Oil Shale, Vol. 14, No. 1
pp. 5-18
ISSN 0208-198X

https://doi.org/10.3176/oil.1997.1.01

MANGANESE AS AN INDICATOR OF THE INTENSITY OF ANOXIA DURING THE DEPOSITION OF THE SENONIAN OIL SHALES IN THE NEGEV, ISRAEL

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The geochemical relationship of Mn to organic carbon, iron and alumina was studied in Early Maastrichtian oil shales of southern Israel. The Mn concentration appears to mirror the intensity of anoxia in the bottom waters of the depositional basin. It is proposed that the general trend of increasing Mn stratigraphically upward through the organic-rich sequence is a reflection of fluctuating redox conditions during the transition from an anoxic to a more oxidizing regime.

Introduction

The Oil Shale Member of the Ghareb Formation [1], of Early Maastrichtian age, is widely encountered in the sedimentary succession of the Negev (Figs. 1 and 2). Typically, the oil shales are restricted to the subsurface, though some surface exposures are known. The oil shales are found in synclinal structures [2-3]. The Early Maastrichtian was a time of marine transgression [4]. The various synchronous deposits probably represent a system of depositional basins characterized by anoxic bottom waters that helped preserve the organic detritus. These "oil shales" are massive chalks, rather than true shales, that are enriched in organic carbon (1-18 %, Fig. 2). A large bibliography on this sequence of rocks has been presented by Nathan *et al.* [5].

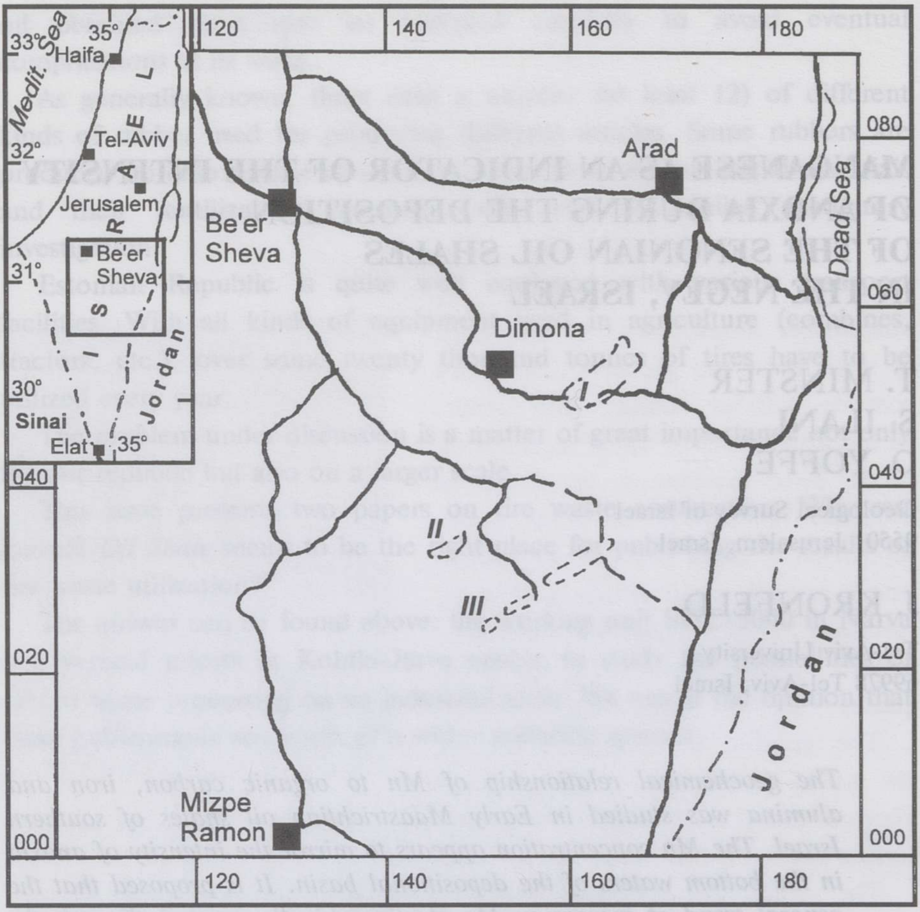

Fig. 1. Location map of the oil shale basins from which samples for Mn analyses were collected: *I* - Mishor Rotem; *II* - Oron; *III* - Nahal Zin

