oxide minerals are common in both sedimentary and hydrothermal deposits. Below is a more detailed description of the textures and mode of occurrence of Mn oxides and carbonates in the deposit, pyrolusite, psilomelane, manganite, cryptomelane and rhodochrosite. Mineralogical results were obtained from microscopic investigations of polished and thin sections.

Pyrolusite,  $MnO_2$ , mostly occurs in the high-grade portion of the mineralized zone. In general, the nodular concretions of the massive ore contain pyrolusite contents above average. In some places, pyrolusite can reach 95 percent of the mineralized zone volume. It is the most common manganese ore mineral of the Binkılıç deposit and was detected in almost all of the ore samples investigated by X-ray diffraction analysis.

Especially, the lowermost parts of oolitic and pisolitic ore appear to be enriched in formation of pyrolusite. The mineralogical evidence obtained from optic observations indicates that at least some of the pyrolusite is associated with replacement of the manganite. Pyrolusite exhibits mostly cryptocrystalline grains, but rarely radial grains.

Psilomelane, chiefly a mixture of manganese minerals, occur most commonly in the massive ore and is second most frequent constituent of the manganese ore. The psilomelane-rich ore is predominantly composed of fine-grained psilomelane and manganite and exhibits dark brown colors. Botryoidal texture, as a tool in identifying the psilomelane -rich ore appears to be one of the most important aspects. Psilomelane without botryoidal texture is similar in appearance to manganite and wad. Therefore, it is possible that some of psilomelane was previously noted to be manganite or wad in the massive ore zone.

Manganite,  $\alpha$ - $MnOOH$ , occurs most commonly in the oxidic ore and exhibits steel-blue colored, fine- and medium-grained crystals. Manganite, like pyrolusite, was detected in almost all of the samples from the oolitic and pisolitic ores. Rarely, it occurs as subhedral crystals in a blackish brown ground-mass of psilomelane and wad. Together with pyrolusite fill small fissures and cracks in the massive type ore. Manganite usually forms radial grains and with increasing depth in the deposit, its content shows a marked decrease.

In thin and polished sections of some samples, diagenetic reactions of primary carbonate minerals to manganite are seen clearly. These samples exhibit the preserved initial textures.

Cryptomelane,  $K_2Mn_8O_{16}$ , occurs locally as micro- or cryptocrystalline grains. It was detected only in several manganese ore samples. These grains are generally more or less intensively intergrown with microcrystalline psilomelane. Apparently, the cryptomelane-psilomelane association was observed in massive ores. In fact, cryptomelane is similar in appearance to psilomelane. In light of the identification of cryptomelane in the deposits, it is possible that some of what was previously reported to be psilomelane in the oxide ore-levels of the deposits may actually be either one or both of these minerals. Although there is no detailed petrographic and mineralogical data of the cryptomelane in the deposit, it is mostly represented by cryptocrystalline masses as well as by fine-grained fibrous aggregates.

