Chapter 6
Manganese Deposits of Turkey

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Abstract Turkey comprises different types of manganese deposits which were identified by the Mineral Research and Exploration Institute of Turkey (MTA) in 1965 (MTA. Manganese ore deposits of Turkey. General Directorate of Mineral Research and Exploration. Pub. No: 120, 38 p. (In Turkish), 1972). After many research works conducted on the formation and genesis of marine pollymetalic oxides that occur in the modern oceanic sediments, a new genetic classification of the marine ferromanganese manganese deposits was made by several workers (Frakes LA, Bolton BR. Geology 12:83–86, 1984; Rona 1992). Based on newly acquired knowledge, the manganese deposits of Turkey were divided into four main types according to host rocks, geological-tectonic settings and formation processes by Öztürk (Geol Eng 43:24–33. (In Turkish with English abstract), 1993a; Öztürk H. Ore Geol Rev 12:187–203, 1997; Öztürk H, Hein JR. Econ Geol 92:733–744, 1997). These types are (1) Black shale – hosted deposits, (2) Radiolarian chert – hosted deposits, (3) Oligocene – hosted deposits, (4) Volcanic arc – hosted and/or vein -type deposits. Although radiolarian chert – hosted type Mn oxides mineralization is widely distributed, they generally are small occurrences associated with ophiolitic mélanges but some of them may be of economic value. Economically important Mn deposits are in the black shale rocks in southwestern Turkey and in the Oligocene sediments in the Thrace Basin. The Oligocene deposits are connected to the Black Sea region deposits, including Varna (Bulgaria), Nikopol (Ukraine) and Chiatura (Georgia). Exploration studies by drilling programs have been made by MTA for the Oligocene – hosted Binkılıç deposit of the Thrace Basin (Bora E. Binkılıç ve Sefaalan Bölgesinin jeolojisi ve manganez yatakları. [The geology and Mn deposits of the Binkılıc¸ and Sefaalan area]. M.Sc. Thesis, Istanbul University, 47 p. (In Turkish, unpublished), 1969) and black shale – hosted Ulukent Mn deposit in Tavas region (Doğan H, Turkmen H. Ulukent – Tavas çevresindeki manganez yataklarının jeoloji Raporu. [Geological report of the manganese deposits of the

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Ulukent-Tavas and surrounding area]. General Directorate of Mineral Research and Exploration Report No: 345, 87 p. (In Turkish, Unpublished), 1983).

The representative manganese deposits or occurrences of each type are identified in this chapter on the basis of their age, host rocks, mineralogy, geochemistry and reserve – grade relationships. The distribution of the manganese mineral systems and the location of the important deposits in Turkey are shown in Fig. 6.1. The Mn ores of the main deposits were sampled and analyzed by ICP- MS at Acme laboratories in Canada, in 2015 exclusive for this chapter.

6.1 Introduction

Turkey is located in the Alpine – Himalayan orogenic belt and includes E-W trending manganese deposits that formed related to the evolution of Tethyan ocean. Most of deposits occur in a radiolarite-shale alternating deep sea sediments which have been subjected to broad mining activities. However, these occurrences or deposits occur as tectonic sheets or blocks in the accretionary complex of Cretaceous age and very rarely reach an economic grade. Only six deposits have been defined as economically viable among the more than 200 surveyed occurrences. Black shale – hosted manganese carbonate – silicate deposits also occur in passive margin sediments on the Taurus belt. A few hundred thousand tonnes of ore were extracted from these deposits, however, mining has stopped in these ore beds due to the

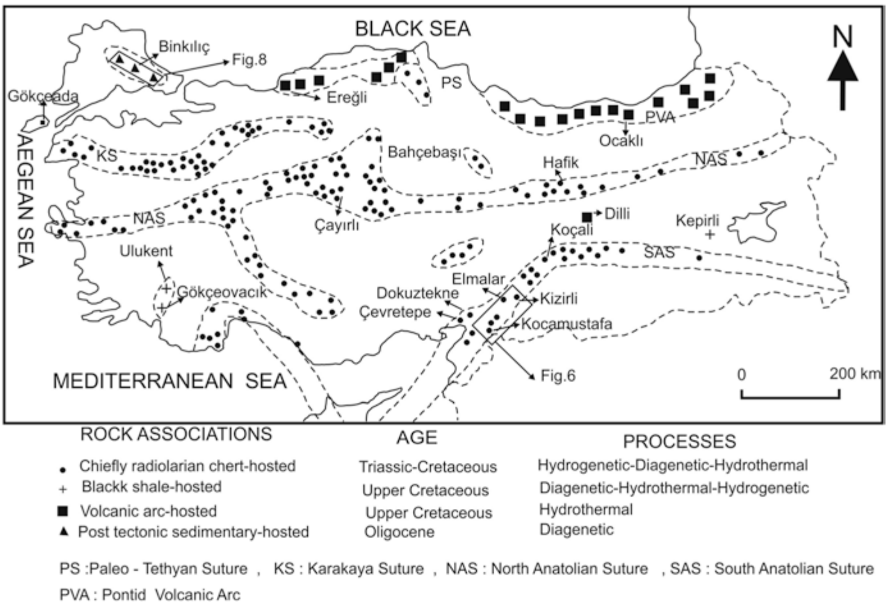

Fig. 6.1 Distribution and types of the manganese deposits in Turkey according to rock associations, ages and processes of formation. The map also shows the location of Figs. 6.6 and 6.8

increase in the stripping ratio. The licenses of these deposits belong to iron and steel factories of Turkey (Oyak Group) and the deposits have not been sufficiently investigated. In the Pontides, manganese ore deposits related to arc magmatism are seen along the Black Sea margin. A limited ore production was obtained from these hydrothermal veins and exported. Sedimentary manganese oxide beds of Oligocene age are located in the Thrace basin, NW Turkey where mining still continues. The geology, mineralogy and geochemistry of four types of manganese deposits are presented in this study.

6.2 Black Shale: Hosted Type Mn Deposits

Black shale-hosted Mn deposits are the most important in Turkey and annually 20,000 tonnes of ore are produced from the Ulukent deposit from 1980s to 2000s and a few hundred thousand tonnes of ore were obtained from the Gökçeovacık deposit from 1930 to 1950s.

6.2.1 Ulukent and Gökçeovacık Deposits

Black shale – hosted manganese deposits of Turkey are located in the western part of Tauride Mountains. The largest one of this type is the Ulukent deposit licensed to the Erdemir Mining Industry & Trade Inc.. Exploration studies of the Ulukent deposit have been carried out by MTA with a total of 54 drill holes (Doğan and Türkmen 1983). Kirmanlı and Nasuf (1998) made a reserve calculation for the Ulukent deposit using 42 drill hole data. According to the authors the Ulukent deposit includes a total of 6,922,714 tonnes of ore of which 3,428,303 tonnes are above the cut- off grade (32% Mn) whereas 3,494,411 tonnes of below this cut-off. Approximately 240,000 tonnes of ore with 25% grade has been mined form the Ulukent deposit with open pit method and sold to the Erdemir Iron and Steel factory. Owing to increased stripping ratio, mining was abandoned in 2001. The other important deposit of this type is Gökçeovacık deposit that occurs the south of the Ulukent deposit (Fig. 6.2).