A recent study [6] of the concentrations of Mn in the marine carbonate succession of Israel has indicated that the Oil Shale Member of the Ghareb Formation is among the more Mn-poor (20-100 ppm, averaging 40 ppm Mn) sedimentary sequences in Israel. This stands in sharp contrast to the much higher Mn concentrations (averaging 812 ppm, SD - 615 ppm) encountered in the overlying non-bituminous Ghareb Formation chalks and chalky marls of Middle to Late Maastrichtian age, and to the fact that these oil shales are otherwise the most trace-metal (Co, Cu, Cr, Ni, V, Zn) enriched of the marine carbonate sequence [7].

In nature Mn can exist in several valence states. The Mn^{+2} specie is more soluble compared to the more oxidized Mn^{+3} and Mn^{+4} species. The environmental redox strongly influences this speciation. Lower Eh

(= redox potential) facilitates the reduction to the lower ionic specie and thus increases the Mn solubility. Iron, that may enter the basin of deposition along with Mn, is less sensitive to the Eh. Thus the magnitude of the Fe/Mn ratio in sediments has been considered as an indicator of paleo-redox conditions [8-10]. Aluminum, found in the sediment, is not redox sensitive; it is mainly associated with insoluble alumino-silicates minerals. Thus, Al/Mn ratio represents a detrital relation, while Fe/Mn can be considered to signify the redox influence.

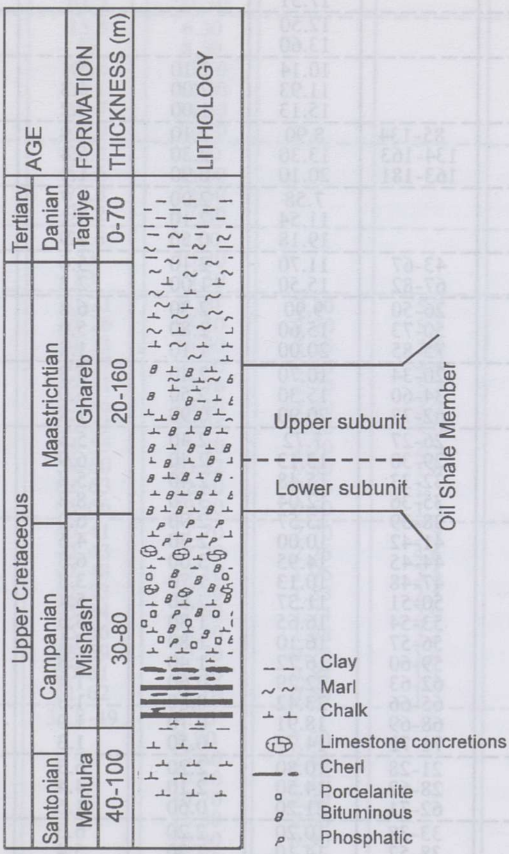

Fig. 2. Schematic geological section of the studied sequence

The oil shales of the Negev are a potential energy source and therefore much effort has been expended in their study. The most extensively studied deposits are those of the Mishor Rotem, Oron and Nahal Zin, located in the Northeastern Negev; the studied samples were from those three basins.

Table. **Mn and Related Analytical Results from Various Oil Shale Samples, Southern Israel**

