Rare Earth Elements Geochemistry of the Cambrian Shallow Marine Manganese Deposit at Wadi Dana, South Jordan

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Abstract

The Cambrian manganese deposits of Wadi Dana were investigated for their REE geochemistry, contents and patterns. Compared with other manganese ore types the studied ore is REE depleted. However, such depletion can be applied to the high-grade ores, while the low-grade ores bears higher REE due to the detrital contribution. The horizontal variation throughout the basin is insignificant, while, the vertical variation is pronounced. Vertically. The $\sum$REE and many individual REE's are increasing upwards except for Yb and Eu. Moreover, Ce/$\sum$REE and Eu/Sm vertical behavior shows inverse relationship that reflects the increase of oxic diagenetic conditions upwards. The normalization pattern shows that the ore exhibits a high positive Eu and no or small positive Ce anomalies. The REE pattern and content is comparable to similar worldwide diagenetic manganese ores.

Keywords: REE; Spatial variation; Mobilization; Diagenesis; Ce and Eu-anomalies;

1. Introduction

Manganese deposits were known to form since the Archean and are being formed at the present day. It formed in various environments e.g. lakes, internal seas, pelagic, archipelago, shallow marine, deep marine, as well as terrestrial mineralization. This is due to the fact that manganese can be formed by hydrothermal, sedimentary, and supergene processes. Manganese diversity in time and environment of deposition can be of great importance for better understanding of the geochemical processes responsible for its deposition. Furthermore, it can contribute to the on going investigation of the Earth's evolution history, and help in explaining the worldwide phenomena such as the Banded Iron Formation (BIF) (Kimberely, 1989). Huge deposits were discovered around the world (e.g. Nikopol of Ukrania, and at Chiatura of Georgia, and the Groote Eylandt deposit of Northern Australia, (Varentsov, 1982; and Frakes & Bolton, 1992), Hokkaido manganese deposits of Japan (Miura and Hariya 1997) and Thrace deposits of Turkey (Ozturk and Frakes 1995) and Orissa, manganese deposits of India (Nicholson et al. 1997).

The REE geochemistry as a tool and tracer for marine environment and sedimentary processes has been used by many authors (e.g. Elderfield et al. 1981; De Baar et al. 1983; Alpin, 1984; Klinkhammer et al. 1983; Michard et al. 1983; Calvert et al. 1987; Glasby et al. 1987; De Baar et al. 1988 and Rolland et al. 2003). Slight change in REE contents or their patterns may reflect a change in redox potential (Piper, 1974; Elderfield, 1988; and De Carlo, 1991), and might be due to the change in sorption properties of solid phases (Alpin, 1984; Byrne & Kim 1990; De Carlo & Koeppenkastrop 1990; and Koeppenkastrop & De Carlo 1990). Also it can be caused by complexation with major anions of seawater (Byrne & Kim 1990; Cantrell & Byrne 1987; and De Carlo & MaMurtry 1992). Hence the REE mobility is controlled mainly by the redox potential of the environment, therefore REE patterns can be used in tracing out the post-depositional processes (i.e. diagenesis) (Ozturk and Frakes 1995; De Carlo, 1991; and Dymon et al. 1984). Dubinin & Volkov, (1986) found that low Ce/La ratio was found to be indicative for ore deposition by direct precipitation or adsorption from seawater. Moreover, Glasby et al. (1987) found Ce/La ratio a useful redox indicator, when they noticed the increasing trend in Ce/La ratio from the SW Pacific towards the equatorial Pacific; due to the passage of the Antarctic Bottom Water. Ponater (1988) have measured a higher Ce/La ratio (2.5-3.2) in the Urkut manganese deposit of Hungary and used it as an indicator for a terrigenous source of REE, which causes also a

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positive Ce anomaly. Furthermore, conditions that are more oxic would lead to REE enrichment (Ingri, 1985; Ingri & Ponater 1987; Shokoriviz et al. 1992). Additionally, Varentsov (1995) has used Eu/Sm ratio as indicator for supergene ore formation.

Enlightened by these observations the geochemical characteristics of REE were investigated in the Cambrian shallow marine manganese mineralization of Wadi Dana. Cambrian manganese deposits in Jordan were targeted by many previous investigations regarding their petrology, mineralogy, and genesis using trace element geochemistry (G.G.M., 1965; Basta and Sunna, 1970 & 1972; Khoury, 1986; and Shaltoni, 1988). Recent studies reveal that the ore was formed through three genetic stages each of which has its mineralogical and geochemical signature (El-Hasan, 1999; and El-Hasan et al. 2001). However, the REE geochemical signature was not yet been investigated.

