CARBONATE REPLACEMENT TYPE MANGANESE ORE FORMATION DURING THE OLIGOCENE ANOXIA, BİNKILIÇ MANGANASE DEPOSIT, THRACE BASIN, TURKEY

OLİGOSENDEKİ ANOKSİK SÜREÇLERLE İLİŞKİLİ KARBONAT ORNATIM TİPİ MANGANEZ CEVHERLEŞMESİ, BİNKILIÇ MANGANEZ YATAĞI, TRAKYA HAVZASI, TÜRKİYE

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Abstract : The Binkılıç Mn deposit of Oligocene age, occurs in northern part of the Thrace Basin of Turkey, which is the lateral equivalent of the manganese giants such as Chiatura, Nikopol, and Varna. Petrographic, mineralogical,and geochemical studies indicate that Binkılıç manganese deposit of the Oligocene was formed as a result of interaction between manganese - rich anoxic basin water and underlying calcitic sediments. Manganese diffusion downward resulted in the dissolution of the calcitic material and precipitation of manganese carbonate, iron oxides,and manganese oxyhydroxides, depending on Eh - pH, from the sediment - seawater interface into the sediment. The formation of manganese ore was lithologically -controlled by the deposition of the carbonates. Regional uplifting resulted in marine regression, dehydration and complete oxidation of the primary carbonatic ore. High grade hard ore and infiltrated ore are thought to have formed during that time .

Key words : Oligocene, diagenetic replacement, manganese

Özet: Trakya Havzasının kuzey kıyımında bulunan Oligosen yaşlı Binkılıç manganez yatağı, Chiatura, Nikopol ve Varna gibi yüksek rezervli manganez yataklarının yaş ve tektonik konum itibariyle yanal eşdeğeridir. Binkılıç manganez yatağında yapılan petrografik, mineralojik ve jeokimyasal çalışmalar manganez cevherleşmesinin manganezce zengin anoksik havza suyu ile tabanda bulunan kalsitik sedimanların arasındaki etkileşme ile ilişkili olduğunu göstermiştir. Manganez iyonlarının kalsitik sedimanların içine doğru göçü, yukarıdan aşağıya doğru Eh ve Ph değerlerindeki değişime bağlı olarak sırasıyla manganez karbonat, demir oksit ve demir - manganez oksihidroksitlerin oluşumuna neden olmuştur. Bu bağlamda manganez ceherleşmesi karbonat çökelimiyle ilişkili litoloji kontrolllü bir özellik göstermektedir. Bölgesel yükselme ve deniz çekilmesi birincil karbonatik cevherin tamamen dehidratasyonunu ve oksitlenmesini sağlamıştır. Yüksek dereceli sert cevher ve infiltrasyon türü cevherleşme bu süreçlerle ilişkili olmalıdır.

Anahtar kelimeler : Oligosen, diyajenetik ornatım, manganez

Introduction

The Oligocene is known as one of the major epochs for the formation of the manganese giants in Earth history. The Binkılıç manganese deposit of Oligocene age occurs on the northern side of the Thrace Basin, Turkey (Fig.1), which is genetically connected with the manganese giants of the Paratethys region, Chiaturi (Georgia), Nikopol (Ukraine), Varna (Bulgaria), etc. Although they include large reserves (over a few billion tons ore) their formation enigma remains to be solved. Chemical and isotopical stratigraphy of the ore section and detailed descriptive study of these deposits have not been made, especially in western literature. But, some studies were carried out at the Chiatura - Georgia,(Bolton and Frakes 1984), at the Nikopol - Ukraine, (Hein and Bolton 1992) and at the Binkılıç - Turkey, (Öztürk and Frakes 1985). The Soviet investigators have considered that the manganese accumulations during the Oligocene has been formed by redox - controlled synsedimentary processes (Varentsov and Rakhmanov 1978). Bolton and Frakes (1984) and Frakes and Bolton (1992) postulated that manganese accumulation at the Oligocene basins were formed related to transgression - regression cycles. They relate the mineralization to sea regression associated with oxygenation of the basin water. However, Öztürk and Frakes (1995) recently showed that the manganese accumulation at the Thrace basin was not formed by redox - controlled synsedimentary processes and/ or short term oxygenation of the sea water .

The purpose of this study is to determine the geochemical character of the manganese deposits through the ore section and to offer a conceptual model for the formation of the manganese deposit at Binkılıç in the light of its petrographic, mineralogical and geochemical features.

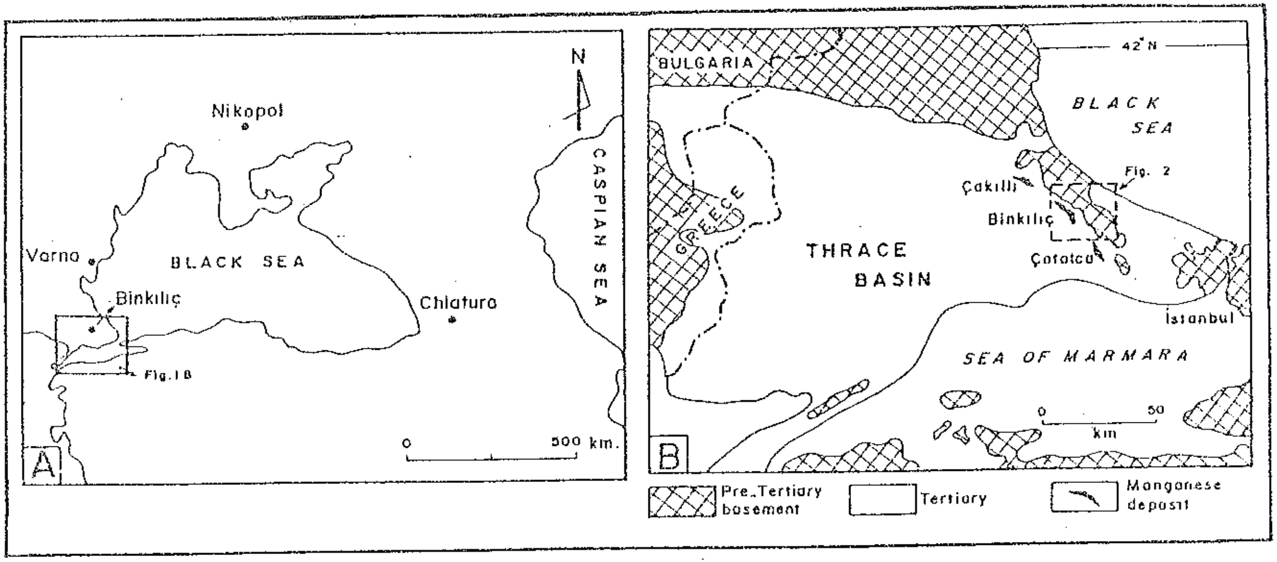


Figure 1. Location map of the principal early Oligocene manganese deposits of the Black Sea region (A), simplified geological structure of the Thrace Basin and positions of manganese deposits (B).

Şekil 1. Karadeniz Bölgesinde Alt Oligosen yaşlı önemli manganez yataklarının konumları (A), Trakya Havzasının basitleştirilmiş jeolojik yapısı ve manganez yataklarının konumu (B).

Material and Method

This study investigates the Çatalca, Binkılıç and Çakıllı manganese deposit of the Thrace basin. A geological map of the Binkılıç- Çakıllı region was made and the host rock lithologies of the deposits were studied. The Binkılıç manganese deposit was sampled from base to top , and the ore types were determined in the field.

Geochemical analysis for major and minor elements, including rare earths were made by ICP at the Centre de Geochimie de la Surface, Strasbourg, France. Mineralogical - petrographical studies have been carried out on thin sections and polished sections. XRD analyses were done using a Philips diffractometer with Cu Kalpha radiation and a curved crystal carbon monochronometer. Microprobe analysis were done using a computer automated jeol 733 electron microscope.