Borehole/ Sample	Depth (m)	EOM (%)	Fe_2O_3 (%)	Al_2O_3 (%)	Mn (ppm)
		Mishor Rotem			
Bit-1	18-36	12.04			70
	36-55	14.62			92
	55-75	19.76			24
Bit-4A		10.68			49
Bit-4B		13.20			43
Bit-4C		17.51			48
Bit-6A		12.50			33
Bit-6B		13.60			53
Bit-45I		10.14	2.10	5.1	48
Bit-45II		11.93	2.00	4.3	45
Bit-45III		15.13	1.00	2.2	31
Bit-53	85-134	8.90	2.10	4.9	50
	134-163	13.30	2.30	5.4	48
	163-181	20.10	0.90	1.4	24
Bit-54I		7.58	2.00	4.7	66
Bit-54II		11.54	2.10	5.1	50
Bit-54III		19.18	0.50	1.9	29
Bit-78	43-67	11.70	2.10	5.6	46
	67-82	15.50	1.00	2.3	32
Bit-85	26-50	9.90	2.30	6.8	45
	50-73	15.60	2.80	5.0	55
	75-85	20.00	1.10	1.8	27
Bit-87	20-34	10.70	2.40	5.3	50
	34-60	15.30	2.50	5.0	55
	62-78	20.90	0.90	1.8	23
Bit-94	26-27	7.72	2.40	5.5	47
	29-30	13.13	2.40	6.9	45
	32-33	15.48	2.40	5.8	38
	35-36	12.04	3.70	8.8	72
	38-39	13.57	2.90	6.0	75
	41-42	10.00	2.30	4.6	54
	44-45	14.95	3.00	6.3	68
	47-48	10.13	1.70	3.3	68
	50-51	11.37	2.80	5.4	78
	53-54	16.65	1.80	3.5	53
	56-57	16.10	1.80	3.1	47
	59-60	16.72	1.40	2.8	51
	62-63	22.29	0.60	1.4	24
	65-66	23.42	0.60	1.3	21
	68-69	18.91	0.70	1.9	35
	71-72	14.77	0.50	1.3	36
Bit-95	21-28	10.80	2.20	6.3	46
	28-62	14.50	2.10	4.4	47
	62-71	21.20	0.60	1.6	20
Bit-97	33-38	10.20	2.20	6.3	47
	38-52	14.10	2.30	5.4	60
	53-69	18.60	0.80	1.8	20
Bit-102	32-42	19.00	0.50	1.5	19
Bit-250I		20.03	0.80	1.8	79
Bit-260	30-44	11.90	3.20	7.3	55
Bit-263	66-114	9.10	2.30	6.2	51
	114-140	13.60	2.40	5.6	51
	140-158	19.30	1.10	2.0	38
M-228*		23.70	0.40	1.2	13
M-272*		11.70	2.10	5.0	54
PM-5I		13.60	0.80	4.7	62
PM-5II		17.42	2.00	2.3	34
PM-5III		21.49	1.10	1.1	33

* Samples from the open-pit mine.

Table (cont.). Mn and Related Analytical Results from Various Oil Shale Samples, Southern Israel

Borehole/ Sample	Depth (m)	EOM (%)	Fe_2O_3 (%)	Al_2O_3 (%)	Mn (ppm)
		Mishor Rotem			
F-88	32.5	11.30			25
	35.3	13.00			40
	48.5	19.20			25
F-89	22.5	10.40			71
	42	14.80			40
	61.2	21.70			20
F-90	15.5	6.30			40
	32	8.50			70
	47.4	15.50			20
	62.1	12.30			40
	80.7	14.50			20
	25.9	12.50			100
F-94	32.4	7.80			25
	53.6	15.00			40
	73.3	12.50			40
	90.2	17.80			20
F-95	24.8	9.00			25
	33	10.30			20
	83	19.50			20
R-2	20-21	9.20	2.20	5.2	62
	25-26	13.10	2.20	5.1	36
	30-31	16.90	2.10	5.0	32
	36-37	15.00	2.20	4.6	48
	40-41	13.70	2.70	5.7	52
	45-46	13.40	1.60	3.2	50
	50-51	13.95	2.00	4.0	58
	54-55	19.10	1.70	2.9	40
	59-60	20.22	0.80	1.6	21
	62-63	22.80	0.60	1.3	23
	65-66	22.20	0.50	1.3	18
T-1	40-41	11.70	2.70	5.5	66
	42-43	12.20	2.26	4.6	44
	47-48	13.10	1.96	3.5	53
	52-53	16.30	1.53	2.5	55
	53-54	17.90	1.74	2.9	44
	55-56	18.80	1.98	3.2	45
	58-59	20.70	0.70	1.4	19
	60-61	24.40	0.54	1.1	20
	61-62	26.10	0.50	1.3	22
T-2	33.8-49	8.15			74
1		9.90	2.30		45
2		15.60	2.80		55
3		20.00	1.10		27
4		10.70	2.40		50
5		15.30	2.50		55
6		20.90	0.90		23
7		10.80	2.20		46
8		14.80	2.10		47
9		21.20	0.60		20
10		10.20	2.20		47
11		14.10	2.30		60
12		18.60	0.80		20

