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Tracing the sources of sedimentary Cu and Mn ores in the Cambrian Timna Formation, Israel using Pb and Sr isotopes



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ABSTRACT

Diagenesis and epigenetic remobilization frequently obscure the original depositional environment of sediments that have been affected by Cu- Mn- mineralization. Such is the case for the sedimentary Cu and Mn ores of the Cambrian Timna Formation in Southern Israel, where different interpretations of field, petrographic and geochemical data have led to conflicting genetic models. In this study we show how Sr and Pb isotopic data can help unravel the origins and complex processes involved in the sedimentary-hosted Cu- Mn- mineralization. Applying Pb and Sr isotopic systems to the various host rock types, two petrographical and chemically distinct types of Mn nodules (referred to as A and B) and reduced and oxidized Cu minerals of the Timna Formation indicates that two major solution types were involved. The first solution is depleted in Th and enriched with U, with a constant ²⁰⁸Pb/²⁰⁴Pb ratio and single U source as reflected by the correlation between ²⁰⁶Pb/²⁰⁴Pb vs. ²⁰⁷Pb/²⁰⁴Pb. The second solution has higher Th and lower U concentrations; thus ²⁰⁸Pb/²⁰⁴Pb ratios significantly vary whereas the ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁷Pb/²⁰⁴Pb ratios remain relatively constant. The low Th/high U solution is associated with the deposition of Type A Mn nodules, whose 87 Sr/ 86 Sr ratio of 0.7093 \pm 0.0005 matches that of the Cambrian Sea. Thus, in keeping with previous petrographic and mineralogical evidence, the isotope data are consistent with primary Mn nodule formation under oxidizing conditions during early diagenesis. In contrast, the second high Th/ low U solution is associated with the transformation of primary Type A to epigenetic Type B Mn nodules. During these later processes, U was leached from Type A Mn nodules to form secondary Pb enriched Type B nodules. The Pb isotope composition of these nodules clearly shows that the epigenetic solutions were significantly different from those of a major phase of Oligocene-Miocene Fe- mineralization that affected the bedrocks adjacent to the Dead Sea Transform. Cu- Mn- mineralization exhibits more complex isotopic signatures. Cu-sulfides (mainly covellite) deposited during early diagenesis under reducing conditions, and although their ⁸⁷Sr/⁸⁶Sr ratio in places is 0.709, as a whole, their Sr-isotope ratios reflect their location rather than the Cambrian sea water signature, as clearly evident from their Pb isotope compositions. During later epigenetic stages, copper sulfides were altered to form malachite and paratacamite, whose Pb isotope compositions show that the oxidizing solutions underwent fluid-rock interaction with their host rocks, particularly during the transport of Pb in lower pH chloride solutions. Overall, it is evident that the combined use of the Sr and Pb isotope systems allows clarification of the various primary and secondary processes involved in the Cambrian Timna mineralization Cu- Mn- mineralization, and particularly the important identification of the involvement of Cambrian sea water in the primary ore formation processes. © 2017 Elsevier B.V. All rights reserved.

1. Introduction

Sedimentary Cu- Mn- mineralization involves complex geochemical processes. In particular, the original sedimentary environment of the Cu- Mn- mineralization is often masked by diagenesis and epigenetic remobilization processes. In order to elucidate the complex geochemical record of such sediments, and to separate primary sedimentary isotopic signatures from those of later processes, we show here how application of the isotopic systems of Pb and Sr to Cambrian sedimentary ore minerals and their host sedimentary rocks can considerably help clarify the geochemical evolution of such complex systems. Owing to its long and complex exposure and geological history, the Cambrian Timna Formation of the Timna Valley, Southern Israel (Fig. 1) provides an excellent setting for tracing stages in Cu- Mn- mineralization and their sources by means of isotopic geochemistry of Cu and Mn ores. The coupled use of the Pb and Sr isotopic systems, in combination with selective dissolution methods, potentially allows unraveling the various stages of evolution of the Cambrian metalliferous ore deposits,

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Fig. 1. Geology and sample location; (a) General location map of all sites of interest (b) a composite section of the Cambrian, including Timna Formation (after Segev, 1986) and (c) Sampling locations superimposed on the geological map of Timna Valley.

from the time of deposition to later subsurface leaching and migration processes.