Geological Setting

The Oligocene manganese deposits of the Thrace Basin occur at the northwestern part of Turkey, close to the Black Sea. The Thrace Basin has an eliptical geometry,and displays a well developed zoned pattern of the sedimentary formations which are surrounded by metamorphic massifs (Fig. 2). Metamorphic basement rocks consist of two major tectonostratigraphic units, high grade metamorphosed core rocks, possibly Precambrian in age,and the low grade epimetamorphic cover units of the early Mesozoic. Metamorphic core rocks consist mainly of gneiss,quartz schist,and meta granite, whereas cover units mostly consist of phyllite and marble. A phyllite horizon of the epimetamorphic cover units includes a stratiform ferromanganese deposit at the Kestanepınar, 4m. in thickness and 200 m. in length. This deposit was mined during the first world war and already has been exhausted. Manganese silicate is an important accessory mineral of the metamorphic core rocks of the Thrace Basin which was described by several investigators (Bora 1969).

Sedimentary formations of the Thrace basin exhibit differences in the south and the north. In the southern rim of the basin, an ophiolitic melange of Cretaceous age is overlain by Palaeocene and Eocene formations that are mostly clastic (Sümengen and Terlemez,1991). The Eocene is conformably overlain by organic -rich shale of Oligocene age. Unlike the south, deposition began in the Eocene in the north and the sedimentary pile is represented by well matured sandy basal clastics which gradually pass up to biohermal and bioclastic limestone. The Oligocene is divided into two series in the north which are congerian serie at the bottom and fish serie above (Akartuna 1953). Congerian serie shows terrigenous character and unconformably overlays the Eocene at the northeastern part of the basin, whereas represented by congerian limestone and conformably overlays that of the Eocene at the northwest. Fish series consist of gypsum nodule - bearing, organic mattter -rich and hence dark brown - black colored claystone in the northeastern part of the basin associated with low grade Mn ore, whereas it is represented by green clay, silty shale on the northwestern side. Fish and shark fossils are locally concentrated in the claystone (İlkümen 1964) which occurs at the top of the ore horizon. Coal deposit - bearing sediments of the Miocene (Fig. 2) unconformably overlay the older rocks. Basaltic domes of the Upper Miocene and Pliocene age (Ercan, 1992) were intruded into the Miocene sediments in the central part of the basin.

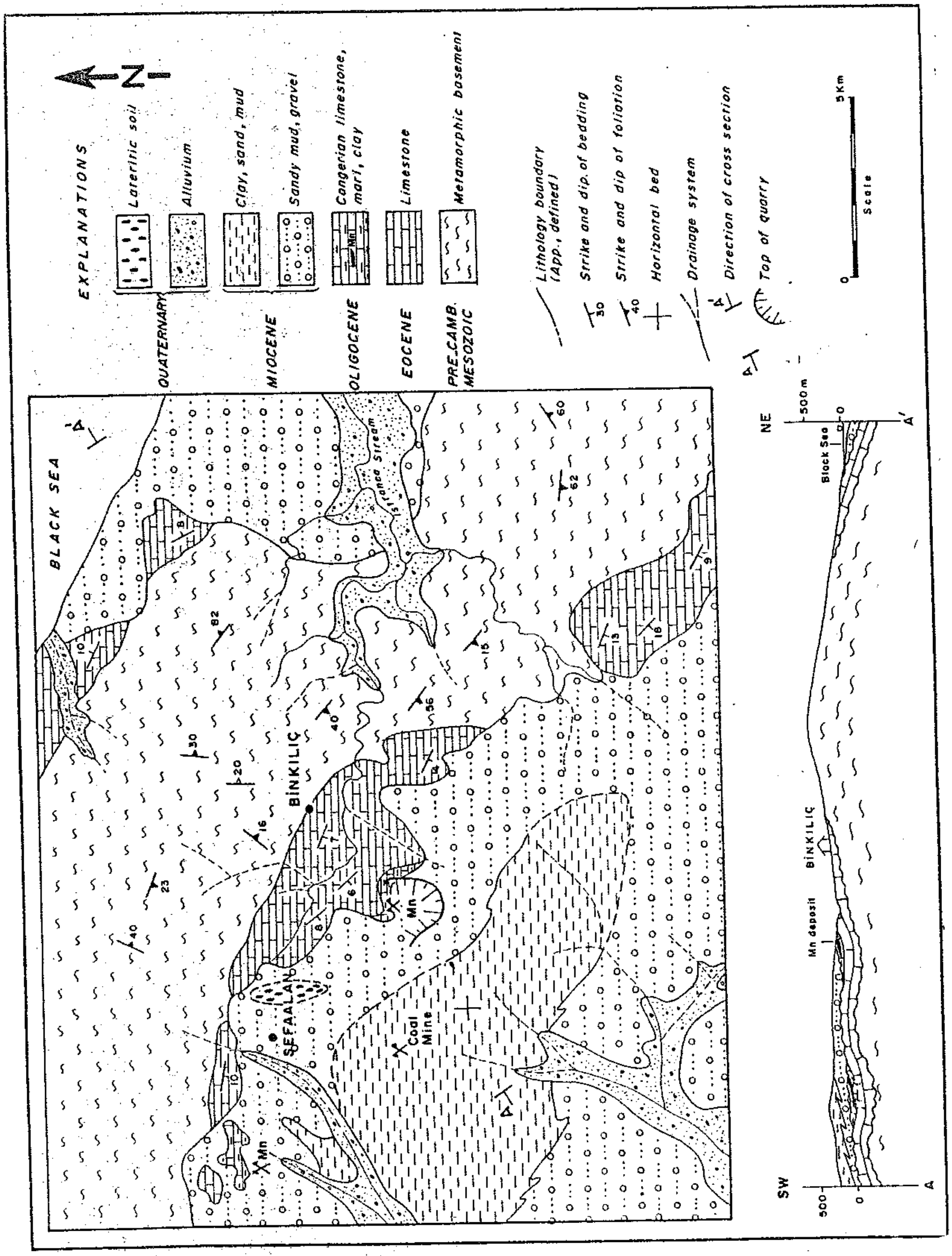


Figure 2. Geological map and cross section of the Binkılıç manganese deposit.
Şekil 2. Binkılıç manganez yatağının jeoloji haritası ve enine kesiti.

The manganese deposit

The manganese ore at Binkılıç is nearly horizontal and the main ore level occurs between Congerian serie and fish serie. There are also several other horizons , intercalated with claystone of the fish serie. The ore thickness varies between 0.6 - 1.3 m. and exploration studies indicate that total ore reserve are nearly ten million units, with 30 % Mn grade .The ore types and petrological - textural aspects of the ore are discussed in detail by Öztürk and Frakes (1995). The congerian serie occur at the base of the ore and mainly consist of congeria fossils -rich limestone. The limestone is well bedded, highly porous, and discontinous along strike. The Oligocene paleoenvironment possibly was a lagoon or bay. At the Binkılıç region congerian limestone includes gastropod- and ostracod- fossil - bearing spiculite and oolith- pisolith levels at the top of the section. Congeria fossils are homogenous in size, generally 2 cm. in length. These were reported to be an indicator of a non- marine depositional environment (Cox et al. 1969). Congerian limestone generally includes manganese oxide infiltrations as a key stratigraphic level. Mineralization begins at the bottom as low grade soft ore consisting of reworked Mn pisolites - mineralized Congeria fossil debris. This ore passes upward into the high grade - hard ore (mangcrete) levels or mangcrete patches -bearing pisolitic ores and ends with a concretional level. This concretional ore level is one the distinctive feature of the Mn deposits of the Thrace basin, occuring at the top of the main ore horizon. The concretions of the ore protolith consist of gypsum and kutnahorite lamination. The manganese concretions are nearly equal in size, roughly 5 cm.

Sometimes their core and cortex consist of gypsum or calcite and the rim formed by very thin Mn oxide laminations. The concretional ore level is overlain by local fish fossil- bearing silty claystone,and concretional ore - claystone alternations are common (Fig. 3). High limonite and hematite content of the concretional ore gives a reddish -brown colour to it. Green claystone formations consist of well laminated silty clays, and their bedding surfaces and micro fractures include manganese oxide dendrites. Claystones include plant, fish and shark fossils,and gypsum nodules. Claystone is overlain by secondary carbonate concretions - bearing sandy mud of the Miocene.