Table (end). Mn and Related Analytical Results from Various Oil Shale Samples, Southern Israel

Borehole/ Sample	Depth (m)	EOM (%)	Fe_2O_3 (%)	Al_2O_3 (%)	Mn (ppm)
		Mishor Rotem			
Feed*		15.20	1.30	3.3	26
		17.60	1.60	3.8	63
		17.50	1.20		22
		15.30	1.60		37
		16.00	1.50	3.6	34
		20.50	0.40	1.2	12
		16.50	1.20		25
		17.80	1.30	3.0	27
		15.10	1.80	4.2	41
		15.90	1.10		31
		20.00	0.90	2.0	45
		19.30	1.00	2.2	29
		18.30	1.00	2.1	27
		15.30	1.30	3.0	29
		20.50	0.30	1.2	11
		20.60	0.50	1.5	17
		17.00	1.10	1.9	29
		19.00	0.60	1.7	21
		20.80	0.50		26
		15.60	1.90	4.9	31
		15.70	1.90	4.7	28
		18.30	0.90	2.4	55
		14.60	1.80	4.0	35
		13.20	1.40	3.2	33
		13.70	1.20		27
		14.80	1.30	3.1	31
		14.70	1.40	3.1	36
		12.50	2.10	4.6	45
		9.20	1.90	4.1	46
		13.70	1.30	3.2	30
		Oron			
NG-127	31-32	14.30	2.60	5.2	60
	33-34	11.50	1.40	2.9	68
	37-38	13.30	2.00	4.4	49
	41-42	17.10	1.60	2.8	39
	45-46	16.20	1.40	2.5	35
	49-50	18.80	0.80	1.7	23
	53-54	22.40	0.60	1.4	22
	57-58	20.20	0.60	1.8	24
OS-9	12-13	9.80	2.60	7.9	60
	15-16	7.70	2.20	6.0	78
	19-20	8.10	2.10	6.1	55
	22-23	13.50	2.50	7.3	52
	27-28	11.90	1.80	4.7	78
	31-32	18.50	1.50	2.8	32
	36-37	19.30	1.10	2.0	25
	39-40	22.20	0.60	1.7	22
	43-44	17.00	0.50	1.6	19
		Nahal Zin			
ZS-11	12-13	0.20	2.90	6.5	94
	14-15	3.30	2.70	6.0	80
	18-19	14.22	1.70	3.4	40
	21-22	16.33	1.10	2.2	27
	24-25	18.65	0.40	1.1	18
3355	36-38	27.05	0.58	1.3	20
3369T	36-36.6	28.89	0.62	1.4	15
	36.6-37	31.65	0.56	1.5	18
3363	35.4-37.4	30.30	0.48	1.5	21
	37.4-38.8	30.82	0.54	1.6	18

* Samples from the open-pit mine.

Although the oil shales of the Early Maastrichtian age (Ghareb Formation) have been studied in detail, geochemical investigations were not previously employed to delineate palaeo-environmental conditions. In the present study, changes in the Mn concentration in the stratigraphic profile were investigated to evaluate the possibility of using the change in the concentration of manganese in conjunction with iron, alumina, and organic matter content to detect variations in redox conditions, in what could be considered an otherwise uniform depositional environment.

Sampling and Analytical Method

Seventy-five oil shales samples collected from boreholes (both core and cuttings) representing three basins were studied. Most of these samples were from the Mishor Rotem basin, though representative samples from the neighboring Oron and Nahal Zin basins were also studied. All of the samples were unaltered, free of visible manganese mineralization or staining. Microfossils were found to be well preserved, indicating that post depositional diagenetic processes and alterations were negligible. These samples were dried and ground to less than 200 mesh size followed by acid (4 ml HCl : 6 ml HNO_3 concentrated solution at 90 °C in an agitated water bath for 1 hour) dissolution. Mn and Fe, as well as Al, in 49 samples from Mishor Rotem, were analyzed by the ICP-AES (Jobin-Yvon JY-46 polychromator) at the geochemistry laboratory of the Geological Survey of Israel. The organic matter content was measured as the easily oxidized organic matter (EOM = easily oxidized material, determined by the potassium dichromate method). Other analyses of organic matter, carried out on samples from the equivalent intervals from which our manganese samples were collected, which were previously analyzed by the same method [11-12], were incorporated into the Mn data-base. Likewise, our data-base was expanded to 134 samples by including Mn values with some EOM and Fe data, previously reported by Spiro [13] and Shirav [14] from the Oil Shale Member of the Ghareb Formation, from the Mishor Rotem basin.