	1	2	3	4	5	6	7	8	9	10	11	12	13
SiO <sub>2</sub>	36.34	25.07	9.69	10.01	5.30	7.00	15.17	6.50	7.63	6.57	9.06	11.89	3.20
TiO <sub>2</sub>	1.15	0.08	0.32	0.60	0.30	0.50	0.20	1.05	1.10	0.60	0.16	0.41	0.30
Al <sub>2</sub> O <sub>3</sub>	15.32	8.90	1.39	3.50	1.15	2.60	0.98	5.10	8.05	2.60	2.20	7.02	0.90
Fe <sub>2</sub> O <sub>3</sub>	2.50	8.80	3.09	4.00	3.97	2.90	2.50	1.05	8.10	2.65	12.40	7.27	0.70
MnO	13.04	11.01	53.19	47.00	55.01	49.00	44.30	55.00	39.47	50.94	23.90	17.91	15.50
MgO	0.80	0.65	1.12	1.04	1.18	0.71	1.31	1.08	0.92	0.96	1.35	0.90	1.50
CaO	18.01	31.66	15.62	17.50	16.00	22.01	19.60	14.43	16.03	21.63	25.93	16.48	44.75
Na <sub>2</sub> O	0.90	0.80	0.43	0.50	0.20	0.86	0.27	0.13	0.40	0.36	0.21	0.55	0.10
K <sub>2</sub> O	0.40	1.10	0.34	0.24	0.22	0.33	0.18	0.37	0.35	0.39	0.60	0.10	0.40
P <sub>2</sub> O <sub>5</sub>	0.25	0.44	0.97	1.10	0.60	0.95	0.90	1.05	0.96	0.78	0.66	0.57	0.60
Loss at 800°C	8.01	10.02	12.23	10.52	12.95	11.17	12.66	12.73	15.68	11.07	22.27	35.19	26.41
Loss at 110°C	3.00	1.10	1.58	1.33	2.22	1.35	1.15	1.44	1.05	1.28	0.90	2.63	4.48
Ba	2130	3092	2616	3106	2448	3269	2251	2196	2967	2814	3310	985	10793
V	10	67	30	18	42	31	28	35	21	33	122	93	47
Cr	4	19	15	15	13	18	16	20	14	16	3	10	5
Co	42	64	149	95	94	85	65	55	90	96	20	83	15
Ni	216	90	330	360	375	270	310	340	260	275	291	50	194
Cu	68	83	120	98	95	103	110	120	106	112	110	20	79
Zn	67	42	85	71	65	60	45	40	80	75	108	29	34
Pb	27	40	53	33	51	38	42	68	30	56	33	10	59
Sr	430	743	490	316	376	437	522	588	563	487	3093	1150	1300
Y	3	13	10	5	15	8	12	10	13	16	9	5	11
Zr	42	33	65	63	66	57	66	49	73	60	17	25	32

Table 1. Chemical compositions of the Binkılıç sedimentary manganese deposits (Major elements in wt percent, trace elements in ppm).

Rhodochrosite, MnCO<sub>3</sub>, is the most common manganese carbonate ore and mainly found at the lower of the manganese horizon. It occurs as hard, medium- or coarse-grained, subhedral to euhedral crystals in a fine grained matrix of the oxide and carbonate ores. Rhodochrosite in comparatively large masses is gray, light gray whereas in thin section it is colorless. Under the microscope, it differs from calcite in its higher index of refraction and by comparatively intense cracking related to rhombohedral cleavage. Rhodochrosite observed in the oxide ore is mostly associated with pyrolusite and mainly occurs in the cracks of this min-

erals. The grain size of Mn carbonate minerals ranges between 0.05 to 5 mm and locally reaches up to 1 cm.

## Chemical characteristics

### Major Elements

The analytical results of the samples taken from the Binkılıç manganese oxide ores are given in Table 1. The average MnO content of the deposit is 36.55 with 9.30 standard deviation. The highest values for manganese are determined in the oolitic and pisolitic (42.58 % Mn) and massive ore (41.17 %Mn). The

Table 2. Correlation Coefficients for Major and Trace Element.