The black shale – hosted manganese province of the western Anatolia has a large ore potential because of good outcrops of the both shale – carbonate rocks and associated mineralization which extend from the Ulukent to the Fethiye region (Kuşçu and Gedikoğlu 1989; Öztürk and Hein 1997). Despite large outcrops of the host carbonates, post mineralization tectonism has highly deformed and metamorphosed the ore zone associated with nappe emplacements in the Paleocene (Graciansky 1968) and also related to the extensional tectonism in the Miocene. Exploration and mining of these deposits reveal some difficulties owing to these multi stage tectonic deformations which resulted in modification of the original stratigraphic position and chemical mineralogical composition of the ore body.

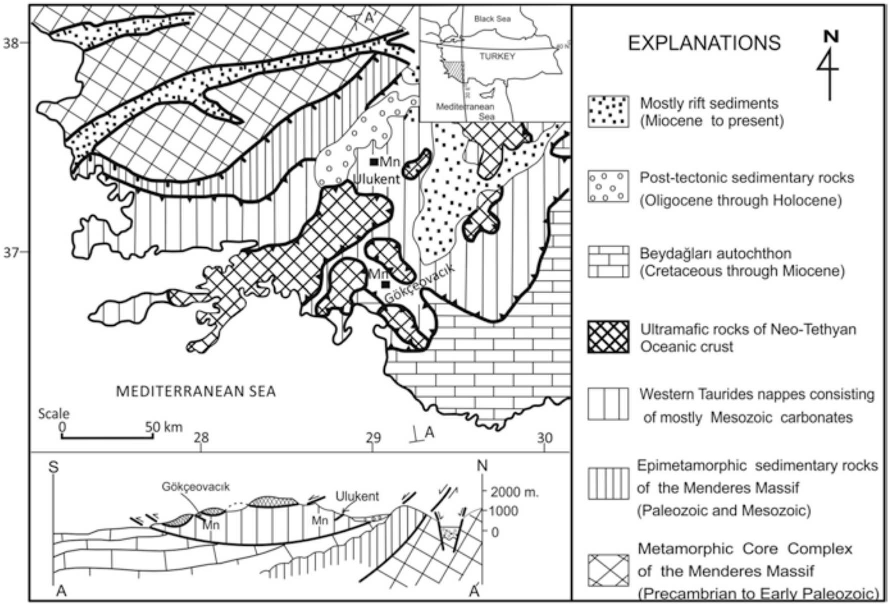

Fig. 6.2 Regional geologic map showing major tectonostratigraphic units of the western Taurides and locations of the Ulukent and Gökçeovacık Mn deposits. (Modified from Öztürk and Hein 1997)

The ore zone is situated between two shale units in the thick bedded passive margin carbonates (Fig. 6.3). Black bituminous shale at the base, includes coarse and cataclastic pyrites up to 15 mm in size. This black shale horizon also includes chalcedony – quartz veinlets. Gray colored shale does not include and large pyrites and silicification. The ore section begins with pisolitic – bauxitic low grade ore (detrital phase) at the bottom gradually passing to the carbonate – silicate ore and lastly oxidized ore. The brownish – pinkish bauxitic ore represents a sudden terrigenous input from the land into the sea associated with tectonic activity. This ore horizon mainly consists of anatase, diaspore, hausmannite, kutnohorite and hematite.

Silicate-oxide-carbonate is the most common ore type of the Ulukent Mn deposit and is composed of bustamite, tephroite, braunite, and hausmannite, the lesser amounts of jacobsite, kutnohorite, rhodocrosite, and Mn calcite. Gangue minerals include epidote, calcite, dolomite, quartz and stilpnomelane. Primary bedding planes within the ore can be seen in the both hand specimens and in polished sections. Silicate – oxide – carbonate ore shows very strong magnetism and XRD analyses indicated that the main magnetic mineral is hausmannite.

High-grade oxidized ore represents the supergene oxidation product of the silicate-oxide-carbonate ore, which locally caps the ore horizon with a thickness of up to 5 m. This high grade and porous ore shows a weak magnetism. This ore zone

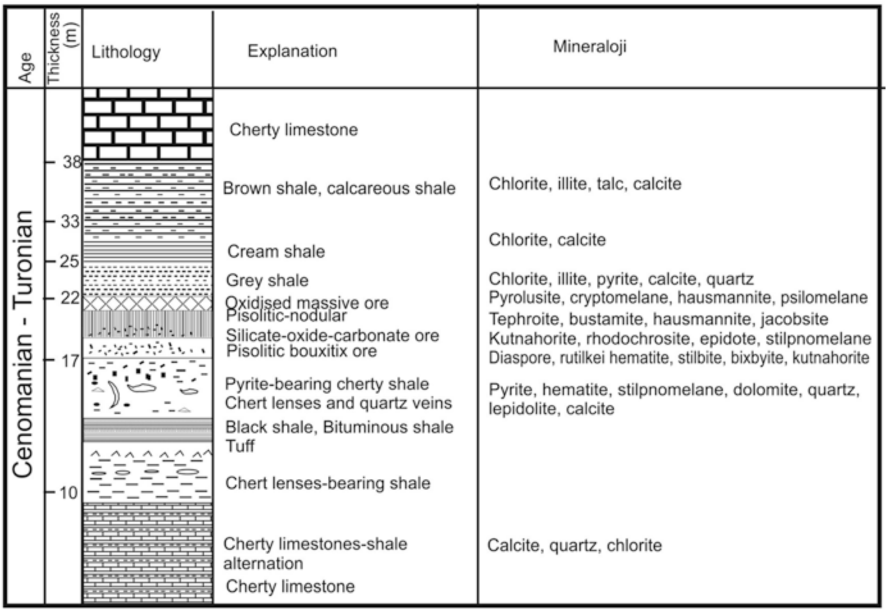

Fig. 6.3 Measured stratigraphic section of the Ulukent manganese deposit showing the main ore types, ore and gangue minerals

especially well developed along the fracture – fault zone that crosscuts the ore body and gained porosity due to alteration processes. This high quality ore zone consists of pyrolusite, psilomlane, limonite and lesser amounts of hausmannite and ranciete.

The Ulukent deposit displays some similarities and differences to well-known black shale – hosted Mn deposits, for example the Jurassic Urkut deposit in Hungary (Polgari et al. 1991), Molango deposit in Mexico (Okita 1992; Okita et al. 1988), and Taojiang deposit in China (Fan et al. 1992). The mean $\delta^{13}C$ and $\delta^{18}O$ values of eight ore samples which consisted of rhodoscrosite and kutnohorite are −12.2 and −4.5 per mil (PDB), respectively (Öztürk and Hein 1997). These values are so close to the Molango deposit of Mexico a world class black shale – hosted Mn deposits. $\delta^{13}C$ values of the Ulukent manganese deposit is lower than the Oligocene – hosted the Binkılıç manganese deposit whereas $\delta^{18}O$ values is higher. The C and O isotope systematics suggest a role of fresh water during the formation of the Binkılıç manganese deposit, whereas marine and more reducing conditions would have been more important during the formation of Ulukent manganese deposit (Fig. 6.4).