Results

The Mn, Fe, Al and EOM contents of samples taken at various intervals in boreholes from the three oil shale basins studied are presented in the Table. The Mn concentrations range from 13 to 100 ppm, averaging 44 ppm. Iron concentrations for the corresponding samples range from 0.4 % to 3.7 %, averaging 1.73 %. A positive correlation (r = 0.8; N =

= 134), is noted between Fe and Mn. Likewise, for where data is available, in the Mishor Rotem deposit, a similar positive correlation (r = = 0.76; N = 49) is noted between Al and Mn. On the other hand, there is a negative correlation (r = −0.71; N = 110) between Mn and EOM (Fig. 3). Though most of the samples were taken from the Mishor Rotem basin, the average Mn concentrations do not differ significantly, either in magnitude nor in the geochemical association, among the basins. There appears to be a decrease in the EOM and a concomitant increase in the Mn going stratigraphically up the organic-rich sequence, culminating in a sharp jump in Mn concentration in the overlying non-bituminous part of the Ghareb Formation.

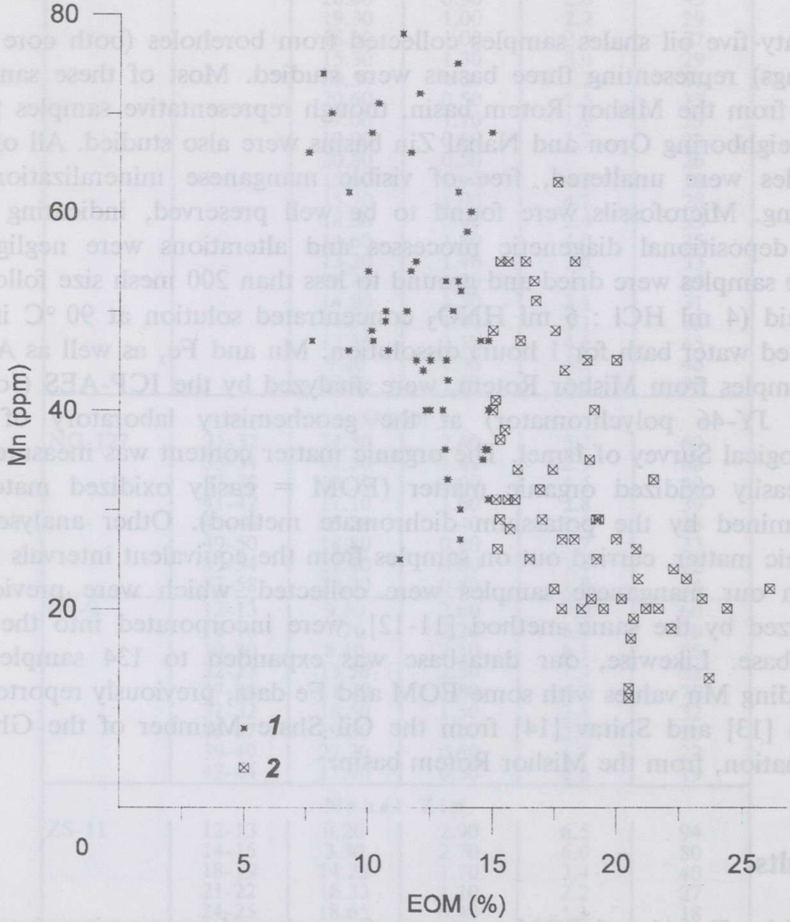

Fig. 3. Correlation between manganese and organic matter (EOM - easily oxidized material) in the studied oil shale samples of the Oil Shale Member (*1* - upper subunit, *2* - lower subunit) from Mishor Rotem, Ghareb Fm. N = 110, r = −0.71