	Al <sub>2</sub> O <sub>3</sub>	Ba	CaO	Co	Cr	Cu	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	MnO	Na <sub>2</sub> O	Ni	Pb	P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	Sr	TiO <sub>2</sub>	V	Y	Zn	Zr
Al <sub>2</sub> O <sub>3</sub>	1.000	-0.319	-0.179	-0.185	-0.182	-0.459	0.174	0.283	0.494	-0.552	0.469	-0.409	-0.494	-0.538	0.814	-0.153	0.886	-0.150	-0.458	-0.105	-0.221
Ba		1.000	0.869	-0.477	-0.362	0.018	-0.266	0.150	0.518	0.300	-0.345	-0.085	0.939	-0.099	-0.316	0.177	-0.214	0.002	0.155	-0.193	-0.232
CaO			1.000	-0.522	-0.344	-0.314	0.011	0.490	0.312	-0.576	-0.120	-0.398	0.221	0.178	-0.061	0.351	-0.459	0.286	0.176	-0.257	-0.516
Co				1.000	0.564	0.205	-0.134	-0.295	-0.324	0.625	0.175	0.272	0.013	0.463	-0.120	-0.564	0.010	-0.377	0.164	0.204	0.678
Cr					1.000	0.402	-0.240	0.079	-0.424	0.606	0.104	0.202	0.344	0.581	-0.197	-0.606	-0.024	-0.375	0.387	-0.253	0.565
Cu						1.000	-0.161	0.119	0.241	0.681	-0.356	0.791	0.662	0.622	-0.347	-0.067	0.049	-0.320	0.487	0.522	0.536
Fe <sub>2</sub> O <sub>3</sub>							1.000	0.440	-0.141	-0.397	0.111	-0.329	-0.569	-0.218	0.106	0.675	-0.284	0.244	0.001	0.418	-0.436
K <sub>2</sub> O								1.000	-0.310	-0.467	0.280	-0.358	0.117	-0.377	0.377	0.270	-0.260	0.725	0.237	0.076	-0.409
MgO									1.000	0.105	-0.863	0.391	0.388	0.157	-0.494	0.421	-0.325	0.209	0.198	0.094	-0.088
MnO										1.000	-0.333	0.812	0.491	0.779	-0.576	-0.430	0.144	-0.445	0.360	-0.225	0.779
Na <sub>2</sub> O											1.000	0.092	-0.548	-0.332	0.689	-0.301	0.158	-0.192	-0.469	-0.039	-0.054
Pb												1.000	0.809	0.310	-0.420	0.580	-0.035	-0.292	0.580	-0.063	0.277
Ni													1.000	0.609	-0.396	-0.180	0.161	-0.425	0.212	0.507	0.638
P <sub>2</sub> O <sub>5</sub>														1.000	-0.639	-0.231	0.137	-0.316	0.132	0.171	0.595
SiO <sub>2</sub>															1.000	-0.126	0.188	-0.132	-0.433	-0.063	-0.229
Sr																1.000	-0.374	0.869	-0.097	0.356	-0.742
TiO <sub>2</sub>																	1.000	0.559	-0.284	0.059	0.300
V																		1.000	-0.022	0.073	-0.793
Y																			1.000	0.062	0.335
Zn																				1.000	0.180
Zr																					1.000

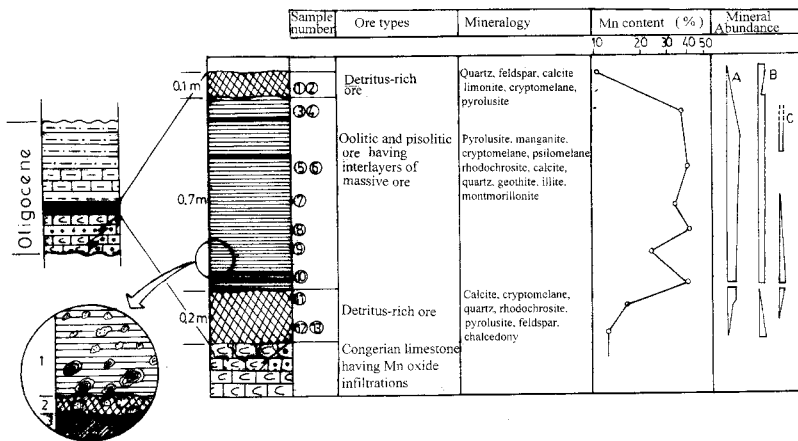


Figure 4. Columnar section showing ore type and associated minerals, Mn content, and mineral abundance. A-Mn oxide minerals (usually pyrolusite), B-Detrital minerals (Quartz, calcite and feldspar), C-Rhodochrosite.  
 1) Oxide ore including generally inversely graded Mn and ooliths and pisoliths.  
 2) High grade, hard massive ore with spicules and voids representing dissolved pisoliths.  
 3) High grade oxide ore including manganese pisolith debris in places.

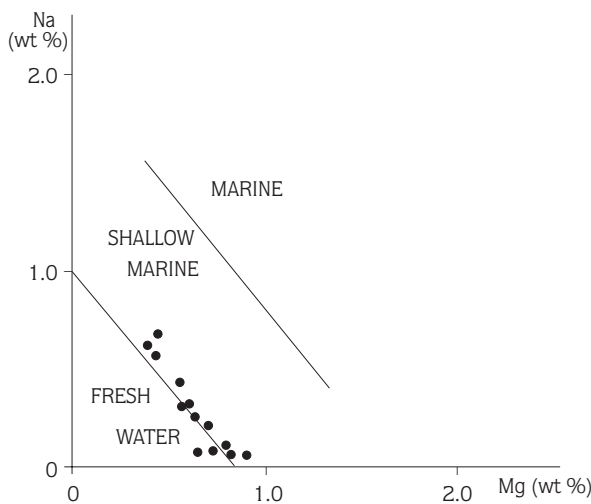


Figure 5. Diagnostic plot to differentiate marine and fresh water deposits (after Nicholson 1992). All of the samples from the Binkiliç mine, except for one sample, plot in the shallow marine field.