The black shale – hosted type Mn ore deposits are associated with anoxic basins with precipitation of primary mineral Mn carbonate silicate ore. Submarine volcanic activity may have been introduced the Mn into the sea water. A thin tuff unit at the bottom of the Ulukent manganese ore suggests such an activity. The primary

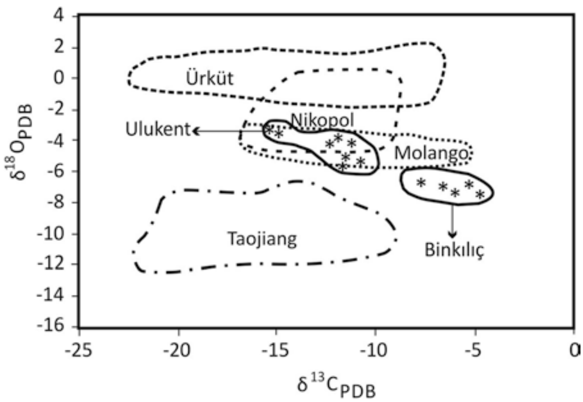

Fig. 6.4 Diagram of carbon vs oxygen isotopes of important Mn carbonate deposits of the world compared with the Ulukent and Binkılıç Mn deposit. (Data are from Oligocene Binkılıç (Öztürk and Frakes 1995); Cretaceous Ulukent (Öztürk and Hein 1997), Oligocene Nikopol, Ukraine (Hein and Bolton 1992), Jurassic Molango, Mexico (Okita 1992), Jurassic Urkut, Hungary (Polgari et al. 1991), Ordovician Taojiang, China (Fan et al. 1992))

carbonate silicate ore was buried and was subjected to greenschist facies metamorphism. The outcropping metamorphosed silicate and carbonate ore was then oxidized to the trivalent and tetravalent Mn oxides. The Ulukent manganese deposit is located close to the suture zone of nappe tectonism, Gökceovacık Mn deposit at the southern margin of the region was not significantly affected by metamorphism because of its lesser involvement in nappe tectonism (Öztürk and Hein 1997). Geological and mineralogical features of the Ulukent deposit indicate that the ore can be explored such as geophysical exploration by magnetic (magnetic hausmannite), gravity (due to gravity contrast with limestone) and electric methods (due to the bottom pyrites).

The Gökçeovacık manganese deposit represents the southward continuity of the Ulukent deposit because of the presence in a similar shale units of thick carbonates section (Fig. 6.2). This deposit is located the 70 km south of the Ulukent deposits. The ore body continues for 600 m on the surface with 1 m in thickness and was underground mined during the World War I. The ore was transported to the Göcek port by a wire line system 4 km long. Today the Gökçeovacık Mn ore zone is in a special protected area. The ore of the Gökçeovacık consists of two ore seams each about 0.4 m in thickness and the main ore mineral is braunite. Manganite, pyrolusite, hematite and chalcedony are minor. The bottom limestone is cherty, whereas limestone is at the top calciturbiditic, including fragmented algea fossils and lime clasts associated with oxygenation of the basin.

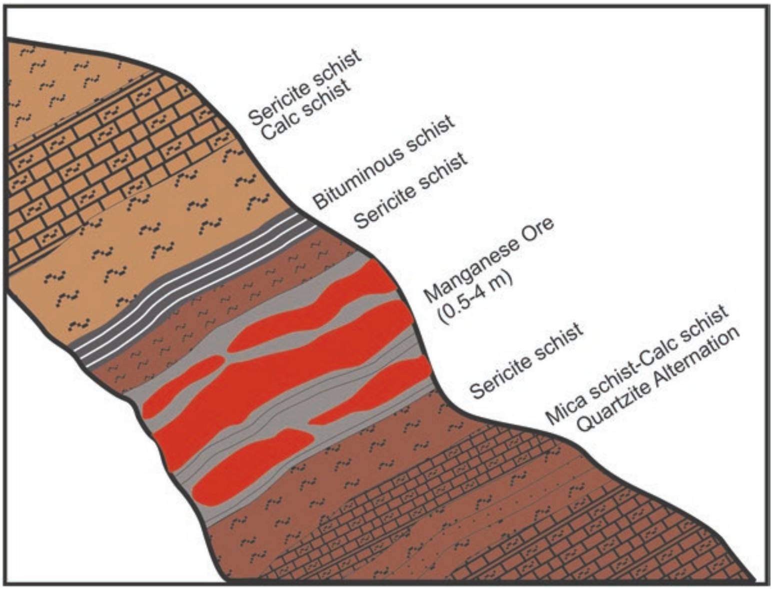

Fig. 6.5 Cross section (not-to-scale) showing the host rock relationships of the Kepirli manganese mineralization in the Bitlis metamorphic massif

6.2.2 The Kepirli Mn Mineralization

This mineralization is defined as a black shale – hosted deposit that occurs west of Kepirli Village (ancient name is Nurs) of the Hizan town of Bitlis city (Fig. 6.1). The ore body is hosted in the metapelitic rocks of the Bitlis Metamorphic Massifs in Eastern Anatolia (Fig. 6.5). The thickness of ore body varies between 0.5 and 4 m and extends for 350 m on the surface. A few thousand tonnes of ore has been mined with 30% average grade. Chemical composition of the ore body is characterized by high silica (7–25%) and iron (9–7, %). The chemical compositions of the Kepirli ore is shown in Table 6.1.

Rock associations of the ore consists of calc-schist, chlorite schist and bituminous schist that indicate a black shale associations deposited in semi closed or closed basins like the modern Black Sea and the Baltic Sea.