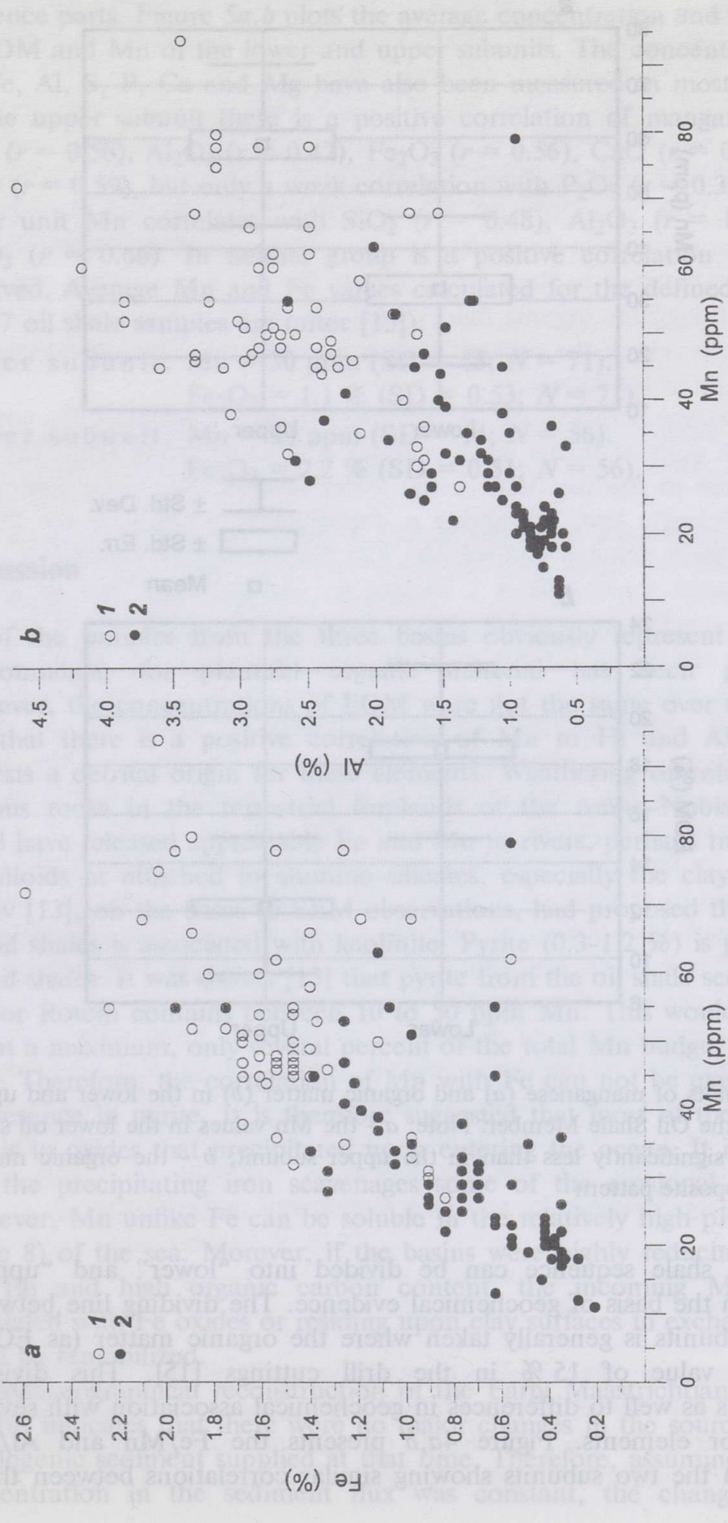

Fig. 4. Correlation between (*a*) manganese and iron (*1* - upper subunit, $r = 0.4812$; *2* - lower subunit, $r = 0.6412$), and (*b*) manganese and alumina (*1* - upper subunit, $r = 0.4166$; *2* - lower subunit, $r = 0.5661$) in samples of the Oil Shale Member from the studied basins, Northern Negev. $N = 127$