Copper ores in the Timna Valley, mined since biblical times (Rothenberg and Shaw, 1990), predominantly occur together with manganese deposits in sands and shales of the Timna Formation (Bentor, 1952, 1956; Strum, 1953; Parnes, 1971; Bartura and Wurzburger, 1974; Segev and Sass, 1989). The sequence of events, timing of formation and the source material for the Cu- Mn- mineralization in the Timna Formation are the main issues addressed in this study. One of the key issues of the study is the relation between syngenetic-diagenetic and epigenetic Cu- Mn- mineralization, about which there has been considerable scientific debate (e.g. Segev and Sass, 1989; Bar-Matthews, 1987; Bar-Matthews and Matthews, 1990; Shlomovitch et al., 1999). A related question is which ore minerals, if any, preserve primary sedimentary signatures of the Cambrian Sea?

The isotopic composition of Pb was used in many studies to identify source rocks for Cu- Mn- mineralization and to trace multi-stage history of ores, including the pioneering study of Doe and Deleveaux (1972) and others (e.g. Brevart et al., 1982; LeHuray et al., 1987; Kiippel and Schroll, 1988; Dixon and Danny, 1991; James and Christopher, 1993; Doe et al., 1996 and references therein). Arribas and Tosdal (1994), for example, utilized Pb isotopes to study the complex geological history and Cu- Mn- mineralization ages of Fe-Pb-Zn (Ba) deposits in various host rocks (carbonates) in the Betic Cordillera, Spain. In contrast, the use of Sr isotopic composition for the same purpose is less common, and Sr is primarily applied for dating (e.g. Nakai et al., 1993). In the case of the Cambrian Timna Formation, unraveling the Sr isotope record of Cu- Mn- mineralization may shed light on the Cambrian sea water ⁸⁷Sr/⁸⁶Sr values. These data are of considerable importance in the light of potential contribution of high Sr ⁸⁷Sr/⁸⁶Sr material to the Cambrian Seas due to the massive erosion of the Pan African Orogeny (e.g. Derry et al., 1989, 1994; Asmerom et al., 1991; Kaufman et al., 1993; Burns et al., 1994; Montanez et al., 1996).

2. Geological setting of the Cambrian Cu- Mn- mineralization

Copper and Mn-mineralization occurs in Cambrian sediments of the Timna Formation, which outcrops in the Timna Valley in Southern Israel and extends south into the Sinai Peninsula, and to the north is found in the Sinaf borehole some 30 km north of the Timna Valley (Fig. 1a). This formation is also exposed in Jordan in a ca. 70 km transect along and east of the Arava Valley, a segment in the Dead Sea Transform. The maximum thickness and exposure of the Timna Formation are found in the Timna Valley which is a horseshoe shaped erosional cirgue truncated on its eastern side by a series of structurally lower blocks, which are part of the Dead Sea Transform (Fig. 1). The Timna Igneous Complex (TIC) exposed in the center of the Timna Valley is the northernmost tip of the Arabian - Nubian shield in Israel. The TIC comprises gabbroic rocks in its core and alkali K- syenite to granitic rocks at its margins (600-625 Ma; Beyth, 1987; Beyth et al., 1994; Beyth et al., 1997). The sedimentary sequence, exposed in the cirque's floor and walls, is Cambrian to Cenomanian in age (Fig. 1c). At the base of the sedimentary section, the fluvial Cambrian Amude Shelomo Formation consists of conglomerates, arkoses and coarse sandstones. The overlying Timna Formation represents the Cambrian marine transgression (Parnes, 1971) and consists of dolomite (dolomitic lithofacies), sandstone and shale. This formation hosts the Cu- Mn- mineralization, mainly in the sandy- shaly lithofacies (Fig. 1). Previous works suggested that the age of the Timna Formation was Early-Middle Cambrian (Parnes, 1971; Cooper, 1976; Soudry and Weissbrod, 1995). However, the Cambrian fauna of the Burge Formation in Jordan (which is equivalent to the Timna formation) was inferred to be earliest Middle Cambrian (Rushton and Powell, 1989), equivalent to ca. 520 Ma (Geyer and Landing, 2004).