6.3 Radiolarian Chert: Hosted Manganese Deposits

Radiolarian chert-hosted manganese deposits and occurrences of Turkey are in four belts that represent deep sea sedimentary rocks. These four belts from north to south are known as Paleo Tethyan, Karakaya and two branches of the Neotethyan ocean, respectively. The most important Mn deposits occur in the pelagic sediments of the

Table 6.1 Major oxides (%) of the selected Mn deposits of Turkey

Deposits	SiO2	Al2O3	Fe2O3	MgO	CaO	Na2O	K2O	TiO2	P2O5	MnO	Cr2O3	TOT/C	TOT/S
Çayırlı	16.66	1.06	1.77	0.06	0.34	0.03	0.06	0.07	0.05	58.12	0.004	<0.02	<0.02
Binkılıç	6,45	2,2	1,65	0,82	8,29	0,36	0,79	0,11	0,26	48,56	<0.002	1,84	0,03
Dilli	2,33	1,01	1,68	0,17	0,42	0,06	0,13	0,06	0,06	64,71	<0.002	0,05	<0.02
Elmalar	25,59	1,38	0,6	0,09	0,27	0,04	0,24	0,06	0,05	52,99	<0.002	0,02	<0.02
Gökçeada	6,03	0,7	12,7	0,64	4,42	<0.01	0,1	0,03	0,02	42,67	<0.002	7,76	0,77
Kepirli	14,65	3,49	10,88	5,02	8,29	0,21	0,74	0,19	0,38	25,81	<0.002	9,8	0,05
Uluk. -o	3,85	1,61	4,31	0.16	2,16	0,09	0,19	0,07	0,31	59,53	<0.002	0,5	0,05
Uluk.-os	15,15	1,63	4,32	2,18	2,65	0,01	0,01	0,06	0,16	53,83	<0.002	3,33	0,03
Çay. nod	7,72	1,64	0,63	0,27	0,39	0,07	2,22	0,06	0,05	61,97	<0.002	<0.02	<0.02

Cayırlı nod Çayırlı Mn nodule, *Ulukento* Ulukent oxidised ore, *Ulukent os* Ulukent oxide and silicate ore

Northern Branch of the Neotethyan Ocean (Izmir–Ankara–Erzincan Suture zone). These deposits are represented by the Çayırlı, the Çorum and the Hafik region deposits. Mn deposits of the Southern branch of Neotethyan Ocean (Bitlis – Zagros suture zone) consist of Koçali, Kilis, Çevretepe and the Dokuztekne region deposits (Erdemoğlu and Yaman 1992; Van and Yalçınalp 2010). These deposits are generally small being 5000–30,000 tonnes of ore reserve with a 20% Mn and high Si (30%) content. These deposits are mined by open pit methods.

Chert – hosted Mn deposits are widely scattered within the reddish- brownish colored radiolarian chert series, displaying tectonically imbricated structure. The most common exploration practice is by using excavators for digging some of the Mn oxide olistoliths or tectonic slices of Mn oxides. Oceanic sediments of the Paleo Tethyan and the Karakaya sutures do not include economically important manganese deposits. The general characteristics of the radiolarian chert – hosted ore deposits are, as follows: (1) limited by faults, (2) enriched by silica associated with hydrothermal quartz or opal – cristobalite tridimite formation or radiolarian fossils, (3) showing well stratified structure or laminations, (4) alternated with thin radiolarian chert and siliceous shale beds (5) include reddish and soft iron oxides – okr levels at the bottom of the manganese oxides, (6) rarely include Mn nodules (Öztürk 1993b), (7) include trace amount of Ni, Co and Cu, (8) ore mineralogy consists of pyrolusite, psilomelane and manganite, (9) reflect a strong post sedimentary deformation, (10) have generally high Mn/Fe ratio.

The most representative chert-hosted deposit of the Izmir–Ankara–Erzincan suture zone is the Cayırlı Mn deposit studied by Oygür (1990). The Çayırlı manganese deposit is one of the largest hosted by the radiolarian chert – radiolarites of a tectonic mélange of Cretaceous Age (Öztürk 1997). Approximately 250,000 tonnes of ore has been mined up till now and still under production with an ore processing plant consisting of jigging separation process. The ore body continues for 200 m and is concordant with thick-bedded reddish brown radiolarian chert and siliceous shale. Reddish and earthy iron oxides occur at the bottom of the manganese oxide zone indicating a gradual increase in redox potential and/or oxygenation of the deep oceanic water. The ore minerals consists of pyrolusite and psilomelane as disseminated and microscopic–submicroscopic grains. Stockworks of secondary ores are also common and these consist of relatively coarse pyrolusites and minor psilomelane minerals. Ore chemistry with moderate Ni, Co and Cu indicate that mineralization was formed by circulating hydrothermal solutions with minor hydrogenetic input according to Oygür (1990).

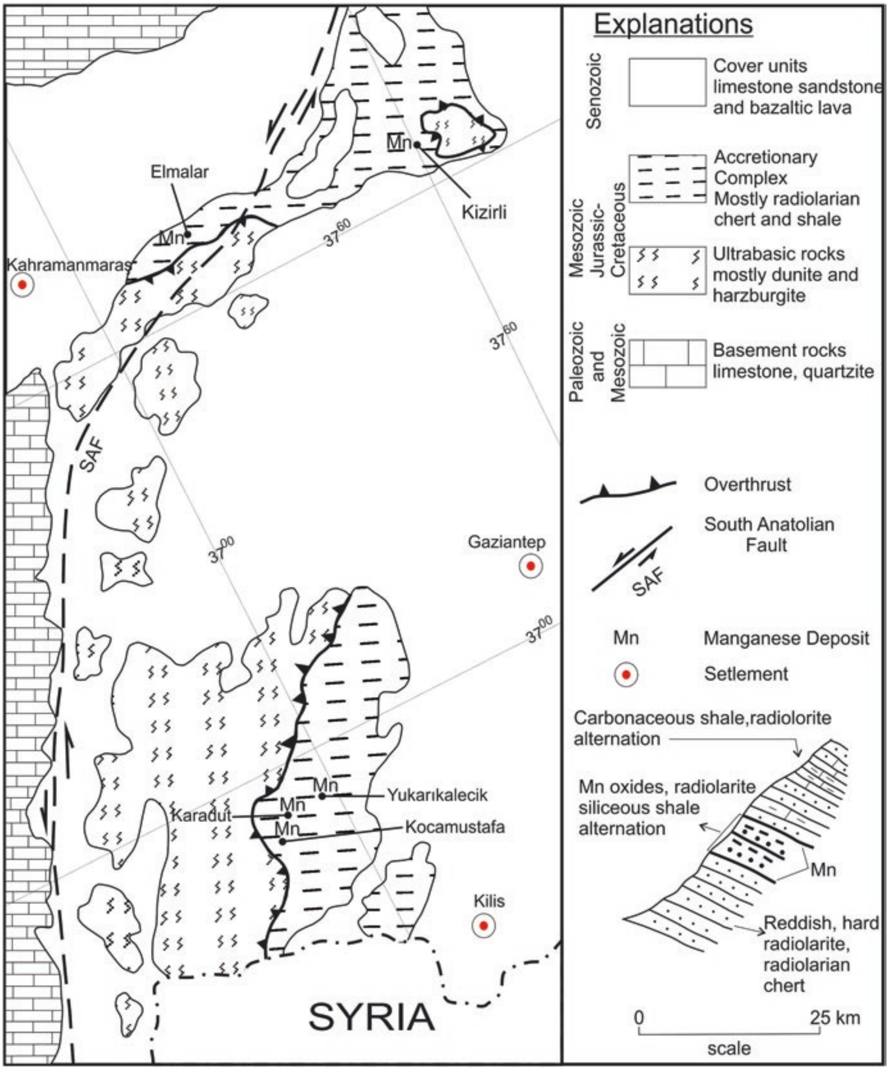

Fig. 6.6 Geological map showing of the Kilis region manganese deposits, and cross section of the Karadut Mn deposit

6.3.1 The Kilis Region Deposits

The Kilis – Maraş region includes three low grade manganese deposits, known as Elmalar, Karadut, and Kocamustafa which belong to the Demeka Mining Co. These deposits are similar to each other in terms of mineralogy, host rocks, chemical composition, and ore grades (Fig. 6.6). The Elmalar manganese ore occurs as concordant seams within the pinkish radiolarian chert and brownish siliceous shale rocks.