Mineralogy and Petrography

The ore minerals of the Binkılıç manganese deposit are pyrolusite, psilomelane, cryptomelane and manganite as oxides and hydroxides and rarely kutnahorite and rhodochrosite as carbonates. Low grade soft ore mainly consists of psilomelane and poorly crystalised manganese oxyhydroxides. The gangue minerals of this ore are calcite, Mg - calcite, quartz, feldspar, chalcedony and montmorillonite. Microprobe analysis of the two feldspar minerals from low grade ore horizon indicate that these are albite and andesine in composition. High grade -hard ore consist of microscopic pyrolusite and lesser amounts of manganite as disseminated - coarse crystals

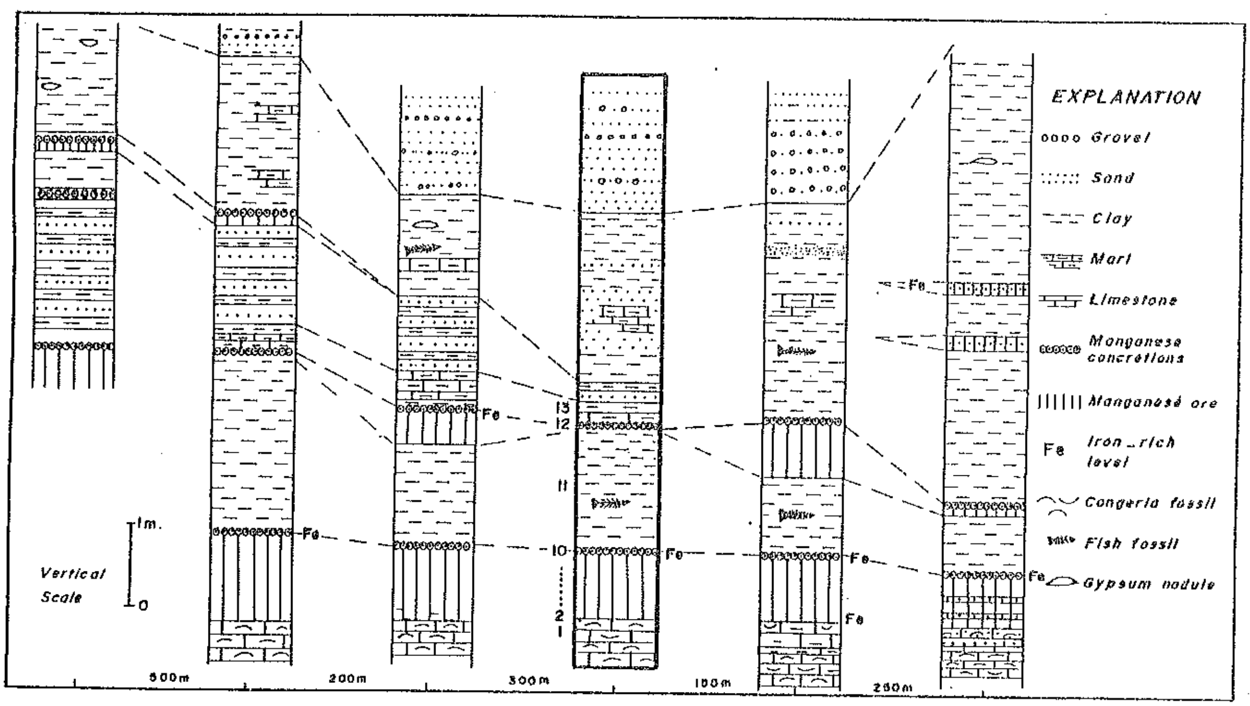


Figure 3. Stratigraphic correlation among the manganese ore levels at the Binkılıç ore deposit. Solid - lined column and numbers indicate sampling horizons.

Şekil 3 : Binkılıç manganez yatağında cevher düzeyleri arasındaki korelasyon. Kalın cizgili sütün örnekleme yapılan düzeylcri göstermekte.

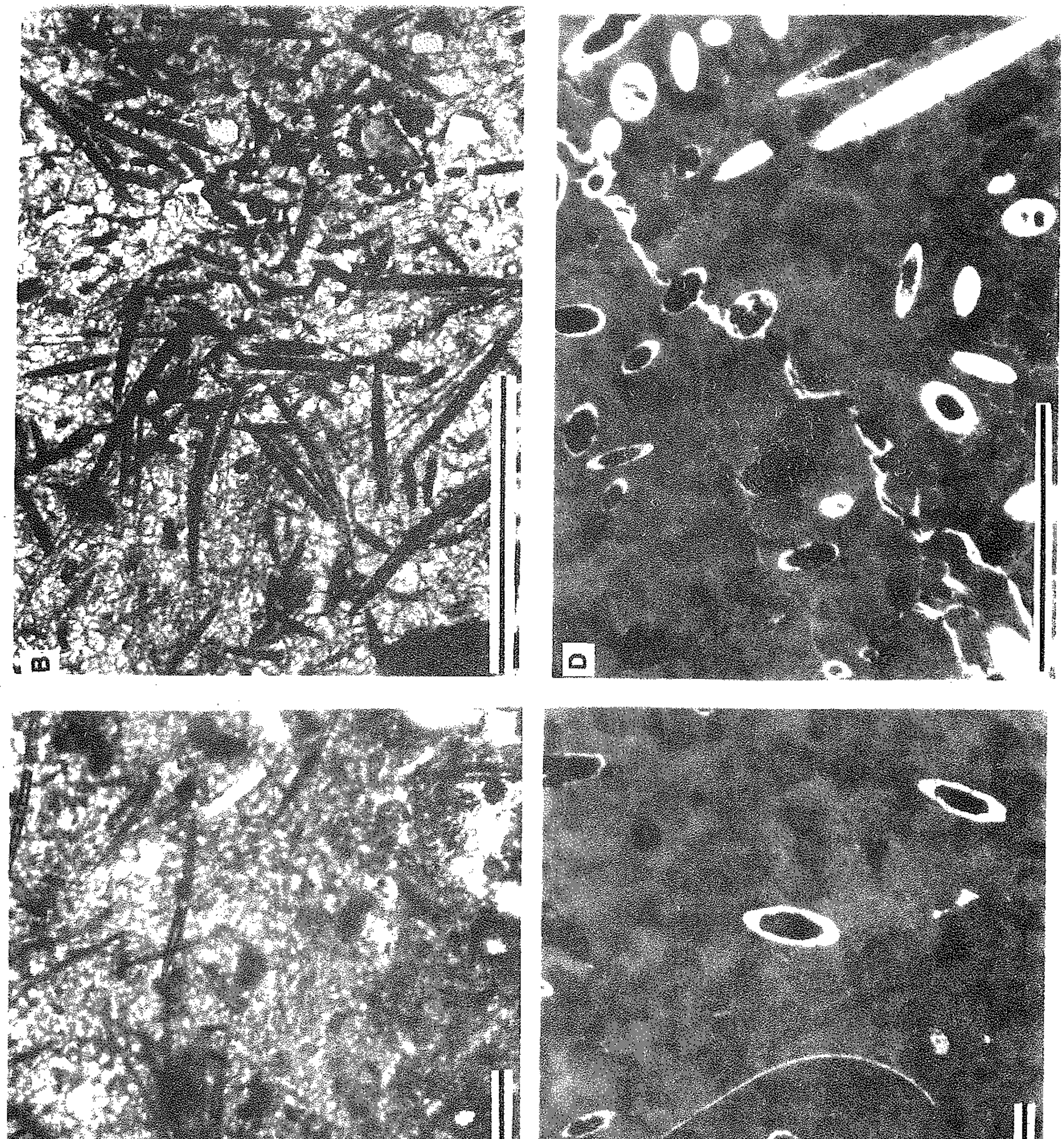
Table 1 : Major and trace element contents of the different units of the Binkılıç manganese deposit. - indicates below of the detection. Remainder is LOI.

Tablo 1 : Binkılıç manganez yatağında farklı birimlere ait major ve iz element değerleri - dedeksiyon limitinin altında olduğunu göstermekte. Kalan değerler kızdırma kaybıdır.