2. Objectives

The aim of this work to investigate the behavior of REE with regard to these genetic stages, and to test the reliability of REE in determining the different evolution history of ore formation of the study area as indicated by the trace element geochemistry (El-Hasan et al. 2001)

2.1. Geologic Setting

The investigated area occupies the north of central Wadi Araba region, where the main manganese outcrops in Jordan are located (Fig. 1). The manganese mineralization is hosted within the Lower and Middle Cambrian formations. The Lower Cambrian consists of bedded arkosic sandstone unit (Saleb Formation) (BASU); is a 20-35 m thick, consisting of vary-colored arkosic sandstone layers, with quartz pebbles and cross-beddings. Clay and shale layers are intercalated within the sandstone beds. The stratigraphic features indicate that it was formed under shallow marine to braided river environment conditions (Bender, 1974; Amireh, 1987 and Rabba', 1994). The manganese mineralization occurs in the form of lenses, concretions, and encrustation (El-Hasan, 1999). The Middle Cambrian dolomitic limestone shale unit (DLSU) or (Burj Formation) consists of three parts, the lower sandy, middle is carbonaceous and the upper is shaley (Amireh et al., 1994). The middle part is composed of dolomite and dolomitic sandstone layers, intercalated with clay and shale beds, whereas the upper part consists of brown – red sandstone with ripple marks and cross-beddings intercalated with red shale. The manganese hosted in this formation was found as disseminations, thin intercalations, lenses, concretions, and bands (El-Hasan, 1999 and El-Hasan et al. 2001).

2.2. Mineralogy of the Studied Horizons:

The mineral assemblage is cryptomelane, psilomelane, pyrolusite, hollandite, todorokite, and coronadite. Rarely manganite and birnessite were detected. Hematite is found as minor mineral in all sites; however, at Wadi Dabah it is a major constituent. Such mineral assemblage usually

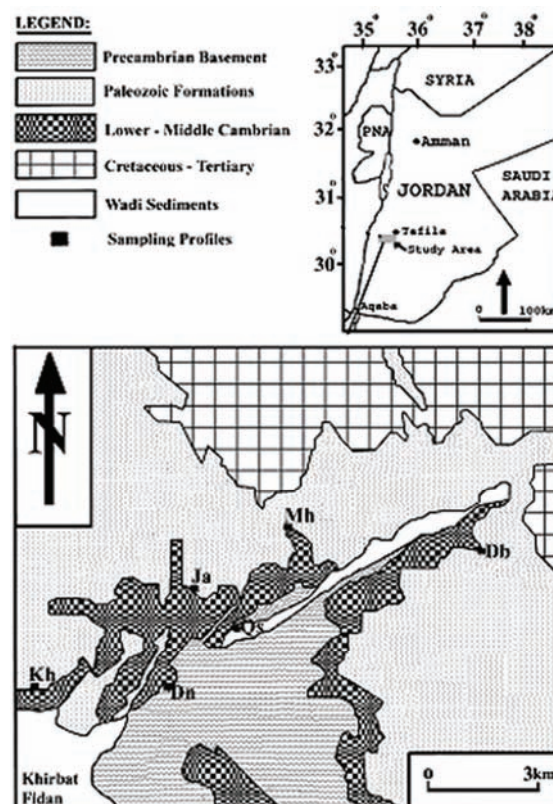found in supergene enrichment (Ozturk and Frakes 1995 and Varentsov, 1995).

Fig. (1). Geological map of the study area showing the location of the six sampling profiles. The sites are from West to East:- Kh: Wadi Khaled; Dn: Wadi Dana Camp; Ja: Wadi Al-Jamal; Qs: Ain Quseibeh; Mh: Wadi Mahjoob; Db: Wadi Dabah.