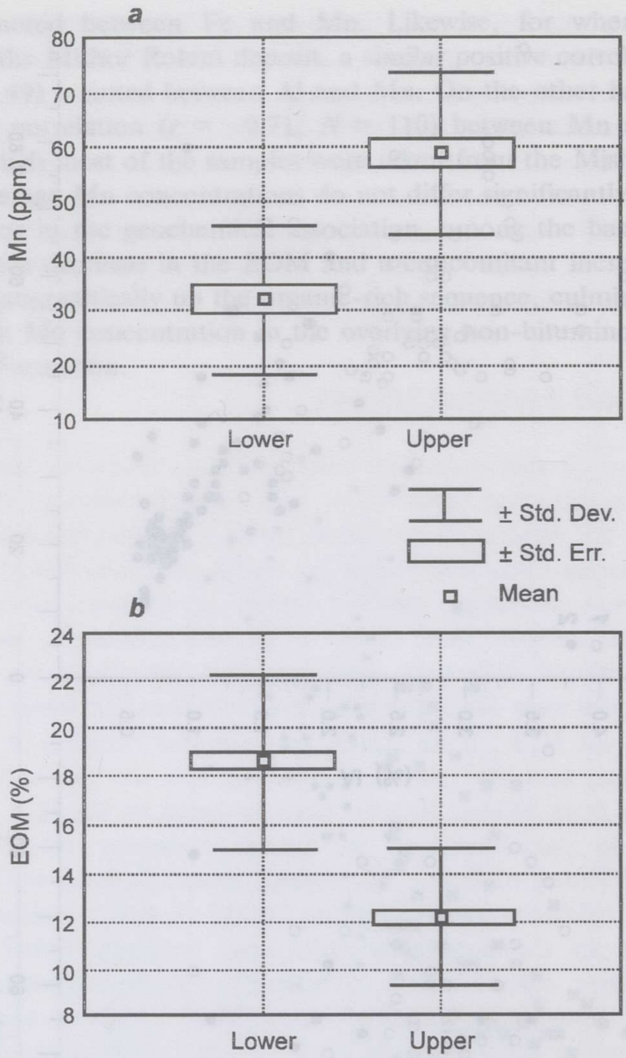

Fig. 5. Boxplots of manganese (*a*) and organic matter (*b*) in the lower and upper subunits of the Oil Shale Member. Note: *a* - the Mn values in the lower oil shale subunit are significantly less than in the upper subunit; *b* - the organic matter shows an opposite pattern

The oil shale sequence can be divided into "lower" and "upper" subunits on the basis of geochemical evidence. The dividing line between the two subunits is generally taken where the organic matter (as EOM) reaches a value of 15 % in the drill cuttings [15]. This division corresponds as well to differences in geochemical association with several other major elements. Figure 4*a,b* presents the Fe/Mn and Al/Mn relations in the two subunits showing similar correlations between those sequence parts. Figure *5a,b* plots the average concentration and the range of EOM and Mn of the lower and upper subunits. The concentrations of Si, Fe, Al, S, P, Ca and Mg have also been measured in most samples. In the upper subunit there is a positive correlation of manganese with SiO_2 ($r = 0.56$), Al_2O_3 ($r = 0.47$), Fe_2O_3 ($r = 0.56$), CaO ($r = 0.68$), and MgO ($r = 0.59$), but only a weak correlation with P_2O_5 ($r = 0.35$). In the lower unit Mn correlates with SiO_2 ($r = 0.48$), Al_2O_3 ($r = 0.59$) and Fe_2O_3 ($r = 0.66$). In neither group is a positive correlation with SO_3 observed. Average Mn and Fe values calculated for the defined subunits in 127 oil shale samples are (after [15]):

Lower subunit: Mn = 30 ppm (SD = 13; $N = 71$).
Fe_2O_3 = 1.1 % (SD = 0.53; $N = 71$).

Upper subunit: Mn = 53 ppm (SD = 14; $N = 56$).
Fe_2O_3 = 2.2 % (SD = 0.51; $N = 56$).