Unit	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	MnO	Fe_2O_3	BaO	SrO	P_2O5	TiO_2
1	2.2	0.5	53.6	0.4	0.1	0.1	0.1	0.2	–	0.2	0.13	0.02
2	2.2	0.4	48.9	0.8	0.1	0.1	4.1	0.6	0.01	0.05	0.66	0.03
3	12.1	3.0	6.6	1.1	0.6	0.4	51.2	1.2	0.12	0.12	0.22	0.14
4	13.2	3.5	6.2	2.4	0.6	0.8	46.3	2.5	2.09	0.81	0.27	0.16
5	7.7	1.1	0.9	1.1	0.4	0.6	69.2	-	1.02	0.39	0.25	0.03
6	7.6	2.1	20.3	1.3	0.9	0.43	2.2	2.0	1.84	0.82	0.44	0.08
7	2.7	1.0	1.1	1.3	0.3	0.6	67.9	1.8	1.58	0.51	0.4	0.06
8	11.1	2. 2	1.6	1.1	0.7	0.65	7.8	1.0	1.95	0.81	0.34	0.09
9	4.3	0.9	20.0	1.3	0.1	0.1	32.7	0.4	0.08	0.03	0.25	0.04
10	12.2	3.0	21.9	1.4	0.8	0.5	29.7	1.4	1.44	0.67	0.35	0.11
11	49.4	15.5	4.9	3.0	2.2	0.6	0.1	6.2	0.03	0.02	0.18	0.18
12	2.5	0.6	16.8	0.4	0.1	0.1	37.9	12.7	0.33	0.11	0.3	0.06
13	11.3	3.3	43.7	0.9	0.4	0.2	1.0	2.0	0.1	0.03	0.25	0.15

	C %	S %	V ppm	Ni ppm	Co ppm	Cr ppm	Zn ppm	Cu ppm	Y ppm	Zr ppm		
1	11.11	< 0.01	7.1	37.2	7.5	9.9	<1.0	1.6	4	30.3		
2	10.94	0.02	25.7	68.5	13.4	26.3	8.6	3.5	11.3	6.9		
3	0.31	0.11	166	297	77.8	<1.0	44.9	8.7	20	28.2		
4	1.07	0.02	172	106	64.6	<1.0	34.6	17.9	13.3	70.4		
5	0.01	< 0.01	77.8	41.8	52.7	12.6	37.4	13.8	13	17.2		
6	4.6	< 0.01	103	291	91.6	4.1	51.4	20.3	31.8	26.4		
7	0.01	< 0.01	122	91.6	83.8	<1.0	44.7	21.8	14	15.6		
8	0.12	<0.01	139	7.1	43.8	9.8	28.9	9.2	15.6	29.0		
9	9.68	0.02	90.8	116	41.4	<1.0	18.1	4.3	12.7	9.2		
10	5.12	0.03	97.1	240	81.2	<1.0	44.9	17.1	23.8	26.5		
11	4.31	2.67	244	496	84.5	198	229	124	23.3	110		
12	4.12	0.01	85.5	295	110	<1.0	80.5	82.4	12.5	7.1		
13	9.49	<0.01	53.4	80	17	65.1	16	9.8	17.5	23.9		

or radiating vug infilling. Manganites are seen as altering to pyrolusite along their margins and micro fractures. High grade- hard ore exhibits relict texture of the sponge spicules, implying a original rock of the high grade hard ore was carbonate which was completely replaced by manganese at first to manganese carbonate followed by manganese oxides (Fig. 4). It is possible to detect all the steps of the mineralization stages from calcite spiculite to calcium-manganese carbonate spiculite and finally to manganese oxide spiculite. Carbonate ore consists of rhodochrosite and kutnahorite in colloform texture with lepidochrosite. Microprobe studies indicate that phosphorus content of the ore is related to carbonate phase. Microprobe study has been carried out from carbonate ore samples which indicate that Mn -Calcite and rhodochrosite is Mn 0.8 -0.2 Ca 0.2-0.8 CO_3 in composition. Concretional ore is generally composed of compositionally banded pyrolusite,psilomelane, limonite and cryptomelane minerals and especially occurs at the rim of the concretion. The cortex of the concretion consist of scattered manganese oxides in the spary calcite matrix. The core of the concretion consists of carbonate matter not exhibiting laminated texture. Green claystone is composed of mainly montmorillonite, calcite, quartz, gypsum and pyrite. Pyrite has been determined by X-ray diffraction and occurs as very fine grained mineral.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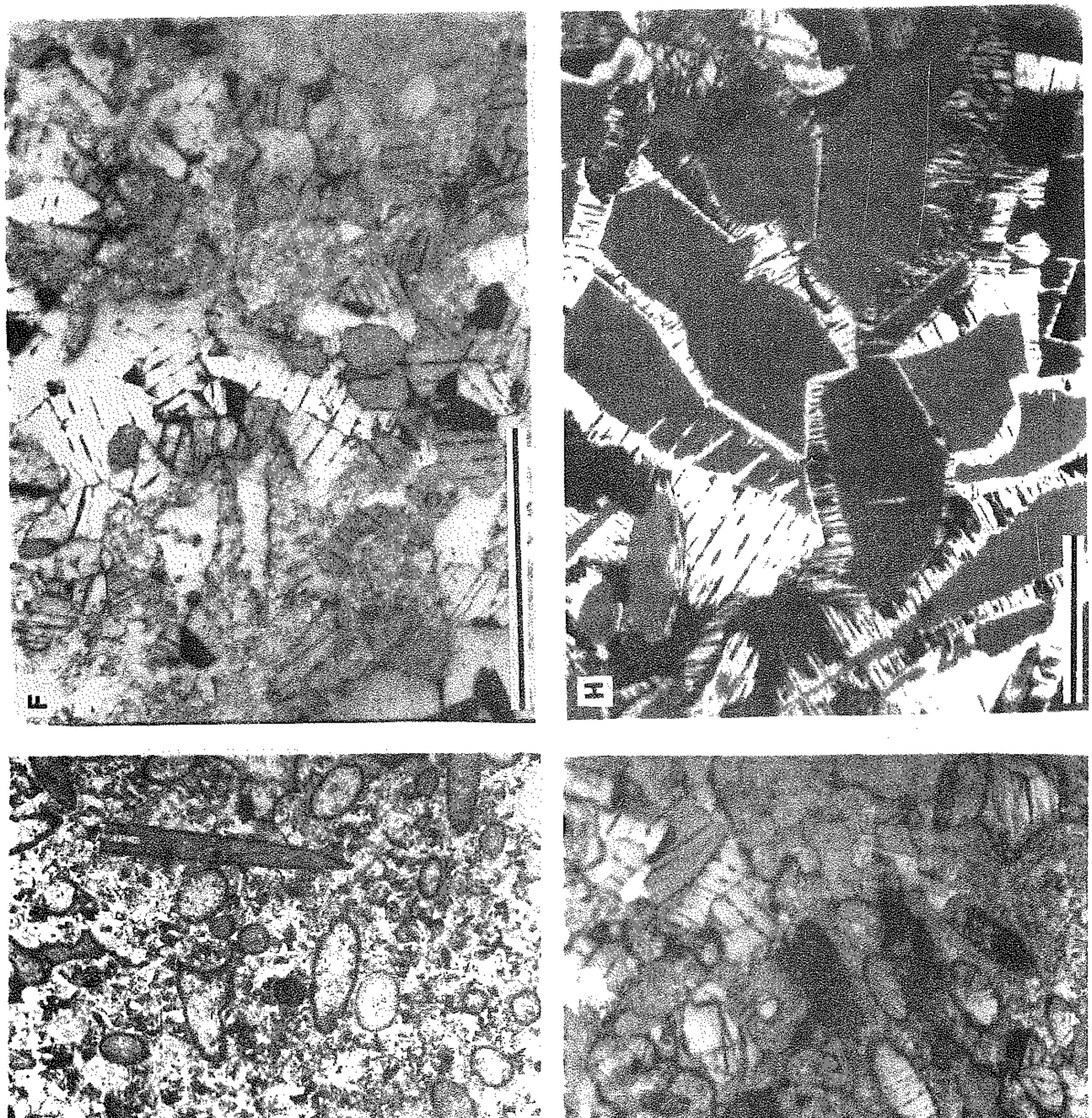
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Figure 4 : Thin and polished section photomicrographs of the Binkılıç manganese deposit. A- Thin section photomicrograph from calcite spiculite consisting mostly of monoaxon sponge spicules within micritic matrix. B- Thin section photomicrograph from carbonatic manganese ore showing rhodochrositic - kutnahoritic spicules within calcite and Mn- calcite matrix. C- Polished section photomicrograph from carbonatic manganese ore that consist of spicules and ostracoda fossil. D- Polished section photomicrograph from carbonatic ore showing advanced stage of the replacement and begin of the oxide mineral development (white is pyrolusite). E- Polished section photomicrograph from high grade massive ore, showing well - preserved relict spicule structures. The basal sections of the spicules are circular or eliptical whereas, the longitudinal sections are needle. The ores consist complete of microscopic - submicroscopic pyrolusites. F- Polished section photomicrograph from high grade oxidised ore consisting of medium -sized pyrousites with twin lamella. G- Polished section photomicrograph from high grade - hard ore (mangcrete) showing relict spicule structures despite successive recrystalization events. Vug infilling type mineral growth is common that represented by lamella twins - bearing pyrolusites (polianite). Black is quartz. H- Polished section photomicrograph from oxidised ore showing manganite (gray) agregates as altering to pyrolusites (white) along their rim. All scale bar represent 0.2 mm. Polished sections photomicrographs using polarised light and oil immersion, and thin section photomicrographs using polarised light .