Detailed mineralogical investigation carried out by (El-Hasan, 1999; and El-Hasan et al. 2001) showed that the ore had been evolved through three stages. First is the primary sedimentary ores, which characterized by the presences of todorokite and birnessite in the form of oolites found as remnants in the lower Cambrian BASU (Saleb Formation). Secondly the supergene-enrichment ores, which characterized by the presence of cryptomelane, psilomelane, hollandite, pyrolusite and hematite. It is the dominant phase of the middle Cambrian (Lower Burj Formation). Finally, the epigenetic ores that most likely formed as result of lateritization; its main mineral phases are coronadite, hollandite-coronadite solid solution, barite and geothite. This phase is confined to the upper most portions of Middle Cambrian DLSU (i.e. Middle Burj Formation). The tentative paragenetic sequence of the three ores is shown in Fig. (2). Moreover, the distribution of these ores within the lithilogical columnar section was illustrated in Fig. (3).

| | Primary Sedimentary | Secondary Supergene | | Epigenetic Lateritization |
		Early Diagenetic	Late Diagenetic	
Quartz	---------------			
Dolomite	---------------			
Kaolinite	--------------			---------
Smectite-Illite				------------
Todorokite	---------			
Birnessite	--------			
Manganite	----------			
Apatite	-------------			-------------
Cryptomelane		------------	-------------	
Psilomelane		-----------	-----------	-------------
Hollandite		-----------	-----------	
Pyrolusite		-----------	----------	
Hematite		-----------	-----------	------
Goethite			----------	----------
Barite			----------	----------
Calcite		-----------	----------	-----
Kutonahorite	--------			
Ankerite	----------			
Coronadite				-----------
Chrysocolla				-----------

Note: Number of dots in dotted lines shows the degree of abundancy of the mineral phases in each stage

Fig. (2). Paragenetic sequence of Wadi Dana manganese ore deposits, including the gangue minerals *(After El-Hasan et al., 2001).*
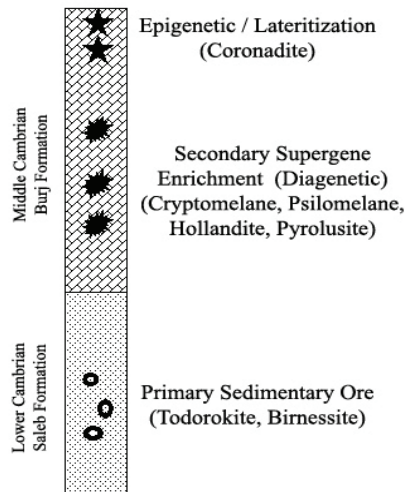

Fig. (3). Schematic lithological columnar cross section showing the distribution of ore types and their correspondent mineral phases within the studied area.

3. Analytical Methods

Thirty-six selected ore samples from six profiles along Wadi Dana mineralized area were analyzed for their content of REE using ICP-MS (Yokogawa, PMS-2000) at the Analytical Center of the University of Tsukuba. Because high REE content was expected, the samples were not pre-concentrated. The powdered samples were dried in the oven for at least 6 hours, and digested following the procedure of mixed acid (Yamaguchi, 1994). 0.05 g of the sample powder was treated with acid mixture of 0.2 ml $HClO_4$, 0.6 ml (1:1) HNO_3, and 1 ml HF. The Teflon beaker was closed tightly and kept overnight at 105 °C. In case of incomplete decomposition, samples were treated again with the same acid mixture. After total digestion was achieved, 5 ml of (6N) HCl were added to the residue and the beaker was closed tightly again and heated for at least 8 hours. The samples solutions were completed up to 100 ml with de-ionized water and transferred into polyethylene bottles. Solutions with different concentrations were prepared in order to match the standardization of the ICP-MS machine. JMn-1, JR-1, JB-1a, and JLK-1 of the Geological Survey of Japan (GSJ) standards were used. These standard samples were repeatedly analyzed every 10 samples to monitor any shift or change in the setup. The calculated error was less than ± 2% range. The results were then normalized against the North American Shale Composite (NASC) (Haskin and Haskin 1968). Detailed mineralogical investigation was conducted for selected samples using the SEM-EDS (JOEL-JSM 5400), at the Geosciences Institute; University of Tsukuba.

4. Results

The analytical results of all selected ore samples from all studied profiles are listed in Table. (1).

In this table the total REE (∑REE) is slightly decreasing from west to east, in other words from low-grade towards high-grade ores. The high-grade ore mineralization especially at Wadi Mahjoob and Wadi Dabah is relatively depleted in REE, particularly in Ce and La, but they are relatively enriched in Eu.