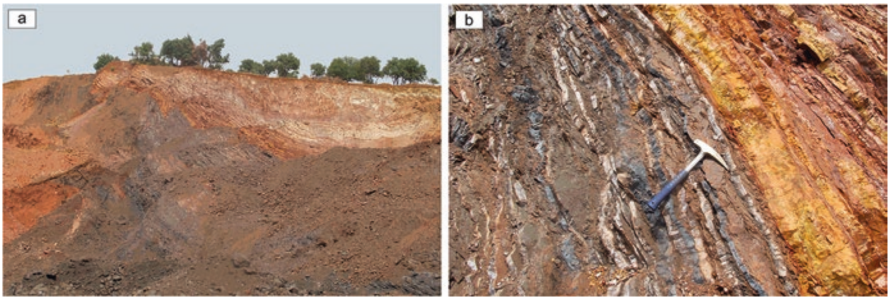

Fig. 6.7 (**a**) Outcrop of chert – hosted the Karadut manganese deposit showing highly deformed deep sea pelagic sediments with thin bedded manganese oxide layers. (**b**) Details of the alternations of the syn sedimentary Mn oxide bandings (3–10 cm in thickness) with radiolarian cherts (reddish brown) and with brownish siliceous shales in the Karadut mine. The upper yellowish red layer consists of Fe oxide- rich clay and siliceous shale

The Mn ore minerals are pyrolusite and minor psilomelane. The ore zone extends for 200 m with 6 m average thickness and dips to NW with 45°. A few tens of thousand tonnes of ore with 12% Mn average grade has been mined from this deposit. The ore is carried to the Türkoğlu processing plant by a 45 km road. The ore material is first crushed to 3 cm then concentrated by the jigging method. Concentrated ore with 57% Mn which is gained by an average 60% recovery. Approximately 1 tonne of concentrated ore is obtained from 9 tonense of bulk ore. The ore is characterized by high Mn and low iron content as shown in Table 6.1. The mining being carried out at Elmalar by open pit method with a stripping ratio of about three. The ore reserve as provided by the company is 120,000 tonnes. However, owing to tectonic structural repetition, some additional new reserve can be found by drilling in or around the license area.

The Kocamustafa deposit is located 3 km north of the Karadut deposit. This deposit was investigated by MTA which defined a few hundred thousand tonnes of ore with low grade. The ore zones extends N 30 W and dips 75° to NE. The general features are similar to the Karadut deposit. A few thousand tonnes of ore was produced by open pit mining. The Karadut deposit exhibits all characteristic features of a chert – hosted ore (Fig. 6.7). The deposits extends for more than 400 m on the surface with an average thickness of 8 m and probable reserves of 620,000 tonnes of ore with 11% Mn. The ore consists of manganese oxide and SiO_2 trace amounts of Al and Fe.

Owing to its wide distribution, some researchers recently studied the chert-hosted manganese deposits (Türkyılmaz 2004; Özküz 2011). These authors defined a similar geochemistry in their studied deposits in North and South Anatolian suture zone.

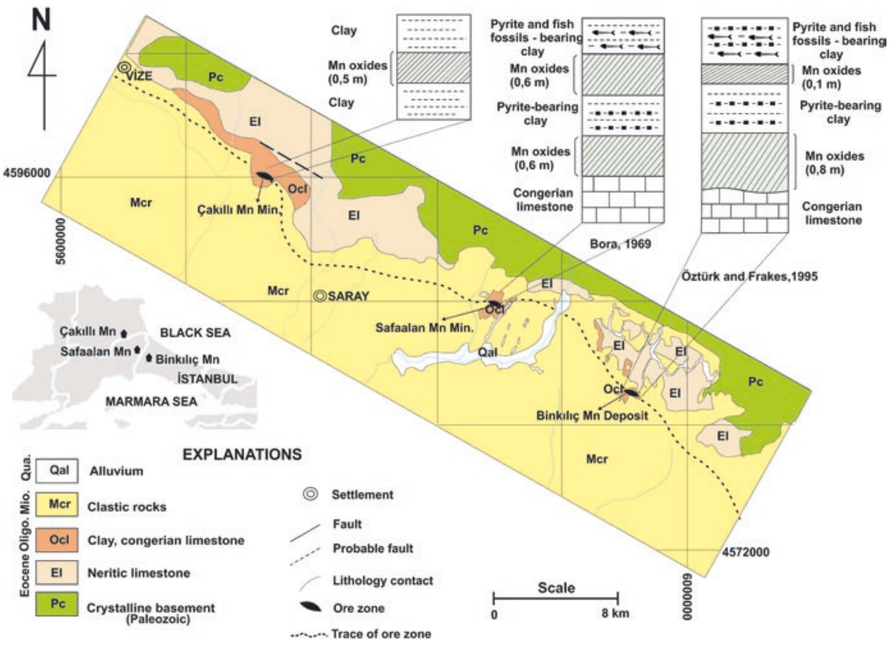

Fig. 6.8 General trends of the Oligocene – hosted manganese mineralizations along the northern rim of the Thrace Basin and the ore – host rock relationships at some locations

6.4 Oligocene: Hosted Manganese Deposits

The Oligocene-hosted manganese deposits form a northwest southeast trend in the Thrace Basin in the northwestern part of Turkey. The ore zone generally occurs between the congeria fossils-bearing limestone and pyrite and fish fossils – bearing clays. Manganese oxide formation begins in Çatalca region and extends to Saray along the 150 km the basin margin (Fig. 6.8). Mn oxides and host lithologies gently dip to southwest, whereas in the Bulgaria these rocks dip to the northeast. This situation suggests more than one isolated basinal conditions during the Oligocene and a stratigraphic control of the mineralization.

6.4.1 The Binkılıç Mn Deposit

Investigation of the Binkılıç and Sefaalan, the latter being the westward continuity of Binlılıç was begun 1966 by MTA for the Tuna Mining company. According to 18 drill hole data a 1.118.293 tonnes of measured ore reserve with 29.4% Mn grade has been defined in Binkılıç (Bora 1969). Beside this, 3.5 Mt and 2.5 Mt of possible ore reserve are also reported in this study for the Binkılıç and Sefaalan deposits, respectively.