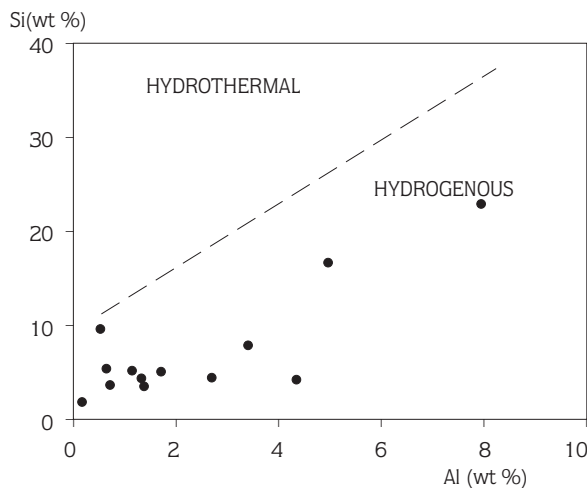


Figure 6. Al-Si discrimination diagram for the Binkiliç samples (after Choi and Hariya 1992). All of the samples plot in the area for hydrogenous deposits.

detritus-rich ore contains low values because of high content of clastic material. In the Binkiliç manganese oxide ores (especially in oolitic and pisolitic ore) iron and manganese are characteristically fractionated, producing high Mn/ Fe ratios. In other words, the oxide ores show a dominance of Mn over Fe (the Mn/Fe ratios range 1.3 to 58 with a mean 16.54 in thirteen samples). When compared with other manganese oxides (Rona 1978, Roy 1992, Chio and Hariya 1992), it can be said that the Mn oxide ores contain lower Mn / Fe ratios than those of hydrothermal, and sedimentary exhalative deposits and are similar to those found in basin margin shallow-water sediments. For a further recognition of genetic origin of the Binkiliç Mn oxide ores, several discrimination diagrams have been used here. These diagrams also allows understand whether there is a hydrothermal metal discharge to sedimentation environment.

The relationships between oxides deposited in the fresh water, shallow-marine and marine environments are given in a Na-Mg discrimination diagram (Fig.5). In this diagram, the Binkiliç manganese oxides mainly fall in the area for shallow marine depositional environment. Figure 6 distinguishes between hydrothermal and hydrogenous oxides, and it is considered to be one of the most important discrimination diagrams to distinguish hydrogenous from hydrothermal deposits, because these tend to plot in distinct areas. The data from the Binkiliç mine plot in the fields characteristic of a hydrogenous origin. Apparently, most of the samples contain low silica values. Roy(1992) suggested that hydrothermal deposits commonly occur in close association with the ferruginous silica gel formed by submarine effusive processes and metal discharge into marine sediments.



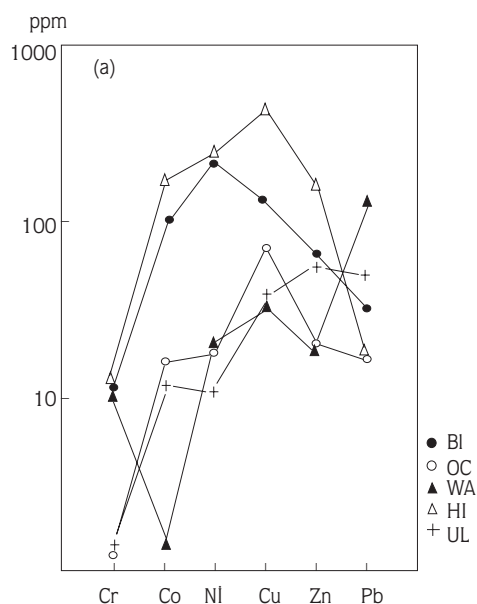


Figure 7. a) Representative trace element profiles for various Mn oxide ores. BI=Binkılıç mine, OC=Ocaklı mine (data from Gedikoğlu et. al., 1985), WA=Wakasa mine (data from Choi and Hariya 1992), HI=Hinode mine (data from Choi and Hariya 1992), UL=Ulukent mine (data from Kuşçu and Gedikoğlu 1989). The Hinode Mn oxide ore is hydrogenous in origin, but Ocaklı mine, Wakasa mine, and Ulukent mine are hydrothermal. The Binkılıç mine is similar to hydrogenous Mn oxide deposits due to relatively high trace element content.