Şekil 4 : Binkılıç manganez yatağından ince kesit ve parlatma kesit mikrofotografları kalsitik spikülitten çekilen ince kesit mikrofotografında mikritik matrix içinde monoaxson tip sünger spikülleri görülmekte. B- Karbonatik manganez cevheri mikrofotografında rodokrosit ve kutnahorit spikülleri kalsit ve mangan kalsit matrix içinde izlenmekte. C - Karbonatik cevherden parlatma kesitte spikül ve ostrakoda fosil yapıları. D- karbonatik cevherde ileri derecede replasmanı belgeleyen oksit mineral gelişimi (beyazlar pirolusit) E - Yüksek dereceli masif cevherde parlatma kesitte oldukca iyi korunmuş spikül yapıları. Spiküllerin bazal kesitleri daireselden ekliptiğe yaklaşan form verirken, parelel kesitleri iğnemsi şekil göstermekte. Cevher tamamen mikroskobik - submikroskobik pirolusitlerden oluşmakta. F - Yüksek dereceli odsitlenmiş cevherden parlatma kesit mikrofotografarında orta irilikte lamel ikizli pirolusitler. G - Yüksek dereceli sert cevher parlatma kesit mikrofotografında tekrarlanan rekristalizasyon olgusuna rağmen relikt spikül yapıları izlenmekte. Boşluk dolgusu tipinde mineral büyümesi lamel ikizli pirolusitlerle (polianit) temsil edilmekte. Siyah kuvars. H- Oksitlenmiş cevherde parlatma kesit mikrofotografında manganit agregatlarının kenarları buyunca pirolusite (beyaz) dönüşümü. Bütün ölçek çubukları 0.2 mm. yi temsil etmekte. Parlatma kesit mikrofotografları polarize ışık ve yağ ortamında çekilmiştir. İnce kesit fotografları polarize ışıkta çekilmiştir.

Geochemistry

The major and trace elements including REEs of the different type of manganese ores, and hosting carbonates and silty claystone were analysed (Table 1). The analytical results show the differences in geochemical features between the manganese ores and host carbonates and the claystone. Geochemical analyses through the ore section reveal five interelemental groups such as Al-Si- Na - K, Fe - Cu- Zn - P, Ba -Sr- V, Co- Ni and, Cr-Ti- Zr (Fig. 5). Mn shows positive correlation with these element associations except with detrital components such as Cr, Ti, and Zr. Mn shows negative correlation with Ca and Fe.

Al- Si- Na and weak K assemblage is related to detrital feldspar represent by albite, andesine and labrador,and mica minerals as sericite, occuring within ores that were detected by thin section and microprobe studies. Al and Si association is also related to clay minerals as shown at the green claystone values (unit 11). Fe- Cu - Zn-P association is mainly related to limonite and/or iron oxides- oxyhydroxides which is relatively enriched in the concretional ore (unit 10-12). Cu and Zn enrichments within the manganese ore may have been related to supergene oxidation of the manganese or ferromanganese deposits which is called "dubhite" by Nicholson (1992). Cu - Zn and P also show positive correlation with Fe and as well as Mn. Co and Ni especially increase in the low grade manganese ore which could be related to wad or weakly crystallized manganese oxyhyroxides and their high absorption capacity of the positive charged metal ions. Co and Ni are enriched in psilomelane and limonite minerals and thus pyrolusite - rich high grade ore relatively poor as Co and Ni. Ba- Sr and V have not individual mineral. Ba closely related to psilomelane and Sr weakly correlate with Na and Si that could be an indicator of the bounding in the crystal latice of celcian feldspar. Cr -Ti and Zr contents of the carbonatic host rocks and the ores are extremely low that indicate low detritial input to the sedimentary basin associated with tectonically stable conditions and /or peneplened an Oligocene paleogeography.

Mn/ Fe ratios of the Binkılıç Mn deposit are generally high which reveals that Mn and Fe completely separated during the formation of manganese deposition. Mn/ Fe values of the low grade ores vary from 60 to 4 , whereas high grade hard ore show high values vary between 500 and 35. Increase of the Mg is a distinctive features throughout the ore succession which is related to Mg - Calcite and Mg - kutnahorite formation as detected by probe from carbonate minerals. S and C (sum of organic and inorganic carbon) contents of the ore succession reflect a very interesting distribution pattern as an increase of S in the mineralization horizon,with depletion of C (Table 1). Decreasing of the carbon content at the ore succession indicate that dissolving calcitic material and removing carbonate from the system. The high S content within the claystone is related to both pyrite and gypsum.

The increase of the Ba, Sr, Na, P and Mg and the certain heavy metals such as Co, Ni, Cu, Zn, and V within manganese ore is a general phenomenon for the manganese - ferromanganese deposits as concluded by several investigators. However, there is not a good published explanation of enrichment mechanism of certain elements especially for P, Na, Mg, Sr and Ba. Very distinctive Mg and Na enrichments within ore horizons of the sediment succession has been reported by Okita (1992) at the Molongo District Mn deposits, Mexico and at the Imini Deposit, Morrocco, (Force et al.1986) at the Urküt Deposit, Hungary (Polgari et al. 1991) and Groote Eylandt Deposit, Australia (Pracejus and Bolton 1992) Urucum district Fe-Mn deposits, Brazil, (Urbàn et

Table 2 : REE contents of the Binkılıç Mn ores and its host rocks (After from Öztürk and Frakes,1995. Note that - indicate less than 0.5 ppm.

Tablo 2 : Binkılıç manganez cevheri ve yankayaçlarının nadir toprak element değerleri (Öztürk ve Frakes 1995 den) - 0.5 ppm den az olduğunu göstermekte.

Unit	1	2	3	4	5	6	7	8	9	10	11	12	13
La	3	16	14	15	10	32	12	17	11	21	27	9	15
Ce	4	20	22	39	17	54	23	25	16	34	54	8	24
Nd	2	12	15	13	9	26	9	14	3	17	27	5	12
Sm	-	2	3	3	2	5	2	3	2	3	5	1	2
Eu	-	1	1	4	2	4	3	4	1	3	1	1	1
Gd	-	2	3	2	2	5	2	3	2	3	4	1	2
Tb	-	-	1	-	-	1	-	-	-	1	1	-	-
Dy	-	2	3	2	2	5	2	3	2	3	4	1	2
Er	-	1	2	2	1	3	1	1	1	2	3	1	1
Yb	-	1	2	2	1	3	1	1	1	2	3	1	1
Lu	-	-	-	-	-	-	-	-	-	-	-	-	-