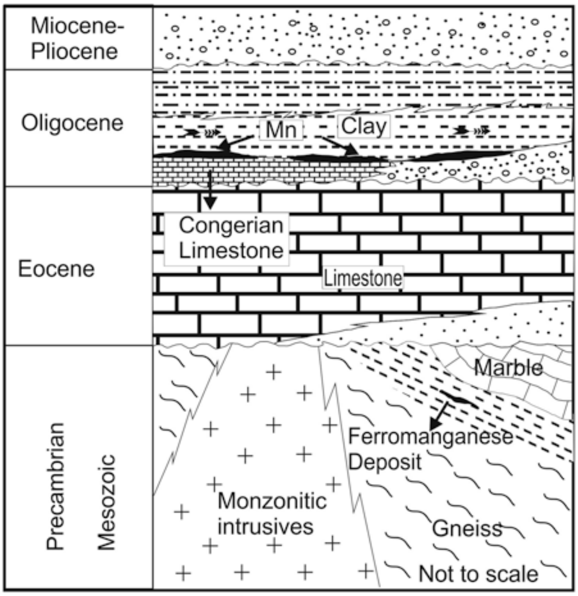

Fig. 6.9 Simplified cross section showing the stratigraphic positions of the Mn deposits of the Thrace basin. (Öztürk 1997)

According to Uzkut (1971) 120,000 tonnes of ore was produced from the Binkılıç deposit from 1952 till to 1970. The deposits has been the focus of studies based on mineral processing (Ateşok 1979) and the ore geochemistry (Gültekin 1998).

At Binkilic, the basement is represented by metamorphic rocks overlain by the Eocene micritic limestone and the Oligocene Congerian limestone rocks (Fig. 6.9). The Miocene is represented by clastic rocks including Mn oxides penetration.

Thickness of the manganese ore seams varies from 0.2 to 1 m. The ore zone includes soft and low quality ore and hard and high quality ore levels or patches, pisolitic, oolitic and concretionary ore types. The ore mineralogy consists of pyrolusite, psilomelane, manganite, rhodochrosite, kutnohorite, limonite and goethite, and gangue consists of Mn calcite, quartz, calcite, montmorillonite and illite.

Average major oxide composition of the ore is 45% MnO, 1.5% Fe_2O_3, 8% SiO_2, 2% Al_2O_3, 5%CaO, 1.3% MgO, 0.4%K_2O, 0.6% Na_2O, 0.06%$\dot{T}O_2$, and 0.3% P_2O_5. Major oxides of the ore show a low terrestrial input and/or chemical depositional process or diagenetic replacement of carbonatic parental rocks. The phosphorus content of the ore is not high for the iron and steel industries. High Ba and Sr are remarkable whereas low amounts of Ti, Cr, Zr and Al indicate a limited terrigenous input. Heavy metals such as Co, Ni, Cu, V and Zn are relatively enriched in the ore possibly associated with absorbing mechanism on to the manganese oxides. Rare earth element contents of the ore is lower than the NASC and the Chondrite values. Chondrite normalized REE pattern of the ore is characterized by negative Ce and positive Eu anomalies. $\delta\ ^{13}C$ values from the rhodocrosite and kutnohorite in the ore zone vary between −7%0 and −5%0, PDB which indicates fresh water environment.

Formation of the Oligocene rocks hosted manganese deposits around the Black Sea is explained as due to sea level change by Bolton and Frakes (1985) and then

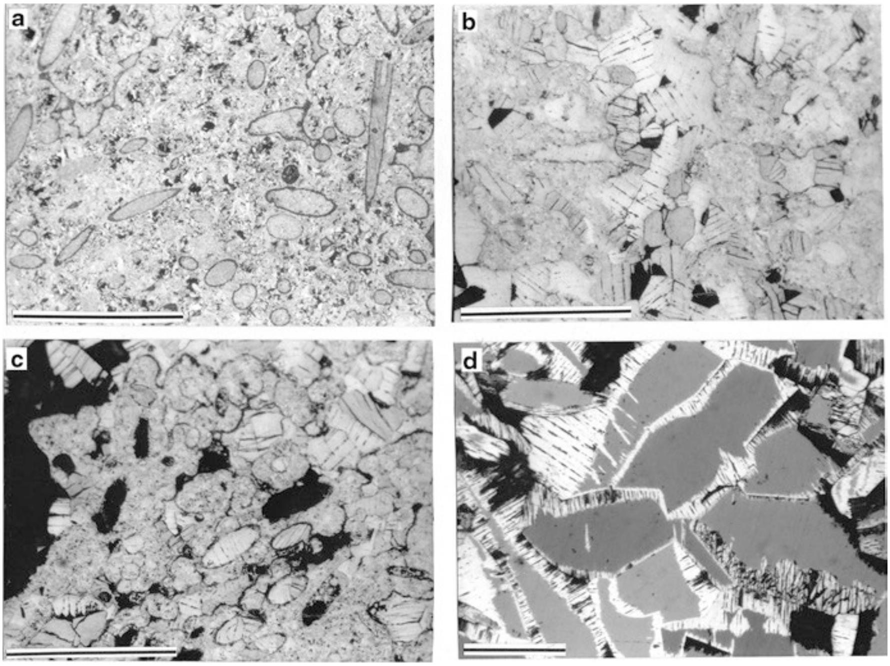

Fig. 6.10 Polished section photomicrographs from the high grade and hard ore of the Binkılıç manganese deposit showing very well preserved diagenetic replacement features of the mono axon sponge spicules by manganese ions. Sponge spicule structures reveal needle or circular shape in relation to the section planes (**a**–**c**): Oxidation of open space forming manganites (dark gray) to pyrolusite (white) and formation of dehydration fissures in pyrolusites. All scale bars indicate 1 mm (**d**). Black area is quartz. Unbroken spicules indicate a quite water conditions like a lagoon for carbonate deposition

diagenetic replacement process by Öztürk and Frakes (1995). Monaxon sponge spicule relics in the high grade ore clearly indicates the replacement of spiculite or spicule – bearing limestone by manganese (Fig. 6.10). Manganese is possibly concentrated in an isolated lagoon lake or marsh environment under both anoxic and acidic conditions was possibly created by volcanic ash and/or acid rain in a shallow water body after a volcanic eruption in the northwestern Anatolia. Manganese carbonate and oxides may have been deposited associated with supergene replacement process as a reactions of downward diffusing or lateral flowing Mn – bearing water. Mn deposition is associated with Eh and pH increase after the reaction between the anoxic Mn – rich surface waters with the host Congerian limestone.

6.5 Vein: Type Manganese Deposits

These Mn deposits mostly occur within the volcano-sedimentary rocks of the Upper Cretaceous age along the Black Sea coast and rarely in eastern central Anatolia and the Gökçeada Island. A volcano-sedimentary rock sequence was formed by the subduction of the Neo-Tethyan oceanic crust beneath the Pontide plate. Volcanic arc rifting during that time with bimodal volcanism and the related Mn deposits formed as metasomatic, hydrothermal and stratabound types in the Pontides. Rock associations of the Mn deposits in this region include dacitic tuff, reddish limestone and hemipelagic-claystone, marl and shale. Similar small – sized Mn mineralization is related to Tertiary magmatism and hydrothermal activity around the Çanakkale city and the central Anatolia.