Previous studies have proposed that the sources of the Mn- and Cuwere the igneous intrusive and extrusive rocks of the Precambrian basement, which is exposed on both sides of the Dead Sea transform (e.g. Bentor, 1952, 1956; Strum, 1953; Bartura and Wurzburger, 1974; Bigot, 1981; Sneh et al., 1998). In general, Cu- Mn- mineralization was proposed to have initiated in a coastal or lagoonal shallow marine environment at temperatures of 25–55 °C, where Mn replaced Ca in primary syngenetic and diagenetic dolomite, while Cu formed copper sulfides. Both diagenetic and epigenetic processes in the overlying sandstones and shales have been proposed to account for the formation of Mn nodules and oxidation of Cu sulfides (Bentor, 1956; Bar-Matthews, 1987; Bar-Matthews and Matthews, 1990; Shlomovitch et al., 1999).

2.1. Mn mineralization

The Mn mineralization in the Timna Formation occurs in a variety of forms and host rocks (e.g. Segev, 1986; Bar-Matthews, 1987): Mn as a replacement in the dolomite forming Mn-dolomite and as Mn nodules in the sandy-shaly rocks in the uppermost part of the Timna Formation. The Mn nodules range in size from a few mm up to 10 cm in diameter. The main minerals identified in the Mn nodules are coronadite, hollandite, pyrolusite and rarely mottramite (Gross and Bartura, 1984; Bar-Matthews, 1987). Based on their petrography, mineralogical and chemical composition, Bar-Matthews (1987) classified the Mn nodules into two types: syngenetic-diagenetic (Type A) and epigenetic (Type B),

and suggested that Type A Mn nodules formed under near-surface oxidizing conditions at the Cambrian sediment-water interface, whereas Type B Mn nodules formed by later epigenetic processes. This difference is well conveyed in their mineralogy and chemical composition. While Type A Mn nodules consist of primary sedimentary-diagenetic pyrolusite-hollandite and are U-rich (up to 1700 ppm), Type B Mn nodules consist of secondary coronadite-hollandite and are U-depleted (<240 ppm) and Pb-rich (0.7–10%). The distinction between the two types of the Mn nodules was confirmed by their different Pb isotope composition (Ehrlich et al., 2004).

An alternative model of Cu- Mn- mineralization events was proposed by Segev (1986), Segev and Sass (1989) and Segev (1992), based on an interpretation of the complex field relationships between three different lithofacies of the Timna Formation (dolomitic, sandy, and shaly lithofacies). They suggested that dolomitization occurred soon after deposition in the Cambrian and that the sandy lithofacies is the insoluble residue of Neogene epigenetic dissolution of the dolomitic facies. In their view, the Mn- mineralization precipitated from epigenetic solutions and could have occurred at any time after deposition. In this

Table 1		
Sample location and	general	data.

Sample	Location (Site no. on Fig. 1)	Host rock	Phase analyzed
Mineralized host rocks			
MT-1	Plant gate (6)	Dol.	Dol., calc., clav
MT-3	Mt. Michrot (2)	Dol.	Dol., clay
MT-17	Pitriya (4)	Dol.	Dol., clay
MT-25	Mt. Timna (3b)	Dol.	Dol., calc., clay
MT-26	Mt. Timna (3b)	Dol.	Dol., calc., clay
MT-27	Eden (10)	Dol.	Dol., calc., clay
MT-28	Pitriya (4)	Dol.	Dol., calc., clay
CMDS 2	Plant gate (6)	Dol.	Cu
CMDS 9	Mt. Michrot (2)	Dol.	Cu
CMDS 15d	Plant gate (6)	Dol.	Cu
CMDS 17c,d	Plant gate (6)	Dol.	Cu
CMDS 18, 19, 30	Mt. Michrot (2)	Dol.	Cu
CMDS 33	Plant gate (6)	Dol.	Cu
CMDO 17-19	Mt. Michrot (2)	Dol.	Cu
CMDO 32	Plant gate (6)	Dol.	Cu
CMDO 20, 21, 27	N. Mangan (1)	Dol.	Cu
CMDO 23-25	Step faults (5)	Dol.	Cu
CMDO 22, 26	Pit K (7)	Dol.	Cu
CMDO 28	Pitriya (4)	Dol.	Cu
CMSS 5, 6	Pit D (8)	Shale	Cu
CMSS 9, 10	Pit D (8)	Sands.	Cu
CMSS 14-26	Pit K (7)	Sands.	Cu
TICO 3, 10,12, 14, 17	Mt. Timna (3a)	Qz. p. dike	Cu
TICS 3, 10, 13	Mt. Timna (3a)	Qz. p. dike	Cu
TIC 1,2	Mt. Timna (3a)	Qz. p. dike	Wr.
HA 1,3	Mt. Timna (3a)	Granite	Wr.
Mn nodules			
MT-7	Mt. Michrot (2)	Mn	Mn (B)
MT-8	N. Mangan (1)	Mn	Mn (B)
MT-9	N. Mangan (1)	Mn	Mn
MT-10	Mt. Michrot (2)	Mn	Mn (A, B)
MT-13	N. Mangan (1)	Mn	Mn (crypt.)
MT-14	N. Mangan (1)	Mn	Mn
MT-15	N. Mangan (1)	Mn	Mn (A)
MT-22	Mn Hill (9)	Sands.	Mn-Fe
MT-23	Mn Hill (9)	Sands.	Mn-Fe
Non mineralized host roo	cks		
MT-5	Netafim C.	Dol.	Calc, dol., clay
MT-6	Netafim C.	Lime	Calc, clay
MT-18	Netafim C.	Qz. dol.	Calc., clay
MT-19, 20	Netafim C.	Dol.	Wr., dol., clay
MT-21	Seismic st.	Qz. dol.	Calc, dol., clay
SST-7	Feinan, Jordan	Dol.	Calc, dol., clay
Sinaf1h	Sinaf borehole	Dol	Calc dol clav