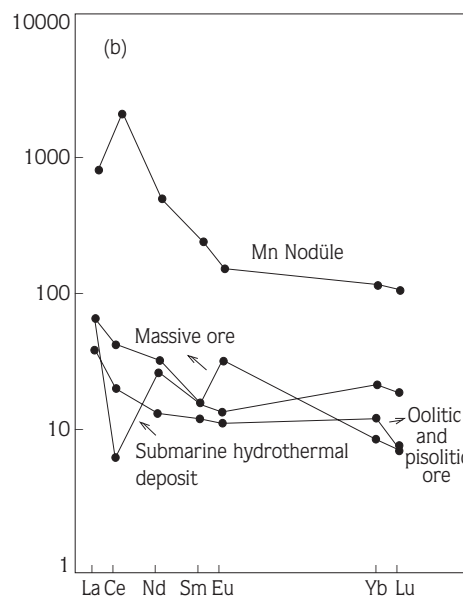


Figure 7. b) Chondrite-normalized REE patterns of the Binkılıç oxide ores compared to those of hydrogenous Mn nodules and modern hydrothermal deposits (Choi and Hariya 1992).

	La	Ce	Nd	Sm	Eu	Yb	Lu
Oolitic and pisolitic ore	*	14	21	10	3	1	3

Table 3. Analytical Results of Rare Earth Elements of the Binkılıç manganese oxide ores (Values in ppm, rounded. \*less than 0.5)

Another characteristic in chemical composition is high Ca content of the Binkılıç Mn oxide ores. The CaO values vary from 14.0 to 45.0 (Tablo 1). Owing to abundant calcite material in the precipitation environment, the carbonate content of the manganese oxide is higher than other similar sedimentary deposits. When correlated to Mn, and some major elements, the Ca shows poor and intermediate correlation coefficients (Table 2, Mn:  $r=-0.576$ , Fe:  $r=0.011$ , Si:  $r=-0.061$ , Al:  $r=-0.179$ ). The Al is generally associated with clay minerals in the deposits, and possess much better values when correlated to Ti ( $r = 0.886$ ). The average  $TiO_2$  value in the Binkılıç Mn oxide deposit is about 0.52 percent. According to Choi and Hariya (1992), the relatively high Ti values in Mn oxide deposits are a reflection of some mixing of det-

rital material during precipitation, producing an extremely good correlation between Al and Ti.

### Trace Elements

The Binkılıç Mn oxide ores show relatively high concentrations of Co, Ni, and Cu (Table 1) compared with concentrations in hydrothermal deposits. In the deposit, trace element contents of the oolitic and pisolitic ore are slightly higher than those of other type ores and most of the samples are characterized by high Co concentrations. Co reaches its strongest concentration in pyrolusite and the psilomelane -rich ores (Sample 3). The detritus-rich ore mostly show a decrease of trace elements. The average Co content of the Binkılıç deposit is 73.31 ppl. In general, the samples from hydrogenous deposits show a strong pos-

itive Co anomaly. The values for Ni and Cu are 258 and 94 ppm, respectively. According to Nicholson (1992), the trace element such as Cu, Ni, and Zn are related to hydrothermal deposits in origin, but hydrothermal oxides are depleted in Cu, Ni, and Co relative to hydrogenous deposits.

The Binkılıç Mn oxide ores are also characterized by high average contents of Ba (3,229 ppm) and Sr (807 ppm). Interestingly, the ore shows low V concentrations with a average of 44.0 ppm, whereas other Mn oxide deposits found in basin margin shallow marine environments contain higher V concentrations. The representative trace element profile for the Binkılıç manganese oxide ore is given in Figure 7a. This Figure allows a further separation of ore origin based on a comparison between the representative trace element patterns of Mn oxide samples. The Binkılıç deposit shows an abundance of the trace element relative to the hydrothermal deposits.