Manganese minerals of the Black Sea region deposits generally consist of braunite, bixbyite, pyrolusite, psilomelane, hausmannite, asbolane, rhodochrosite, Mn-calcite. Gangue minerals of the deposits are barite, quartz, chalcedony, montmorillonite, illite and kaolinite. Distinctive deposits of the province are the Ereğli and Topkirazlar deposits in the west and the Ocaklı deposit in the east. The Topkirazlar and Ereğli ore deposits are the largest deposits in the area which occur in a volcano-sedimentary succession of Upper Cretaceous age. The ore reserve is estimated to be 200,000 tonnes, but near-surface sections of the deposits are generally exhausted (Öztürk 1997).

Volcanic arc hosted deposits are characterized by relatively K, Na, Ba, As, Sb and P enrichment however these elements do not affect the quality of ore (MTA 1972). The hydrothermal origin of the deposits is characterized by its high As, Sb and Pb contents The Ocaklı manganese deposit, and similar deposits of the region, studied by Gedikoglu et al. (1985), are believed to have been formed by hydrothermal replacement and infilling processes.

6.5.1 The Dilli Manganese Deposit

A distinctive vein – type hydrothermal Mn deposit occurs along the tectonic contact between the crystallised limestone and serpentinised ultramafic rocks 2 km SE of Dilli Village of Erzincan city (Fig. 6.11). The serpentinised ultramafic rocks are highly deformed and display brownish green to yellowish green color. The crystalised limestone represents the basement autochthon of the region which is highly brecciated and karstified. The grade of manganese ore is high and shows lenticular geometry with a 4 m average thickness. The ore was mined from the surface to 40 m depth by open pit at the beginning and then by underground methods. The deposit belongs to a private company and approximately 5000 tonnes of high grade (45% Mn) ore mined form the deposit without any exploration study by drilling. The ore

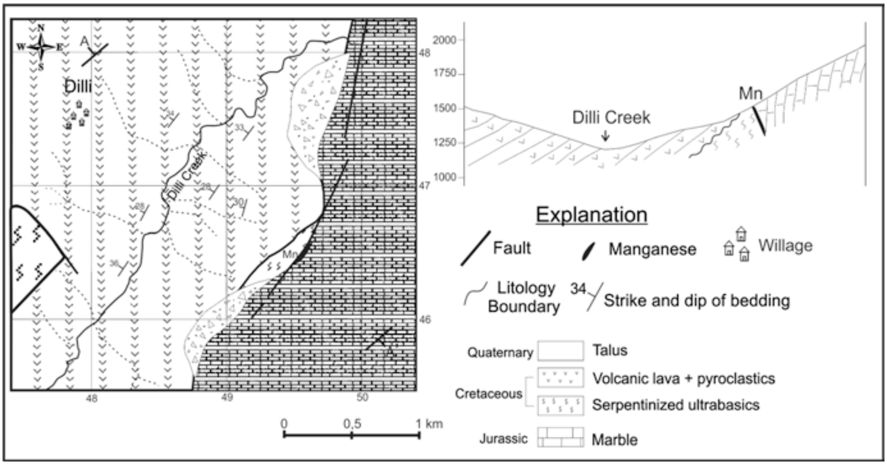

Fig. 6.11 Geological map and cross section of the Dilli manganese deposit

is sold to a zinc metallurgy factory in Turkey which is known as Çinkur Co. The ore minerals of the deposits are pyrolusite and psilomelane. The ore reveals both soft and hard ore which are characterized by Ni enrichments up to 0.5% Ni (Table 6.3). This indicates that the Mn and Ni were scavenged from the serpentinised ultramafics and pelagic sediments of Cretaceous and deposited along the tectonic fabrics related to increase in Eh and pH.

6.5.2 The Gökçeada Manganese Mineralization

This mineralization occurs as a vein up to 1.5 m in thickness and 200 m length in the south of the Gökçeada island in the Aegean Sea. The mineralization occurs in the Oligocene volcanoclastics as a vein with dips of 70–80° to NE. The volcanoclastic rocks around the ore vein display argillic alteration. The geometry of the ore body can be seen in the open pit. Owing to low grade of Mn the mining stopped. The ore minerals are pyrolusite and psilomelene, limonite and goethite. The gangues are calcite, quartz, dolomite and barite. The ore includes high amount of Pb, Zn, Sb and Au (Table 6.3) that clearly indicate an epithermal vein origin.

6.6 Geochemistry

As a major oxides, The Ulukent and Binkılıç deposit reveal high P contents relative to the other deposits (Table 6.1). The highest P_2O_5 contents of the Ulukent deposit could be related to storage of phosphates in the anoxic water column. The Çayırlı manganese nodule includes 2.2% K_2O which is possibly related to cryptomelane or psilomelane. The Ulukent deposit is relatively enriched in iron and silica which is possibly associated with Mn silicate mineral, braunite, and some quartz.

The Kepirli manganese deposit reveals Mg enrichment which is related to dolomite. The chert hosted ores of the Elmalar and Çayırlı reveal high silica associated with radiolaria fossils and chalcedony.

Trace elements are enriched in vein – type hydrothermal deposits such as Dilli, Gökçeada and Kepirli. The Dilli Mn deposit includes 0.4% Ni, 1.3% Ba, 0.1% Sr, 0.104% Co and 0.1% V which suggest that the manganese was possibly extracted from the ultramafic-mafic rocks and pelagic sediments of the ophiolitic mélange (Table 6.2). Contrary to the vein – type hydrothermal deposits, the black shale – hosted type Ulukent manganese deposit includes the lowest amount of trace elements. Ba and Sr elements are enriched in the Binkılıç and Dilli and Mn nodules of the Çayırlı despite their formation conditions is different. Ba and Sr enrichment in the syn sedimentary deposits may be associated with alteration of the feldspars. Uptake of the Ba and Sr from the deep sea sediments may explain the enrichment of these elements in the hydrothermal Dilli deposit. Ba discharges into the sea water from hydrothermal vents is reported by several workers (Rona 1984 and references therein), in this context, the Ba of the Mn nodule could be formed close to sea floor hydrothermal discharge sites. Ba especially enriched in psilomelane, (Ba (Mn^{2+}) $(Mn^{4+})_8$ $O_{16}(OH)_{4,}$ rich soft ore because of Ba enters into the crystal lattice of psilomelane.

The total rare earth elements (REEs) contents of the studied deposits ranges between 342 ppm (Ulukent deposit) and 36 ppm (Çayırlı). REEs are relatively enriched in the Ulukent manganese deposit and show a positive correlation with phosphorous. Both oxide and the oxide – silicate ore of the Ulukent deposit show a typical positive Ce anomaly (Table 6.2). This enrichment may have been related to concentration of Ce^{3+} in the sea water during the anoxia and then oxidation to Ce^{4+} and absorbsion on to the Mn oxides as CeO_2 in oxic conditions.

6.7 Conclusions

Although there are many different types of manganese deposits in Turkey, they do not exceed reserves of a few million tonnes. Potentially and economically two important manganese deposits are black shale – hosted and the deposits of Oligocene age.