Dol. = dolomite, calc. = calcite, wr. = whole rock, lime. = limestone, sands. = sandstone, Mn = Mn nodules, Cu = copper phase, qz. p. = quartz porphyry. Netafim C. = Netafim crossing.

Table 2

Pb and Sr isotopic composition and element concentrations of whole rock and extracts from Timna Valley, Netafim crossing and Sinaf borehole, Israel and from Feinan, Jordan.

			206-1 204-1	207-4 204-4	202-1 204-1	9796 -	-1			-
Sub-sample	Dom. phase	%Cal.	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	⁸⁷ Sr/ ⁸⁶ Sr	Pb	U	Th	Sr
		(*%)					µg/g	µg/gr	µg/gr	µg/gr
Min analized has	ut un alva									
Mineralized nos		02 (02)	10.0040	15 5000	27.004	0 70707	0.00	2.04	1270	110
MI-Ia	Cal	93 (92)	18.0640	15.5980	37.884	0.70707	8.66	2.04	1270	119
MI-ID	Cal	/9	18.6017	15.6606	38.129	n.d.	0.18	0.91	n.d.	n.d.
MT-1c	Cal	n.d.	18.6781	15.6658	38.143	n.d.	9.76	14.04	1.54	n.d.
MT-1d	Cal	87	18.4856	15.6382	38.297	n.d.	0.37	0.80	n.d.	23.2
MT-1a	Dol	37	18.2613	15.6383	37.990	n.d.	1.07	0.74	0.09	17.2
MT-1b	Dol	39	187371	15 6604	38 170	n d	1 10	0.64	0.04	147
MT-1c	Dol	n d	18 72/2	15,6683	38 178	n d	6.00	2.51	1 1 1	n d
IVII-IC	Dul	n.u. 20	10.7242	15.0085	20.251	n.u.	0.99	2.51	1.11	11.u.
MI-Id	Dol	36	18.8251	15.6681	38.251	n.d.	3.10	1.12	n.d.	7.3
MI-1e	Dol	7	18.5312	15.6435	38.256	n.d.	2.12	0.36	n.d.	6.0
MT-1a	IR	<1	18.5559	15.6435	37.984	0.72990	12.00	4.93	2.84	47.0
MT-1b	IR	<1	20.3626	15.7759	38.078	n.d.	2.35	4.56	1.40	13.0
MT-1c	IR	<1	20.0278	15.7610	38.098	n.d.	118.89	2.27	37.27	1.4
MT_3h	Cal	33	18 5206	15,6553	37 003	n d	n d	n d	n d	14.7
MT 25	Del	7	10.3200	15.0555	20 024	n.d.	20.61	7.69	n.d.	14.7
IVII-3d	DOI	/	18.3730	15.0475	38.034	n.a.	28.61	7.68	11.0.	44.6
IVII-3D	DOI	38	18.2613	15.6380	37.999	n.a.	29.59	4.93	120	23.9
MT-3c	Dol	39	18.0959	15.6290	37.992	n.d.	183.42	1.24	10.57	10.1
MT-3a	Dol		20.0245	15.7293	37.988	n.d.	100.00	6.60	0.19	n.d.
MT-3b	IR	<1	21.6219	15.9067	38.011	n.d.	6.73	11.46	0.33	10.8
MT-3c	IR	<1	21 5009	15 8905	37 996	n d	0.32	0 74	n d	0.04
MT_175	Cal	72	18 0151	15 5034	37.850	n d	1 31	1 15	0.04	40.1
IVII-I/d	Cdi	72	10.0131	15.5554	37.830	n.u.	1.51	1.13	0.04	40.1