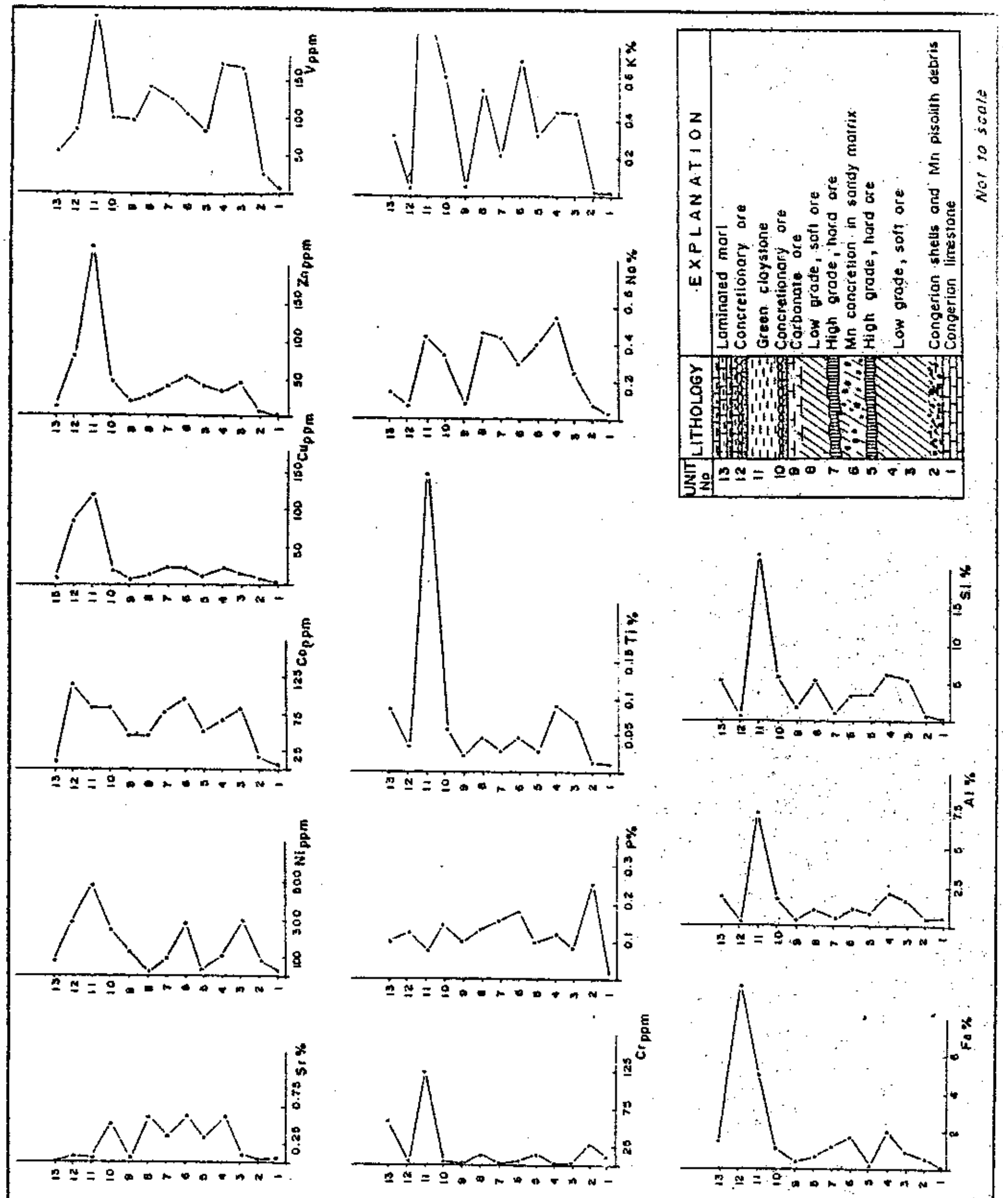

Figure 5. Major and trace element variations through stratigraphical section of the Binkılıç deposit.
Şekil 5 . Binkılıç manganez yatağında stratigrafik kesit boyunca major ve iz element değişimleri.

al. 1992). Force et al. (1986) concluded that the source of the Mg is sea water and both Mn and Mg have been deposited as a result of the interaction of the salty sea water and fresh water at the coastal zone. The saline fresh water mixing zone is known as an area of enhanced calcite dissolution (Back et al. 1979), change in porosity and permeability and favourable places for dolomitization (Randazzo and Bloom 1985). Nicholson (1992) proposed a Mg versus Na diagram for differentiating supergene marine and fresh water deposits. The ores of the Binkılıç Mn deposit fall in the shallow marine field at the Mg versus Na diagram (Fig. 6). However, the author

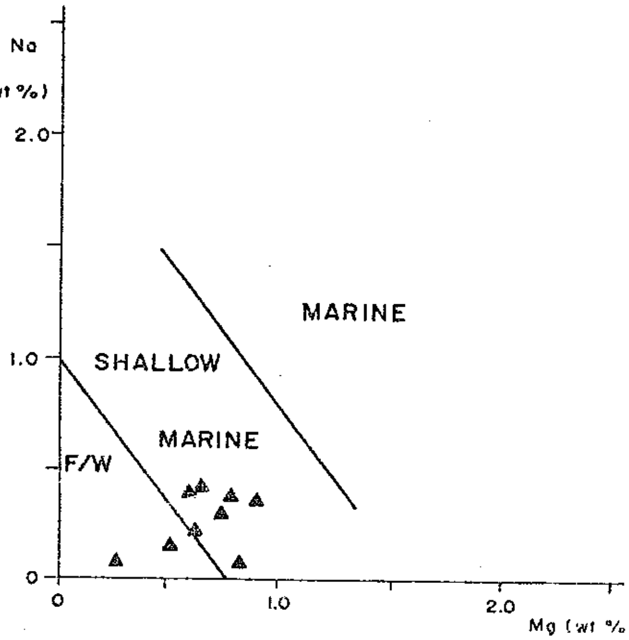

Figure 6. Na versus Mg diagram (Nicholson, 1992) of the Binkılıç manganese deposit to discriminate supergene fresh water and supergene marine deposit.

Şekil 6. Sodyuma karşı magnezyum diyagramında (Nicolson, 1992) Binkılç manganez yatağının tatlı su cevherleşmesi ile denizel cevherleşmesi açısından konumu.

is not sure that this diagram is acceptable for differentiation of the diagenetic replacement type Mn deposits due to complete change of the primary host rock chemistry.

Supergene albitization related to authigenic replacement processes of the detrital K feldspars by Na - bearing fluids has been discussed in detail by Saigal et al. (1988) and Aagaard et al. (1990). The increase of the Na through the ore section might be related to supergene albitization. The source for Na might be halite which could have been dissolved by recharging supergene fluids through the evoporatic carbonates or salty marsh sediments. Replacement of the K feldspars such a reaction K $KAlSi_3O_8 + Na^+$ ------------> $NaAlSi_3O_8 + K^+$ is common. The potassium may react with silca thus cryptomelane, glauconite , illite may have been formed. Orthoquartzite - glauconite- clay association is a characteristic feature for the Oligocene Mn deposits and also for the Cretaceous, Groote Eyland (Oswald and Bolton 1992). However, albite,andesine and other K - feldspar minerals within the ore horizon are seem to be originating from basement rocks based on perthitic exsolution, advanced sericitic alteration, and epidote formation.

High Ba content of the ore may be related to psilomelane due to lack of hollandite. High Ba contents of the Mn deposits are known some of the deposits, (e.g. Imini deposit up to 11 % BaO, Force et al. 1986). High Ba and the strong Ba - Mn association has been proposed to be an indicator of the fresh water manganese deposition by Nicholson,(1992). On the other hand, Morey and Southwick, (1993) argue that Ba mobilised in anoxic water conditions and precipated with manganese when mixing with aerated water. This model generally is in favour for the explanation of high Ba contents and strong Ba and Mn association in the ores.

Low aluminium content of the ore and lack of lithiophorite or gibsite within the ore indicate that long term weathering processes are not closely related to Mn deposition. Al and Si contents of the ores had been plot-

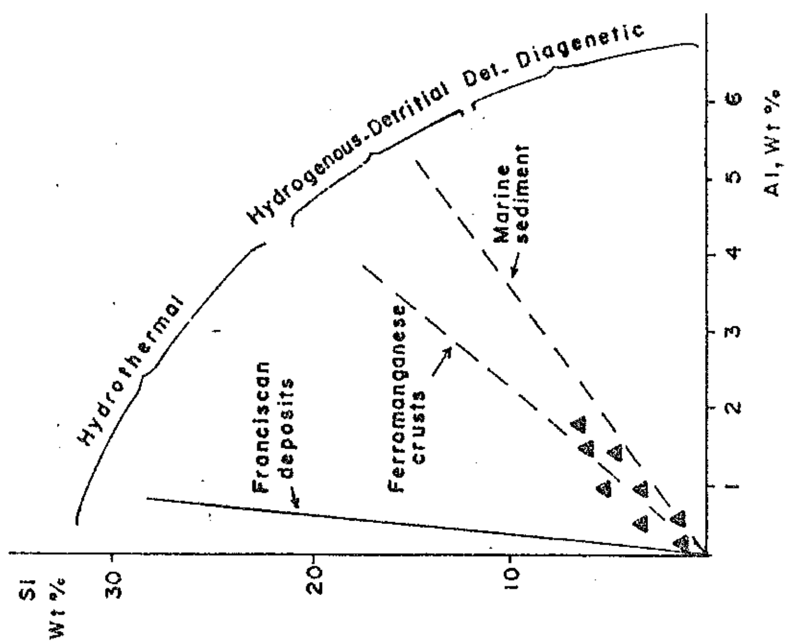

Figure 7. Al versus Si diagram (Crerar et al. 1982) for the Binkılıç Mn ores.