Discussion

All of the samples from the three basins obviously represent reducing environments, for plentiful organic material has been preserved. However, the concentrations of EOM were not the same over time. The fact that there is a positive correlation of Mn to Fe and Al (Fig. 4) suggests a detrital origin for these elements. Weathering of volcanic and igneous rocks in the terrestrial forelands of the Arabo-Nubian Massif could have released appreciable Fe and Mn to rivers, perhaps transported as colloids or attached to alumino-silicates, especially the clay fraction. Shirav [13], on the bases fo SEM observations, had proposed that Mn in the oil shales is associated with kaolinite. Pyrite (0.3-1.2 %) is present in the oil shales. It was shown [13] that pyrite from the oil shale sequence in Mishor Rotem contains between 10 to 50 ppm Mn. This would account for, at a maximum, only several percent of the total Mn budget of the oil shale. Therefore, the correlation of Mn with Fe can not be explained by its presence in pyrite. It is therefore suggested that most of the Mn and iron is in oxides that precipitated upon entering the ocean. It is possible that the precipitating iron scavenages some of the erosional Mn flux. However, Mn unlike Fe can be soluble in the relatively high pH (slightly above 8) of the sea. Morever, if the basins were highly reducing, having low Eh and high organic carbon content, the incoming Mn, either associated with Fe oxides or residing upon clay surfaces in exchange sites, could be remobilized.

Paleogeographical reconstruction of the Early Maastrichtian of Israel [15-16] indicates that there were no major changes in the source or type of allogenic sediment supplied at that time. Therefore, assuming that the concentration in the sediment flux was constant, the change in Mn concentration within the oil shale section can be explained by either a change in efficiency of Mn accumulation or by a dilution of the allogenic sediment.

Within the studied basins, the organic matter varies inversely with the Mn concentration (Fig. 5). A change in the efficiency of Mn precipitation or solution from the Mn flux is needed to account for the difference. The solubility of Mn is affected by the intensity of the reducing conditions in the basin. At lower Eh, more of the higher valence species are reduced to the soluble Mn^{+2}. The Eh is dependent upon the amount of available organic matter, which is in turn dependent upon the efficiency by which the organic matter is preserved. This corresponds to the intensity of the anoxia.

The average iron content in the lower subunit is about 1 %, whereas its average content in the upper subunit is twice as much (Fig. 4*a*). This may be due to the fact that in the lower subunit, the redox conditions were sufficiently low, permitting a considerable portion of the ferrous iron to remain reduced and soluble. The higher iron concentration in the upper subunit might reflect a change to slightly higher pH or greater oxidizing conditions (or both) in the basin waters which would facilitate the ready change of ferrous to ferric iron. This, in turn, would sharply reduce the solubility of iron. A similar small change in pH should have only small effect on Mn solubility. Increasing oxidizing conditions, though, could have a signal affect in decreasing the Mn solubility. In the upper unit, the Mn concentration is greater; though, there still exists a clear negative correlation between the Mn and the EOM ($r = -0.60$). However, in the upper unit Mn is not only associated with detrital clays, as indicated by positive correlations with Al (Fig. 4*b*), Si and Fe, but also with Ca and Mg, indicating possible coprecipitation with the carbonate fraction. There is no significant correlation of Mn in this subunit with P (apatite) nor with S (pyrite and organic sulfur).

As the environment of deposition changed to more oxic conditions during deposition of the upper subunit, (perhaps related to high sea level stand inducing a more intense circulation), less of the Mn attached to the incoming alumino-silicates (clays) surfaces is likely to have been leached. This accumulating Mn was augmented by oxidation of a part of the soluble manganous species and their subsequent precipitation.

Conclusions

The difference in Mn and Fe concentrations exhibited between the lower and the upper subunits of the Oil Shale Member in the Negev, Southern Israel, appears to reflect the degree of oxidizing conditions in the basins, in which the sediments were deposited. The amount of organic carbon preserved in the section is related to the redox conditions at the time of deposition. By tracing the changes in Fe/Mn and Al/Mn throughout the section the trend of changing redox conditions, related to the changing intensity of anoxia, under which the oil shales were deposited are revealed. The Early Maastrichtian oil shales of the Negev thus appear to have been first deposited under more intensely anoxic conditions that gave way, in a fluctuating manner, to a more oxidizing regime up to the Late Maastrichtian.

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Presented by J. R. Dyni
Received July 24, 1996