Although ∑REE is decreasing from low to high-grade ores, the overall spatial distribution for some individual REE's shows slight horizontal variation Fig. (4). As an example La shows insignificant horizontal variation, in spite it is considered as the most mobile REE and used to measure the degree of differentiation between light REE (LREE) and heavy REE (HREE) (Varentsov, 1995). Similarly, Ce and Yb exhibit a steady increase from west to east. Only at Wadi Khaled Ce shows higher values. At Wadi Dabah, Yb shows slightly higher values. On the other hand, Eu is steadily increasing towards the east until it reaches its highest value as at the ore body of Wadi Dabah as reflected by the highest Eu/Sm ratio. Moreover, Ce/La and Ce/∑REE show insignificant changes horizontally, but the values are relatively higher at the western most sites at Wadi Khaled. The La/Yb ratio shows no change up to Wadi Mahjoob, and then it drops towards the ore body of Wadi Dabah, (Fig. 4).

Table (1). REE analytical results for selected Mn-ore samples from all studied profiles along Wadi Dana mineralized area, all are in ppm.
Kh: Wadi Khaled; Dn: Wadi Dana Camp; Ja: Wadi Al-Jamal; Qs: Ain Quseibeh; Mh: Wadi Mahjoob; Db: Wadi Dabah.

|	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Kh2	39.24	348.38	9.91	38.85	7.67	2.16	6.33	0.97	5.37	1.07	2.86	0.5	2.63	0.5
Kh4	26.31	80.61	4.43	15.94	2.94	2.02	2.37	0.37	2.24	0.51	1.36	0.22	1.37	0.25
Kh5	15.4	40.05	2.67	9.2	1.68	0.91	1.35	0.21	1.17	0.27	0.74	0.17	0.83	0.16
Dn2	47.7	81.81	10.94	46.11	8.44	1.32	5.77	0.89	5.13	1.11	2.73	0.45	2.89	0.45
Dn5	11.03	19.14	2.48	10.85	3	0.48	2.65	0.42	2.09	0.44	1.02	0.17	0.94	0.13
Dn7	14.44	25.03	2.78	10.88	2.35	0.37	1.97	0.32	2.33	0.48	1.14	0.23	1.27	0.2
Dn10	19.48	43.55	4.67	19.24	3.92	1.37	2.58	0.39	2.05	0.45	1.03	0.16	0.98	0.18
Dn11	19.08	39.88	4.04	15.86	3.26	2.61	2.19	0.33	1.74	0.37	0.95	0.14	0.96	0.15
Dn13	20.04	63.53	5.14	22.31	6.23	5.25	3.82	0.54	2.54	0.5	0.97	0.13	0.87	0.16
Dn14	2.99	8.88	0.72	3.11	0.76	0.38	0.98	0.15	0.94	0.24	0.56	0.08	0.4	0.08
Ja6	14.06	62.82	2.98	11.19	1.9	2.21	1.76	0.25	1.43	0.36	0.81	0.16	0.85	0.14
Ja8	1.64	1.75	0.3	1.09	0.28	3.84	0.32	0.06	0.33	0.12	0.29	0.05	0.34	0.09
Ja16	20.53	44.38	5.05	20.61	5.22	1.2	3.67	0.55	2.62	0.51	1.09	0.2	0.92	0.15
Qs4	32.66	117.05	9.11	44.88	11.85	4.21	10.51	1.42	6.95	1.29	2.75	0.39	1.81	0.29
Qs5	29.23	68.06	7.22	29.08	4.65	0.99	2.83	0.38	2.17	0.47	1.13	0.22	1.19	0.19
Qs7	19.78	55.89	5.87	26.68	6.77	1.21	5.18	0.85	4.23	0.82	1.9	0.34	1.86	0.28
Qs8	15.66	36.82	3.43	14.28	2.72	0.7	2.27	0.3	1.81	0.36	1.09	0.17	1.04	0.18
Mh1	9.9	25.91	3.29	14.55	3.78	1.47	3.9	0.51	2.6	0.55	1.12	0.17	0.96	0.14
Mh3	10.72	33.32	3.17	12.69	2.9	1.14	1.75	0.28	1.51	0.29	0.71	0.12	0.77	0.11
Mh4	17.3	31.72	3.66	14.25	2.68	0.83	2.21	0.33	1.79	0.37	0.98	0.16	0.98	0.16
Mh6	23.44	44.59	6.19	26.34	4.93	1.81	3.46	0.51	2.47	0.47	1.04	0.15	0.94	0.16
Mh7	51.62	97.84	9.24	35.42	8.38	7.79	10.79	1.97	10.63	2.19	5.51	0.84	5.08	0.83
Mh8	12.89	34.88	2.85	11.08	2.09	1.42	1.91	0.36	2.11	0.16	1.13	0.17	1.17	0.15
Mh9	29.1	61.83	4.98	20.41	3.8	2.69	3.11	0.42	1.96	0.4	0.93	0.14	0.71	0.13
Mh10	21.99	53.73	5.28	17.94	3.14	4.09	2.54	0.41	2.41	0.5	1.43	0.18	1.14	0.18
Mh11	18.63	42.18	4.15	13.42	2.64	6.27	2.19	0.41	2.3	0.52	1.33	0.18	1.23	0.21
Mh13	9.47	22.57	2.12	8.87	2.1	2.81	2.51	0.45	2.44	0.49	1.19	0.19	1.4	0.23
Mh14	11.89	24.41	2.49	9.2	1.68	1.45	1.61	0.3	1.61	0.37	0.93	0.14	0.99	0.15
Db8	10.2	20.3	2.89	14.26	3.58	2.13	5.58	0.93	5.41	1.29	2.92	0.37	1.7	0.32
Db9	9.34	24.49	2.18	9.84	2.1	1.76	2.93	0.46	2.88	0.63	1.42	0.17	0.91	0.16
Db10	15.71	39.26	4.93	22.87	6.26	3.18	6.7	1.12	5.72	1.2	2.78	0.37	1.99	0.32
Db12	7.68	22.36	1.9	8.52	2.17	1.84	2.97	0.46	2.59	0.62	1.36	0.15	0.83	0.14
Db13	3.36	7.66	0.83	4.14	1.05	1.9	1.52	0.24	1.51	0.4	0.8	0.1	0.47	0.09
Db14	10.69	22.09	2.42	10.14	2.32	5.22	1.95	0.36	2.24	0.45	1.25	0.21	1.58	0.3
Db16	9.78	19.03	2.13	7.75	1.13	0.23	0.97	0.22	1.22	0.32	0.74	0.15	1.01	0.17
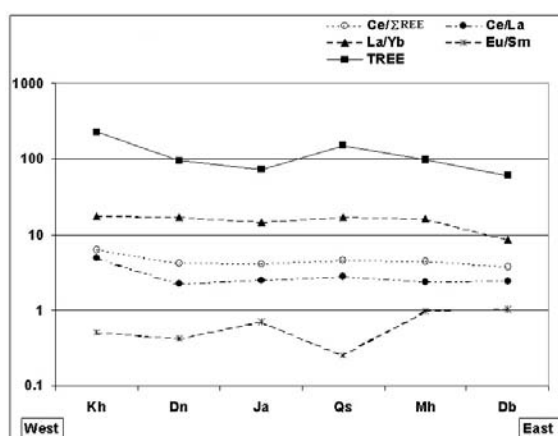
Fig. (4). Plot showing the spatial REE variations (in ppm) along the course of the study area. *(Same abbreviations as in Fig. 1).*