Şekil 7. Binkılıç manganez cevherinin Al-Si diyagramındaki (Crerar ve diğ. 1882) konumu.

ted on the diagram of Crerar et al. (1982) to determine hydrogenic and detritial- diagenetic contributions to the ore formation. The Binkılıç Manganese ores generally fall in the hydrogenous - detrital field rather than diagenetic ones as shown in figure 7. Main explanation of this phenomenon is relatively low clay content of the primary calcitic sediments. The reason for high Si is the presence of detrital quartz within ore. In addition, Si was introduced to the system by supergene silicification represented by chalcedony and secondary quartz.

Rare Earth Element Geochemistry

Rare Earth elements contents throughout the ore section are generally lower than the North American Shale composite (NASC) values with exception of Eu (Table 2). All the stratigraphic units shows characteristic REEs pattern representing by strongly positive Eu and weakly negative Ce anomalies (Fig.8). All the REEs typically increase at the mineralization level. The congerian limestone especially have low REEs content whereas, claystone and marl have nearly similar REEs contents with ores.

Mean values of the Eu is 2 ppm which is higher than that for NASC (1.24 ppm). On the other hand, the mean value of Ce is 26.1 ppm which is three times lower that for NASC. None of the major or trace element shows a linear dependence with REEs. Mean value of the Ce/ La is 1.7 ppm which is very close to NASC values (2.3 ppm).

Interpretation of REE pattern

Although a current studies carried out on the relationship between manganese deposits and their rare earth element distributions, there is neither generally accepted distribution pattern reflecting that the processes of the formation of manganese deposits such as hydrothermal, hydrogenetic, and diagenetic., nor formation conditions such as oxidative or reductive. Two important elements of the rare earths, Ce and Eu especially has been used as an approach for origin of the fluids and redox potentials of the depositional environment. Minor negative Ce anomalies presumed as the indicator of volcanogenic input (Fleet et al. 1976) or to be indication of hydrothermal contribution to sea water (Bender et al. 1971., Dymond et al. 1973) Positive Eu anomalies generally has been accepted as an indication of reflection strongly reducing conditions as shown in banded iron formations (Graf,1978) .Otherwise, Kunzendorf and Glasby (1994) determined positive Ce and mildly negative Eu patterns in modern manganese nodules and crusts at the ocean basin, formed in oxidative depositional conditions .The inverse REE pattern of the Binkılıç manganese ore compared to the oxidative condition products, on the contrary indicate that manganese depositions took place in reducing conditions. However, both secondary mobilisation of the REE elements related to secondary replace-

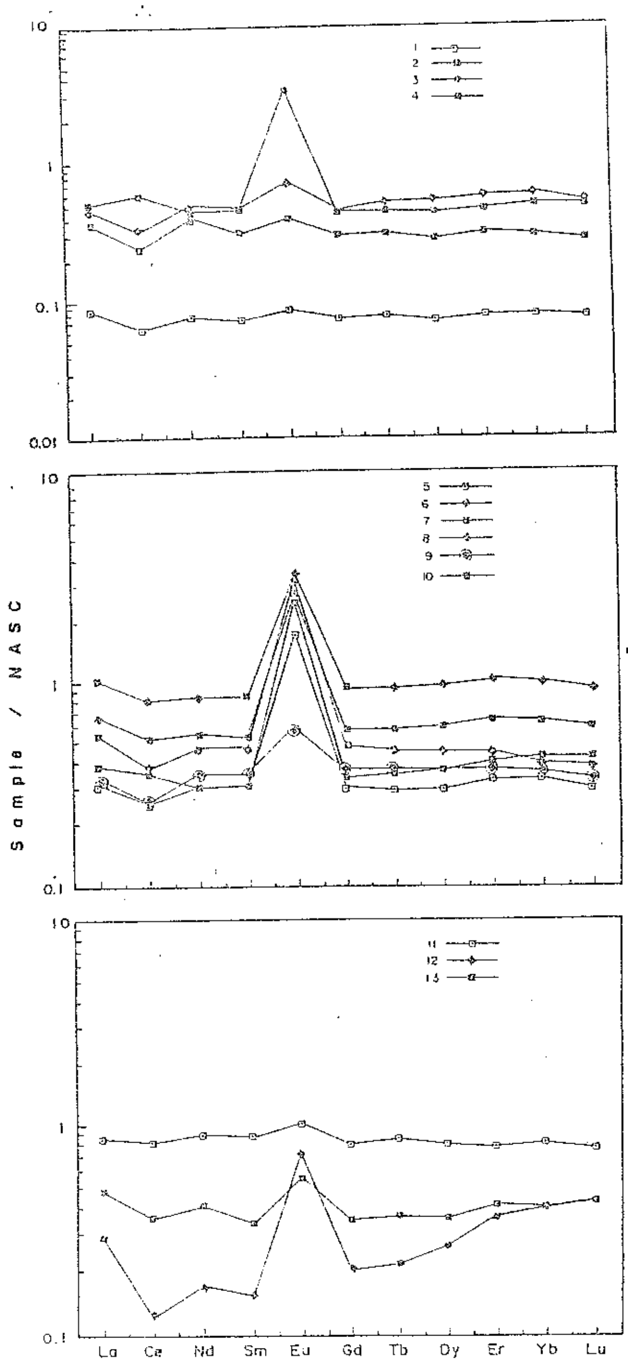

Figure 8. Shale- normalized REE pattern of the stratigraphic units through the ore section.

Şekil 8. Cevher sütunu boyunca Kuzey Amerika Şeyllerine oranlanmış nadir toprak elementlerinin değişim grafiği.