The black shale – hosted Ulukent manganese ores of Turkey were formed in an anoxic basin comparable to today's Black Sea, and similar to the Urkut manganese deposit of Hungry. The primary carbonate ore, consisting of rhodocrocite and kutnohorite, has been undergone regional metamorphism and changed to silicate – oxide ore and gained a magnetic signature. Magnetic hausmanite – rich ore body in the shales and recrystallised limestone offers the best opportunity for geophysical (magnetic) survey.

The Congerian limestone – hosted manganese deposits of Oligocene age and black shale – hosted manganese deposits of Cretaceous age occur as concordant with host shales or limestone and sandy clays. The Oligocene-aged manganese

Table 6.2 REEs values (ppm) of the studied Mn deposits of Turkey

Deposits	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Çayırlı	6,1	14,5	1,35	5,7	1,44	0,39	1,8	0,29	1,59	0,34	1,24	0,14	0,85	0.16
Binkılıç	10,7	15,6	2,28	10,1	1,82	0,23	1,94	0,29	1,65	0,33	0,86	0,15	0,85	0.14
Dilli	10	22,1	1,58	7,3	1,53	0,17	2,1	0,35	2,24	0,5	1,67	0,27	1,97	0.32
Elmalar	11,1	37,4	4,23	18,2	3,91	0,9	4,74	0,65	3,26	0,54	1,48	0,18	1,23	0.17
Gökçeada	8,4	16	2,05	9,6	2,53	1,81	3,86	0,64	3,94	0,93	2,76	0,37	2,32	0.36
Kepirli	57,9	137,1	11,12	44,1	9,5	2,12	10,04	1,47	7,82	1,48	3,94	0,56	3,24	0.45
Ulukent-o	28,4	196,2	7,41	32,9	5,95	1,37	6,33	0,95	5,69	0,96	2,58	0,35	2,03	0.29
Uluk.-os	33,2	234,3	8,82	35,4	6,77	1,49	7,82	1,11	6,04	1,14	3,04	0,4	2,11	0.32
Çay. nod	15,4	16,2	3,02	11,6	2,29	0,42	2,64	0,36	2,2	0,42	1,35	0,21	1,35	0.23

Cayırlı nod Çayırlı Mn nodule, *Ulukento* Ulukent oxidised ore, *Ulukent os* Ulukent Mn oxide and silicate ore

Table 6.3 Trace element compositions of the studied Mn deposits, Hg, Au and Ag are as ppb and the others are as ppm

Deposits	**Mo**	**Cu**	**Pb**	**Zn**	**Ni**	**As**	**Cd**	**Sb**	**Bi**	**Ag**	**Au**	**Hg**	**Tl**	**Se**	**Y**
Çayırlı	122,6	111,2	1,9	102	162,6	48,5	0,1	1,9	<0.1	<0.1	2,4	0,01	2,2	<0.5	14,8
Binkılıç	36,1	16,3	4,5	72	181,3	86,9	0,4	4,6	<0.1	<0.1	1,4	0,4	8,5	<0.5	9,5
Dilli	107,9	633,4	2912	865	4107	198,3	0,2	10,4	<0.1	<0.1	3,3	0,05	61,4	<0.5	11,7
Elmalar	57,1	793,8	15,3	50	30,9	49,3	<0.1	1	<0.1	<0.1	0,6	0,02	2,1	<0.5	13,8
Gökçeada	5,8	47,7	1493	3639	249,5	27,6	4,9	49,6	0,3	4,5	33,2	0,12	2,4	0,9	36
Kepirli	3	38,1	281,4	329	71,1	17,8	3,2	1,3	0,4	0,4	<0.5	0,18	0,1	<0.5	43,1
Ulukent-o	3,4	8,9	151,6	314	60	30,3	0,5	4,5	<0.1	0,3	1,8	0,29	0,5	<0.5	25,4
Ulukent-os	2,2	1,7	3,6	15	15,3	16,7	<0.1	0,8	<0.1	<0.1	<0.5	0,01	<0.1	0,7	25,4
Çayırlı nod	97,6	34,4	2,3	208	175,5	27,1	0,2	1	<0.1	<0.1	2,8	<0.01	23,1	<0.5	13,8
Deposits	**Ba**	**Be**	**Co**	**Cs**	**Ga**	**Hf**	**Nb**	**Rb**	**Sr**	**Ta**	**Th**	**U**	**V**	**W**	**Zr**
Çayırlı	1432	<1	51,8	0,2	58,3	0,2	0,5	1,3	747,6	<0.1	0,3	7,5	281	<0.5	8,6
Binkılıç	13,106	<1	51,2	0,7	47,1	0,5	1,3	9,9	4181	0,1	0,9	9,9	111	1,7	22,1
Dilli	20,310	2	1442	0,2	64,4	0,3	0,2	1,2	1229	<0.1	0,3	9,5	990	1	21,9
Elmalar	3717	<1	192,6	0,2	60,6	0,4	0,7	2,5	352,3	<0.1	0,7	3	48	0,6	17
Gökçeada	839	5	85,5	1,1	35,3	0,2	0,7	5,6	68,9	<0.1	0,8	2,5	33	0,9	8,8
Kepirli	377	3	15,2	1,1	29,5	1,6	9,9	28,3	251,1	0,5	3,3	1	<8	2,4	76,6
Uluk.-o	1471	<1	33,7	1,9	55,1	0,5	1,6	5,5	630,7	0,1	1,3	1,5	22	3,3	26,5
Uluk.-os	830	<1	54,1	0,2	48,4	0,6	1,4	0,8	96,6	<0.1	1,1	0,5	<8	2,2	31,6
Çay. nod	10,619	<1	37,8	0,2	57	0,4	0,8	5,4	3259	<0.1	0,7	2,4	248	0,7	15,3

deposit consists of a horizontal tabular ore body, averaging 1 m in thickness, and annually 60,000 tonnes of ore with 36% Mn are still being open pit mined. These deposit include small amounts of phosphorus, which is an unwanted elements for iron and steel sector (0.35% P_2O_5). The ore deposit was formed by diagenetic replacement processes, in Mn – rich water. Pyrite- rich clays layer (hanging wall rock) indicates a strong reducing conditions during the primary Mn carbonate deposition which was oxidized to tetravalent Mn oxides by supergene alteration. Pyrite-rich bluish gray clay layer, which is so electrically conductive, can be use a guide during geophysical exploration. The Turkish manganese deposits that occurs in the congerian limestone of Oligocene age are genetically and temporally linked to the Ukrainian (Nikopol) and Georgian (Chiaturi) manganese deposits.

Despite the wide distribution of the radiolarian chert-hosted ferromanganese deposits in Turkey, they are small-sized and therefore economically unimportant. Relatively small-sized radiolarian chert hosted -manganese mineralization of Turkey can be economic if mining and ore processing plants are properly planned at a whole regional scale. The same situation is also true for the magmatic arc -hosted hydrothermal manganese deposits.

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