4.1. Normalization

The NASC normalized patterns for all mineralized sites are shown in (Fig. 5).

The quantitative anomalies were calculated using the following equations:

Ce anomaly = Ce*- (2/3La* - 1/3Nd*)

Eu anomaly = Eu*- (1/2Sm* - 1/2Gd*)

Where Ce*, La*,Nd*, Eu*, Sm* and Gd* are the North American Shale Composite (NASC) normalized value of Ce, La, Nd, Eu, Sm and Gd. All sites exhibit a positive Eu anomaly; its highest values are at high-grade ore sites of Wadi Mahjoob and Wadi Dabah. Meanwhile, Ce shows weak positive anomaly; only at Wadi Khaled it has high positive anomaly. This might be due to that samples of Wadi Khaled contain higher detrital material and it is

highly affected by the epigenetic solutions. The Eu positive anomaly is clearly found in all sites, and it increasing toward the high-grade ores (Fig. 5) and (Table 2). This was reflected from the positive correlation between Eu and Mn (Table 3).
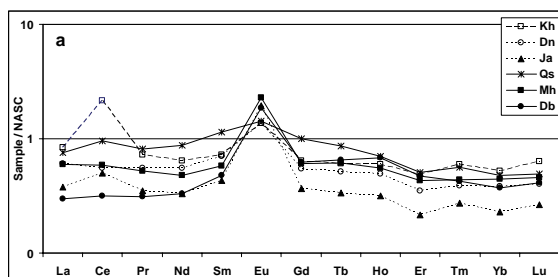

Fig. (5). REE normalizations for all samples from the three ore types for each studied sites relative to NASC (Haskin et al. 1968), *(Same abbreviations as in Fig. 1).*

Table (2). Quantitative Ce and Eu anomalies in all mineralized sites of Wadi Dana area.