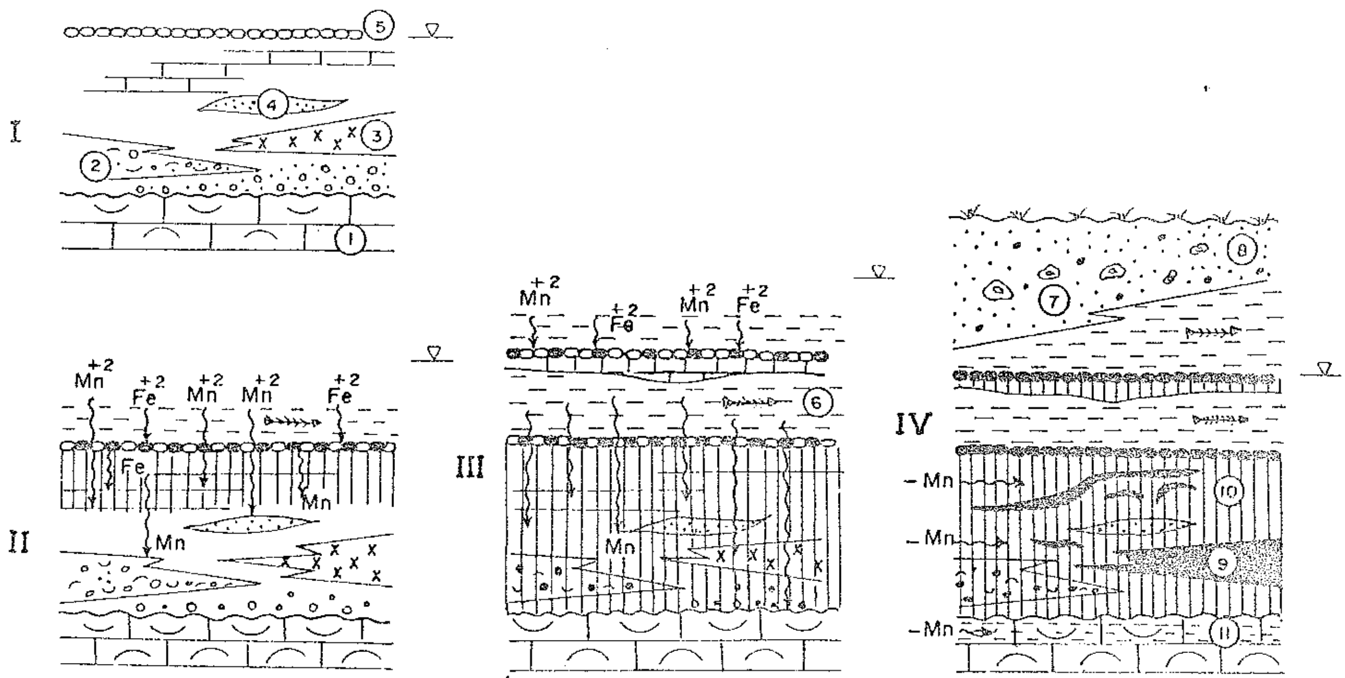

Figure 9. Formation model for the Binkılıç manganese deposit. I: Changing of deposition condition from lagoon or brackish water to marsh and finally - delta environment related to sea regression. Calicification and carbonate concretion might be occurred locally, presumably close to the exposed surface regression related mud plain. II: Claystone deposition were formed under the extremely low sedimentation and anoxic condition, in where aquatic fauna were completely extincted due to basinal anoxia. Iron and manganese rich anoxic fluids moved downward and the first Fe^{+2} has been trapped at the claystone carbonates interface and following Mn has been deposited as a result of gradually increase of pH and Eh. III: Replacement of the carbonatic sediments by Mn^{+2} and certain manganophile elements rich anoxic and possible mildy acidic supergene waters. Fresh water action may have been played a role as carrying both oxygen and metal ions into interaction zone. IV: Downward penetrating supergene solutions and ground water flow has been resulted the manganese oxide infiltrations, late diagenetic manganese enrichments and recrystalization amorph or weakly crystalized wad or psilomelane to pyrolusite. Numbers indicate., 1: Congerian limestone, 2: reworked carbonate pisolites and concretions, 3: spiculite. 4: feldspatic detritics, 5: carbonate concretions 6: claystaone 7: deltaic sand - mud 8: calcite geods 9: high grade - hard ore 10: low grade - soft ore. 11: infiltrated ore.

Şekil 9. Binkılıç managnez yatağı için önerilen oluşum modeli. I: Su seviyesindeki düşme ile havza çökelim koşullarının lagünden acı suya - bataklığa ve delta ortamına dönüşümü. II. Oldukca düşük sedimentasyon oranlı, durgun anoksik ortamda kiltaşlarının çökelimi ve havzadaki anoksia nedeniyle su canlılarında toplu ölümün gelişimi. Demir ve manganezce zengin anoksik suyun dip sedimentlerin içine difüzyonu, Eh ve pH değişimine bağlı olarak, demir +2 iyonlarının ve manganez karbonatların su - karbonatik sediment ara yüzeyinde çökelmesi. III: Karbonatik sedimentlerin +2 değerli manganez ve manganofil elementlerce zengin hafifce asidik süperjen sistem tarafından ornatılması. Yeraltı suyu, etkileşim zonuna oksijen ve metel taşıyarak manganez çökeliminde rol oynamış olabilir. IV: Sediment içine sızan suların derine penetrasyonu mangenz oksit infiltrasyonları, geç diyajenetik zenginleşmeleri ve amorf veya zayıf kristallenmiş psilomelenların pirolusite oksitlenmesini sağlamıştır. 1- Konjeryalı kireçtaşı, 2- yeniden işlenmiş karbonat pizolitleri ve konkresyonları, 3- spikülit, 4- feldispatik kırıntılıları, 5- karbonat konkresyonunu, 6 - kiltaşı, 7- deltaik kum - çamur, 8 - kalsit jeodları, 9- yüksek dereceli sert cevher, 10 düşük dereceli yumşak cevher, 11- infiltrasyon cevheri .

ment processes and also some of the elements could be originating from original lithologies that may have been served to change of the nature of the REEs. The close relationship between REEs contents of overlaying claystone and marls (unit 11- 13) and manganese ore may be an important indicator of the supergene processes or a link between claystone deposition and manganese ore formation. Another reason of the high Eu contents within the ore horizon is presence of the feldspar minerals.

Conclusion

Stratigraphic relations indicate that the Oligocene Binkılıç manganese deposit was deposited in shallow water conditions during the regression, passing from lagoon to brackish water and deltaic sedimentation. The regional uplifting and tectonically stable conditions during the manganese deposition marked by biostromal carbonates and the following very fine laminated claystone deposition. During the claystone deposition basin water was strongly anoxic and therefore fish and other aquatic fauna such as shark had been extincted. This is a general phenomena through the Paratethys deposits,for example similar fossils are found within the Maikop black clays that occur top of the Chiatura manganese ore deposit (Bolton and Frakes 1985). The original source of the manganese was land, that transported to the basin possible during the extensively development of a soil zone under the special climate. The manganese has been concentrated in the H_2S -rich anoxic basin water and its land extension sediments.

Manganese ore formation were lithologically controlled by the deposition and the distribution of the carbonates which formed in lagoon and bay environment of the Thrace basin. Such environment were very favourable places for both primary manganese accumulations and also secondary input by fresh water flow with large volume.

A conceptual formation model for the Binkılıç manganese deposit is seen in figure 9. The mineralization has been formed as a result of the carbonatic host rock replacement by the manganese - rich downwelling anoxic basin water. This time fit to the extensively terrestrial weathering and claystone deposition. The first Mn carbonates and ironoxides has been formed by early diagenetic reactions at the sediment sea water interface and thus iron partly trapped at this level. Diffusion of the manganese to downward and deposition in there as manganese carbonates and oxihydroxides is coeval with claystone depositon. The presence of the fresh feldspar minerals within the both low grade and high grade ore indicating alkaline conditions during the carbonate depositons and fluid sediment interactions In this manner, manganese - bearing supergene solutions were not acidic and organic reactions has not been played major role at the manganese deposition. Complete replacement processes of the carbonatic matter is evidenced essentially by petrographic study. The high grade - hard ore has been formed by ground water action during the late diagenetic stage and ore section has been mostly oxidised.

The negative Ce and positive Eu anomalies, presence of the pyrites and faunal extinction during the claystone deposition indicate that depositional condition was strongly anoxic during the claystone deposition and coeval manganese ore formation However, the reason of the global anoxia throughout the Paratethys during the Oligocene remains as an enigma.

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Özet

Binkılıç manganez yatağı Trakya Havzasında Oligosen yaş konağında bulunmakta, cevher tipi , yaşı, yan kaya ilişkileri, mineralleri açısından Gürciastan (Chiatura), Ukrayna (Nikopol) ve Bulgaristan'daki (Varna) yataklara oldukça benzerlikler göstermektedir. Cevherleşme, altaki karbonatlarla üstteki kiltaşları arasında bulunmaktadır. Karbonatlar oksik ortamı, kiltaşları anoksik ortamı karekterize etmektedir. Oksik süreçten anoksik sürece geçişte gerçekleşen managnez cevcherleşmesi alttan üste mineralojik, kimyasal ve yapısal olarak farklılıklar göstermektedir.

Tavanda kiltaşlarının hemen altında yer alan zon, esas olarak demir oksit ve manganez karbonattan oluşmakta, konkresyonel yapı göstermektedir. Orta düzeylerdeki masif sert cevher bantları pirolusit ve manganitten oluşmakta ve pizolitik yapı göstermektedir. En tabana yakın kesimlerde yumşak cevher ve infiltrasyon cevheri söz konusudur. Bu düzeyin egemen minerali psilomelandır. Yüksek dereceli sert cevher ve infiltrasyon cevheri geç diyejenetik süreçlerin, manganez karbonatlar - oksihidroksitler erken diyajenetik evre ürünü olmalıdır.

Manganez yatağındaki petrogarfik - petrolojik incelenemler cevherleşmenin karbonatik kayaçların replasmanıyla olduğunu göstermektedir. Bu bağlamda, cevherleşme, üsteki havza suyunda zenginleşen manganez iyonlarının tabanda bulunan kalsitik maddeyi replese etemek suretiyle gelişmiştir. Cevher düzeyinde yapılan nadir toprak element analizleri değerleri ve element paterni açısından üstteki kiltaşına benzerlik göstermektedir. Bu durum, anoksik süreçlerle cevherleşme arasında önemli bir bağlantının olduğunu göstermektedir.

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