IVII-I/d	DOI	n.a.	18.5522	15.0590	38.220	n.a.	3.32	1.//	0.28	11.ú
MI-17b	Dol	15	18.9249	15.6309	37.865	n.d.	0.30	5.79	n.d	53.6
MT-17a	IR	n.d.	19.6601	15.7181	38.651	n.d.	0.40	0.28	n.d	1.4
MT-25a	Cal	39	18.1980	15.6484	38.362	n.d.	0.08	0.25	370	7.4
MT-25a	Dol	18 (56)	18,1704	15.6335	38,310	0.70898	0.02	0.08	0.29	18.3
MT_25b	Dol	n d	18 1/66	15 6224	38 268	n d	0.12	0.12	0.76	n d
MT 255	ID	n.d.	10.1400	15.0224	20.200	n.d.	14.90	0.12	<0.05	25.4
IVII-25d	IK	n.a.	18,1181	15.0210	38.182	n.a.	14.80	0.49	< 0.05	35.4
MT-26a	Dol	n.d.	18.0466	15.6358	38.243	n.d.	4.42	0.34	2.30	n.d
MT-27a	Cal	94 (44)	17.8757	15.6171	38.004	0.71121	41.06	0.45	< 0.05	15.0
MT-27b	Cal	n.d.	17.8814	15.6230	38.010	n.d.	n.d	n.d	n.d	n.d
MT-27a	IR	n.d.	17.8807	15.6126	37.984	0.73029	250.00	6.65	3.29	71.6
MT-28a	Cal	94 (74)	17 8752	156134	37 997	0 70720	0.47	0.14	0.25	91
MT_28b	Cal	nd	17 8802	15,6247	38.025	n d	2.36	0.53	1.56	nd
MT 20.	UD UD		17.0052	15.0247	27.025	0.720.42	2.50	0.55	1.50	107
IVII-28d	IK	n.a.	17.8706	15.0172	37.985	0.72043	216.00	2.02	2.57	137
Non mineralized	d bost rocks									
		71	10 4001	15 6200	20.420		0.11	0.02	0.01	
MI-5a	Cal	/1	18.4091	15.6390	38.436	n.d.	0.11	0.03	0.01	n.d.
MT-5b	Cal	<1	18.8522	15.6721	38.928	n.d.	0.18	0.05	0.02	n.d.
MT-5c	Cal	73	18.7091	15.6562	38.679	n.d.	0.06	0.04	n.d.	15.0
MT-5d	Cal	61	18.8977	15.6702	38.930	n.d.	0.62	0.45	0.31	30.7
MT-5e	Cal	28 (56)	18,9390	15.6770	38,983	0.70875	0.33	0.15	0.25	47.0
MT_5f	Cal	n d	18 7102	15 6611	38 179	n d	5 74	1.47	8.45	n d
MT 52	Del	44	10.7102	15,0011	28.040	n.d.	0.41	0.26	0.45	20.9
IVII-Ja	DUI	44	10.0331	15.0740	30.949	11.u.	0.41	0.50	0.29	30.8
IVII-5D	DOI	16	18.8421	15.6686	38.899	n.a.	0.16	0.030	n.a.	13.9
MT-5c	Dol	<1	18.8945	15.6743	38.943	n.d.	0.34	0.05	0.11	29.4
MT-5d	Dol	33	18.9578	15.6792	39.015	n.d.	1.330	0.22	0.49	7.1
MT-5e	Dol	40	18.9458	15.6664	38.977	n.d.	5.10	0.09	n.d.	9.6
MT-5f	Dol		18.9382	15.6713	38,981	n.d.	2.55	0.05	n.d.	n.d.
MT_5g	Dol	40	18 5237	15 6471	38 542	n d	10.64	0.25	0.54	4.0
MT 55	Dol	nd	19,7200	15.0471	20.104	n.d.	4 92	1 50	1 57	-1.0 n.d
IVIT-JII	DOI	11.u.	10.7290	15.0571	20.022	n.u.	4.02	1.50	1.57	11.u.
IVII-Dd		< I 	10.0341	10.000	200.002	0./10/1	19.00	0.58	0.01	52.0