#### Rare Earth Elements (REE)

Table 3 shows the analytical results of rare earth elements of Mn oxide ores from the Binkılıç deposit. Based on these bulk analyses, Mn oxide ores from the Binkılıç deposit compared to hydrogenous Mn nodules and submarine hydrothermal deposits (Fig.7b). The patterns of chondrite-normalized REE from the Binkılıç Mn oxide ores are different than those of Mn nodules and modern hydrothermal deposits. While the analyses of submarine hydrothermal deposits show a strong negative Ce anomaly, hydrogenous manganese nodules display a positive Ce anomaly. The samples of the massive ore from the Binkılıç are characterized by strong positive anomaly for Eu and smaller negative anomaly for Ce. The oolitic and pisolitic ore does not display any anomaly for Eu or Ce. Generally, the REE distribution patterns does not show a precise similarity to those of both hydrothermal and hydrogenous deposits.

#### Discussion

The geological, mineralogical and geochemical data suggested that the Binkılıç manganese deposit has oxide deposition and is a sedimentary mineralization. However, the mode of occurrence of Mn oxides remain uncertain, as one of the most important problems. Whether they formed by upwelling of reducing waters containing abundant organic matter and dissolved Mn to the shallow-marine areas or by diagenetic reaction of carbonates to oxides. According to

the results of this study, Mn oxides directly precipitated from sea water and manganese accumulation is entirely linked to the availability of oxygen in the precipitation environment. On regional scale, as is seen in other Oligocene manganese deposits, marine transgression and regression played an important role in their formations.

Two source are considered that, together or separately, could provide sufficient Mn to form the deposit: a hydrothermal source; and release of Mn by destruction of various minerals containing appreciable Mn during weathering of the metamorphic rocks. At Binkılıç, the first remains uncertain and requires more detailed studies because of absence of the Oligocene magmatism. Therefore the latter seems more meaningful in explanation the manganese source. In the light of this view, it can be said that the major source of the Mn is the metamorphic rocks such as gneiss and schist. Öksüzler(1993) describe Mn-rich garnet and mafic minerals such as biotite resulting from high-temperature and-pressure reactions associated with regional metamorphism within gneisses and schists. The released Mn by destruction of biotite and garnet during weathering processes was carried by solutions to the marine environments and then gave rise to Mn deposits. However, some of manganese may be revealed from primary manganese deposits such as Kestanepinar deposit found in the low grade metamorphic cover rocks of Mesozoic age. Nicholson (1992a) summarized positive correlations of elements with manganese in different genetic types of deposit. Despite some recognized limitation, three correlations were identified as potentially diagnostic, namely Mn-Ba for fresh water oxides; Mn-Pb for dubhites (oxides formed by the weathering of a mineralized sequence), and Mn - As for hydrothermal deposits. According to the author, geochemical associations are related to a given deposit type and normalization of the oxide chemistry against manganese content can be employed as a discriminatory in defining element pattern. In the Çatalca district, the following significant geochemical association is shown in the majority of analyses: Mn-Ba-Co-Cu-Ni. This geochemical association, i.e. the positive correlations of elements with manganese displays a marked element enrichment in the deposit and are similar to supergene marine deposit precipitated directly from sea water, and bedded manganeseiferous sediments deposited in the marine environment.

As mentioned above, the Binkılıç deposit is similar to major sedimentary manganese deposit connected with paratethys, such as Chiatura (Georgia), and Nik-

opol (Ukraine) on the basis of accumulation of manganese mineralization in a oxic zone, the possible association with sea-level fluctuation, associated rocks, and occurrence in a sequence of rocks containing shallow-marine facies, but the Binkılıç deposit is characterized by formation directly on fossiliferous limestones and finer manganese oxide horizon (Sapozhnikov, 1970). This type of deposition is associated with relatively rapid marine transgression and regressions. The oolitic and pisolitic structures of the Mn-oxides suggest that the mineralization formed in a shallow - water agitated environment. The textural signatures showing phase changes from the initial precipitates to more stable species in Mn-oxide accumulation are not well understood and are required more detailed studies on the mechanism of formation of Mn oxide - hydroxides, but it is observed that at least some of pyrolusite and

manganite are secondary. Mn carbonates observed at Binkılıç are mainly formed by early diagenetic reaction of dissolved  $Mn^{+2}$  in reducing waters and diagenetically derived from manganese oxides by reaction with  $HCO_3$ . Similarly, some carbonate relicts transformed by diagenetic reactions to Mn carbonate.