	Ce Anomaly	Eu Anomaly
Kh	1.36	0.69
Dn	-0.03	0.73
Ja	0.14	1.55
Qs	0.15	0.36
Mh	0.03	1.7
Db	0.01	1.31

Kh: Wadi Khaled; Dn: Wadi Dana Camp; Ja: Wadi Al-Jamal; Qs: Ain Quseibeh; Mh: Wadi Mahjoob; Db: Wadi Dabah.

Table (3). Average major oxides for each ore type. All values are in wt%.

	Supergene	*Primary*	Epigenetic
SiO_2	37.25	47.05	54.85
Al_2O_3	2.20	1.93	4.89
TiO_2	0.097	0.064	0.19
Fe_2O_3	6.10	15.48	5.74
MnO_2	23.35	10.75	12.56
MgO	2.00	2.08	0.47
CaO	6.86	11.98	2.66
Na_2O	0.31	0.38	0.06
K_2O	1.01	0.75	1.75
P_2O_5	1.60	0.10	0.56

5. Discussion

Recalling the schematic cross section of (Fig. 3) REE content and ratios are changing vertically according to ore genetic types (i.e. primary, supergene and epigenetic). The REE behavior of the primary ores is rather ambiguous due to the small number of samples. El-Hasan et al. (2001) described Fe-rich layers at Dana-camp and Wadi Mahjoob in the lower Cambrian Burj formation and considered them as the remnants of the primary manganese ores after extensive leaching, they have very low Eu/Sm ratios (0.16-0.31). Therefore, primary ores are believed to be rich in Eu, such result was observed in (Komuro et al. 2006).

However, in the studied primary ores Eu was removed after extensive diagenetic modifications causing very low Eu/Sm ratio. Beside that, primary ores show low values of Ce/∑REE, Ce/La, and La/Yb (Fig. 6). This type of ore showed somehow contradictory observations due to diagenetic alteration processes, which caused REE pattern to be difficult to use as paleoredox indicator (Girard et al. 2002; and Kato et al. 2006).
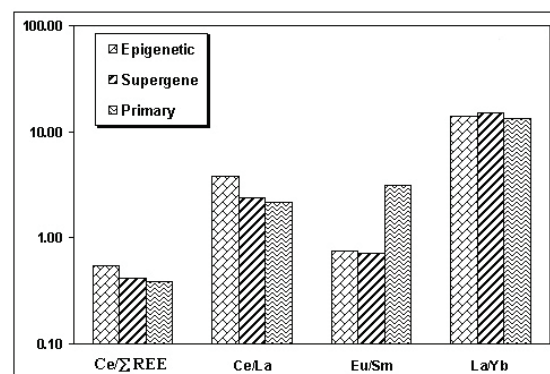

Fig. (6). Histogram showing the REE Ratios behavior among the different genetic stages of the ore.

The supergene ores show relatively high ∑REE; this is due to the upward remobilization from the lower primary ores, and the downward leaching of the upper mineralized horizons by the descending epigenetic solutions. Furthermore, this ore type is characterized by intermediate values of Ce/∑REE, Ce/La, and lower values of Eu/Sm than those of primary ores, and they exhibit the highest La/Yb values (Fig. 6). This might be attributed to higher degree of r modification compared with the primary ores, which have lower La/Yb ratio. The low Eu/Sm values and high La enrichment within this horizon indicate the remobilization of primary ores and their re-deposition under supergene conditions. The lower Eu/Sm was used as an indicator for advanced superegenity of the primary ores and to estimate the degree of alteration of these ores (Wakita et al. 1971; and Varentsov, 1995). Positive Eu anomaly with no distinct Ce anomaly are indicators for oceanic anoxia prevailed through out the early Triassic siliceous claystone from Oritate area southwest Japan (Komuro et al. 2006), Therefore, higher Eu/Sm ratios represent the primary ore then as the alteration proceeds the Eu is removed, causing the Eu/Sm ratio to drop drastically in the Fe-rich layers that is the remnants of the primary ores.   Within the supergene horizon, there is a slight difference in Ce and Ce/∑REE between Mh and Db, where it is relatively higher in the former than in the latter. Similar changes between the two sites were recorded in trace elements particularly in Fe content (El-Hasan et al. 2001). This might be attributed to the difference in the environment parameters between them in terms of Eh and pH. El-Hasan et al. (2001); and El-Hasan & Lataifeh, (2001) shows that Db high-grade ores have hematite as main mineral phase together with Mn-oxides and Mn-melane minerals, more than in Mh ores. The presence of Fe-oxides with Mn-oxides would indicate lower Eh and pH (i.e. mildly reducing) values prevailing in Db (Brookins, 1988). Therefore, such mildly reducing environment would cause Ce depletion and Eu enrichment,