At Binkılıç, there are strong evidence for primary Mn oxides transformed to Mn carbonates. In the microscopic studies, small euhedral rhodochrosite crystals observed within large Mn oxides referred to secondary origin. These are apparently associated with a diagenetic reaction of Mn oxides to Mn carbonates and generated by pore water-mineral interacting. On the other hand, both stratiform formation showing a continuity along strike and absence of the lenticular, anastomosing structure of the manganese-ore horizon on

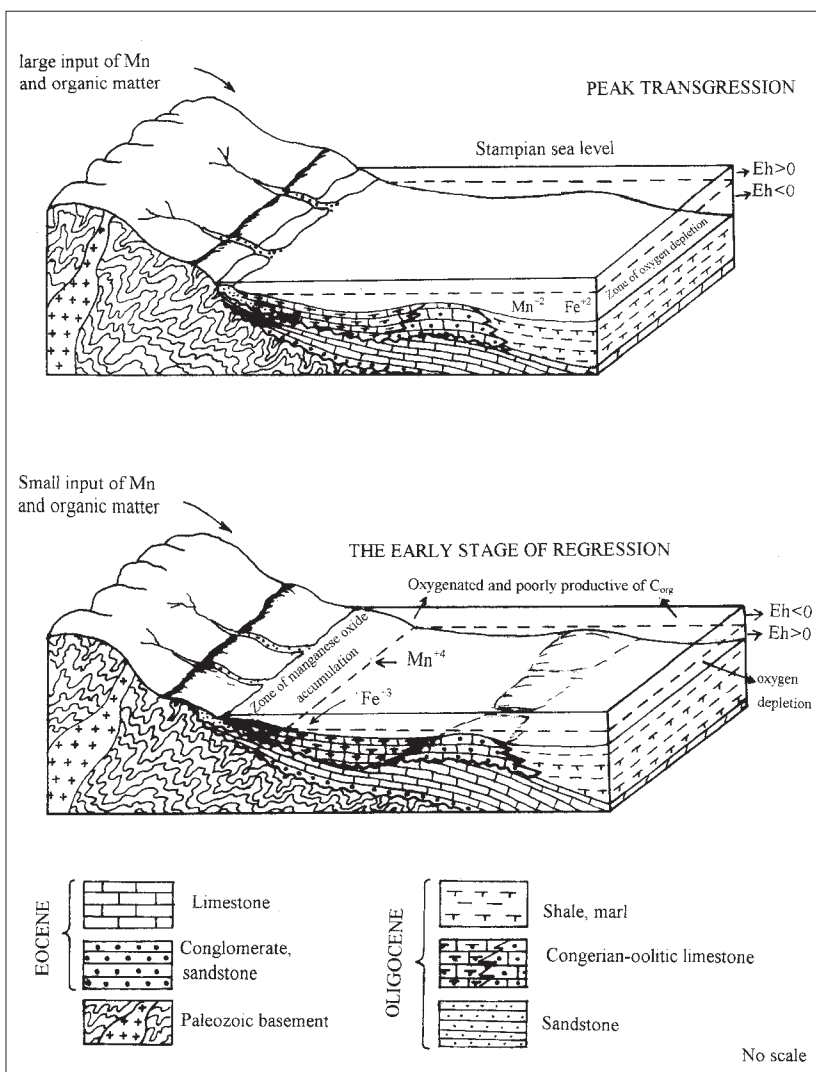


Figure 8. A depositional model for The Binkılıç manganese deposit.

the gross scale suggest that the manganese oxide deposit is primary in origin. In other words, a complex lenticular structure which destroyed the primary structure is not seen at Binkılıç. Also, inverse graded bedding in oolite and pisolite of the manganese horizon represents a primary structure which developed by marine regression. The presence of a carbonate -and detritus -rich zone of 10 -15 cm thickness at the base of manganous bed shows that there is a restricted stratigraphic transition between Congerian limestone below and manganese horizon above. When considered these evidences and the results of diagenetic diagrams together, it can be said easily that the Binkılıç Mn oxides represent a primary origin but, a little of Mn oxide occurred by post-depositional reactions.

The mode of occurrence at transition from limestone deposition below to clastic sediments above and weakly ore relationships to clastic deposition are the most important sedimentation characteristics of the Binkılıç deposit. However, these type manganese ores in the world predominantly related to sands in shallow - water environment. The early Oligocene at Binkılıç is transgressive and is responsible for large input of dissolved Mn and organic matter to sea water. As a result of this, a oxygen minimum zone (anoxic zone) with restricted change with the open sea led to an accumulation of dissolved Mn and Fe, and low Eh values ( $Eh < 0$ ) in a seawater column. In the stage of peak transgression, both oxygen depletion and dissolved Mn reached to a maximum level in the reducing waters. At Binkılıç, Oligocene transgressive sequence are also called as congerian series. Possibly, the upper parts of this series represent a carbonate shoal because the presence of primary calcite pisolites formed in a high - energy environment. Stratigraphic relationships suggest that following transgression, a marine regression sequence are formed in the region. The Binkılıç ores are largely associated with the early stages of this marine regression leading to relative deepening of the oxidation-reduction interface. In this stage, the sea water become more oxic and anoxic deep sea water enriched in  $Mn^{+2}$  has transgressed to a self region containing abundant oxygen. So, manganese ores are deposited within restricted basinal areas reflecting an estuary or lagoon, as a function of gradually raising the Eh and pH. In addition, a markedly decrease in faunal diversity of manganous horizon and an increase in detrital input suggest that marine passages to Paratethys during accumulation of carbonate material are partly closed in accordance with seaward movement of shoreline. Following accumulation of the manganese

layer formed at a short-interval, the sea water depth is again increased and thick sedimentary sequence containing fish bones and plant fossils which represent a marine transgression and reopening of a passage to the Paratethys are developed upon main ore zone. Sedimentation in the late stages of transgression is dominated by the deposition of marl and sandstones. As a function of increasing thickness of sedimentation and the present  $HCO_3^-$  in sea water, some primary manganese oxides transform to manganese carbonates and dissolved manganese again led to diagenetic reactions at the top of congerian series. Probably, some calcite pisolites also transform to manganese carbonates in this stage. All the evidences suggest that both primary manganese oxides and secondary minerals occur entirely in the shallow-water environment of continental shelf. A depositional model for the Binkılıç deposit is given in Figure 8.

The relatively high concentration of trace elements and Mn / Fe ratios of the Binkılıç Mn oxide deposit suggest that hydrogenous and diagenetic processes, together or separately, play a significant role in element enrichment. In general, both hydrogenous and diagenetic processes are responsible for deep-sea sedimentary Fe-Mn nodules (Roy 1992), and early diagenetic process enriches the nodules in Mn, Cu, and Ni. The similar sedimentary processes also occur in the Binkılıç deposit. The diagnostic diagrams and the absence of As indicate that the Binkılıç Mn-oxide deposit is not hydrothermal type. Therefore, the relative metal enrichment, especially Co is considered to be form from sea water. In other words, the trace element concentration may be adsorption mechanism from sea water, but the modes of accumulation of trace elements at Binkılıç ores seem to be complex and this problem has still not been investigated sufficiently. Thus, in the deposit at least partial derivation of some element to the anoxic zone, such as Cu, Ni, and Pb from sea bottom is possible. It is likely that the solutions containing various elements migrated along fault systems and directly discharged to sea water.

## Conclusions

The Binkılıç manganese oxide deposit is pH and redox controlled and was formed when reducing waters enriched in dissolved  $Mn^{+2}$  -  $Fe^{+2}$  welled up on the shallow-water region and mixed with oxygenated surface water above redox interface. The separation of manganese from iron is mainly a function of gradually raising the Eh and pH. The dominant ore minerals are

Mn-oxides and mostly deposited from sea water (hydrogenous deposits). Manganese carbonate was mainly diagenetically derived from primary manganese oxides by reaction with  $\text{HCO}_3^-$ . Three different ore types have been recognized in the form of oolitic and pisolitic, detritus - rich, and massive manganese ores. However, the ore types do not show any variation in their major element composition. The differentiation of the ores is mainly dependent on the their Mn - oxide species. The trace element concentrations and Mn / Fe ra-

tios are similar to those of hydrogenous deposits. During chemical weathering of the metamorphic rocks, manganese solubilized in acid, reducing conditions and carried in surface and subsurface waters to a zone of oxygen depletion. Based on the reservoir of dissolved manganese suddenly gained access to oxygen in associated with transgressive and regressive cycles, the manganese oxides were deposited probably at the coastal parts of a lagoon.

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