which is obvious in Fig (4) where Db ores exhibits a remarkable drop in ∑REE and in Ce/REE to lesser extent, meanwhile it shows an increase in Eu/Sm ratio than the adjacent Mh ores. The changing in Eh, pH and temperature was found to be the cause for Eu and Ce mobility (Alderton et al. 1980; Taylor & Fryer 1980; Sverjensky, 1984; and Parcejus et al. 1990).

The epigenetic ore has the highest Ce content, thus high Ce/∑REE and Ce/La ratios. This was clear from the SEM illustration of (Fig. 7). Meanwhile, Eu/Sm is continuing to decrease upward as shown in (Fig. 6), this confirms the oxic diagenetic environment that affected the upper horizons; at the same time it might indicate the involvement of meteoric water in the continuous leaching process downward (i.e. lateritization) (Ozturk and Frakes, 1995). Moreover, the epigenetic ore shows an intermediate La/Yb value relative to other ores. It is slightly lower than in the supergene, which would reflect a lesser degree of differentiations that might be due to the effect of lateritization. Within this horizon, a clear difference between the western Kh site and the eastern site Mh was recognized. At Kh the ∑REE, particularly Ce, and La are much higher than in Mh (Fig. 4). This difference might be due to the detrital contribution in Kh samples (El-Hasan, 1999).
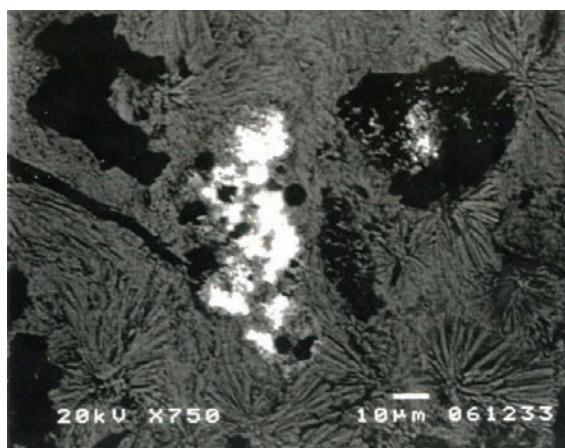

Fig. (7). SEM micro-image showing Ce (White) intergrowth inside the Mn-Oxides radiated crystals (gray).

Generally from the vertical investigation through the three ore types primary, supergene and the epigenetic ores (bottom to top respectively) as shown in Fig. (3), we noticed an upward increase in Ce, Ce/La, Ce/∑REE, in the same time an upward decrease in Eu/Sm ratio, as shown in Fig (6). All these trends are in agreement with each other and would indicate an increasing upward remobilization under oxic conditions, as the upward increase of Ce/La and Ce/∑REE ratios are good indicators for ongoing oxic diagenesis (Glasby et al. 1987; Ingri & Ponater 1987; and Varentsov, 1995). Therefore, it would indicate not only the direction of remobilization, but also the behavior of these REE ratios is in agreement with trace element behavior concluded by (El-Hasan et al. 2001).

The reducing environment that prevailed and affected the primary ores caused the remobilization of Ce upward. Because of the oxidizing environment would facilitate the oxidation of Ce^{+3} to Ce^{+4}, eventually this will develop a

positive Ce anomaly. As the repeated oxic diagenesis continues it would enhances the Ce content in the ore more than other REE's (Glasby et al. 1987). Therefore, the oxidation process would lead to REE enrichment (Ingri, 1985; and Ingri & Ponater 1987). Therefore, the Ce anomaly has been used as redox measure of the environment of deposition by many authors (Glasby, 1973; Piper, 1974; De Baar et al., 1983; Ingri, 1985;Glasby et al. 1987; Ingri & Ponater 1987; Shokoriviz et al. 1992; Varentsov et al. 1993; and Varentsov, 1995).

The Oligocene manganese deposits of the Thrace basin (Turkey) exhibits a REE pattern similar to the studied supergene ore samples (Fig. 8). They have relatively moderate REE content and a positive Eu and Ce anomalies. Its pattern shows clear diagenetic features, probably due to fresh water involvement in the ore formation (Ozturk and Frakes, 1995). The similarity between the two deposits indicates that the studies ores are of diagenetic manganese ore type. On the other hand, (Ozturk and Frakes, 1995) noticed higher REE contents in the intercalating clay layers. These clays may have scavenged the REE from the ore layers. The fact that clay is a good and common scavenger of REE was reported by (Dymond et al. 1984; and Grasselly & Ponater 1988). This would explain the relative depletion of REE in the diagenetic manganese mineralization, as the mobilized solutions rich in REE would be adsorbed onto the clay phases during their percolation; eventually this would create a relatively REE-depleted Mn ores.
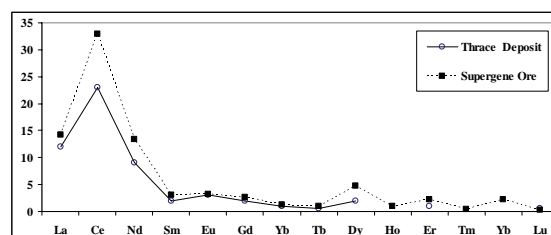

Fig. (8). Plot showing the comparison between the REE-NASC normalized patterns of the studied supergene ore samples of Mh and Db and the Oligocene Tharce manganese deposit of Turkey.

El-Hasan et al. (2001) mentioned that the primary ores characterized by higher Fe_2O_3, CaO and MgO, while supergene ores has the highest MnO_2 and P_2O_5 content beside moderate Fe_2O_3, Al_2O_3, CaO, K_2O, Na_2O and MgO. However, epigenetic ores bears higher SiO_2, Al_2O_3, TiO_2 and K_2O, which might be attributted to higher detrital incrimintation Table (4). Therefore the effect of mineral control on REE enrichment was tested by using a total of 23 high-grade supergene ore samples of Wadi Mahjoob and Wadi Dabah. The correlation coefficient matrix between REE and the possible mineral carriers such as Mn, Fe, P, Ca, Si, and Al are shown in Table (3). There was insignificant correlation between any of the REE's and Fe, P, Ca, Al or Si, and only a slight positive relationship between Mn and Eu. This might indicates that the role of the diagenetic modification is being more effective than the mineralogical control on REE enrichment.

Table (4). Correlation coefficient matrix between the REE and the major and trace elements in the ore samples of Wadi Dana (n=23).

	La	Ce	Nd	Sm	Eu	Gd	Er	Tm	Lu
Mn	-0.28	-0.17	-0.29	-0.28	<u>0.44</u>	-0.14	0.02	-0.13	-0.11
Fe	-0.27	-0.08	-0.17	-0.08	-0.18	0.12	0.24	0.06	0.04
Si	0.15	0.05	0.16	0.16	-0.24	-0.01	-0.17	-0.04	-0.07
Al	0.25	0.37	0.13	0.07	-0.13	-0.03	-0.05	0.04	0.10
Cu	-0.05	0.29	-0.11	-0.13	0.09	0.00	0.19	0.13	0.21
Co	-0.25	-0.11	-0.29	-0.29	0.31	-0.27	-0.26	-0.26	-0.21
Ba	-0.21	-0.21	-0.22	-0.19	0.43	-0.16	-0.16	-0.27	-0.26
Pb	-0.15	-0.11	-0.15	-0.13	0.02	-0.10	-0.12	0.00	-0.03
Zn	-0.08	0.01	-0.15	-0.18	0.43	-0.08	0.11	-0.01	0.04
Ca	0.06	0.02	0.01	-0.02	0.05	-0.09	-0.20	-0.20	-0.20
P	-0.02	0.05	-0.06	-0.10	-0.02	-0.11	-0.14	-0.10	-0.10

At 95% Confidence the significance value is 0.396

6. Conclusions

Generally the REE's content within the studied ore horizons are relatively depleted compared to other manganese ore types. No or weak positive Ce anomaly exist, while a positive Eu anomaly is noticed at all sites. There is a slight lateral variation within REE concentrations; meanwhile vertical variation in REE distribution was more obvious, which was related to the ore genetic evolution. Through genetic ore types; from the primary at the bottom, supergene and the epigenetic at the top, there is an obviuos enrichment of Ce/∑REE which is associated with depletion in Eu/Sm. Mainly due to upward oxic diagenetic process, therefore, high Ce anomaly is commonly associated with supergene ores, while the Eu anomaly is indicative for the primary ores. The REE patterns of the study area indicate the effect of the extensive diagenesis processes on the ore formation. As well it could reflect the different history of ore formation stages.

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