IVII-5D	IK	<1	18.5932	15.6409	38.589	n.d.	20.80	0.50	n.d.	16.0
MT-5c	IR	1.2	18.5227	15.6494	38.541	n.d.	5.90	0.14	0.28	0.4
MT-6a	Cal	99 (58)	17.9457	15.6136	38.278	0.70833	1.21	0.06	0.82	44.0
MT-6b	Cal	99	17.9400	15.6110	38.265	n.d.	4.52	0.20	2.45	n.d
MT-6c	Cal	n.d.	18.2687	15.6296	38.531	n.d.	n.d	n.d	n.d	n.d
MT-6a	IR	27	18 0850	15 4978	38 217	0 76220	16.00	1 17	2 98	46.2
MT_185	Cal	n d	18 3062	15 6296	38 155	n d	5 10	1.07	1 40	n d
MT 10L	Cal	00	10,0000	15.0200	27.007	n.u.	0.02	1.07	1.40	11.U
IVII-18D	Cdi	00	10.0097	13.0015	21.991	11.CL.	0.92	3.21	11.u	80
MI-18a	IK	n.d.	19.5597	15./291	38,682	n.d.	3.28	2.32	n.d	1.2
MT-19a	Cal	77	18.6066	15.6525	38.627	n.d.	0.12	0.04	n.d	15.0
MT-19a	Dol	6	18.9770	15.6836	39.028	n.d.	6.23	0.21	n.d	5.9
MT-19b	Dol	10	19.1278	15.7025	39.170	n.d.	2.56	0.15	490	0.5
MT-19a	IR	n.d.	19.0242	15.6877	39.067	n.d.	10.50	0.24	n.d	0.6
MT_10	W/P	6	10,0500	15 6890	30.077	n d	10.50	0.20	nd	0.5
MT 20-	Dol	u nd	10,0000	15,0000	33.077	n.u.	10.00	1.17	11.u 2.7C	U.J
IVII-20d		n.u.	10.0312	13.0618	20.202	11.CL.	5.35	1.17	2.70	11.d
MI-20b	DOI	6	18,3413	15.6425	38,333	n.d.	1.45	0.78	n.d	2.9
MT-20a	IR	n.d.	18.6213	15.6675	38.344	n.d.	1.85	0.83	n.d	0.5
MT-21a	Dol	n.d.	18.2442	15.6418	38.422	n.d.	1.21	0.310	13.75	n.d
MT-21b	Dol	7	18.0265	15.6020	38.051	n.d.	1.05	0.28	n.d	2.1
MT-21a	IR	n.d.	18,1284	15.6247	38.209	n.d.	3.43	0.52	n.d	0.5
Sinaf 1b	Cal	n d	18 1258	15 6244	38 128	n d	0.72	n d	n d	n d
Sinaf 1b	Dol	n.u.	10.1230	15.0244	20 116	n d	0.72	n.u.	n.u.	d
Silidi ID	DUI	n.u.	10.0091	15.02/4	011.00	n.u.	0.18	n.d.	n.d.	11.U.
Sinaf I b	IK	n.a.	18.0888	15.6296	38.067	n.d.	0.76	n.a.	n.a.	n.d.

Table 2 (continued)

Sub-sample	Dom. phase	%Cal. (*%)	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	⁸⁷ Sr/ ⁸⁶ Sr	Pb μg/g	U μg/gr	Th μg/gr	Sr µg/gr
SST 7 SST 7 SST 7	Cal Dol IR	n.d.	17.8666 17.8713 17.9934	15.6112 15.6124 15.6153	37.962 37.968 37.935	n.d. n.d. n.d.	0.68 0.68 0.87	n.d. n.d. n.d.	n.d. n.d. n.d.	n.d. n.d. n.d.
Whole rocks CMSS1 CMSS2 HA-1 HA-3 TIC-1 TIC-2 CMD1 CMD2	WR(1) WR(2) WR(3) WR(4) WR(4) WR(5) WR(5)		18.0070 18.0220 20.0550 19.2074 18.5453 18.5046 n.d. n.d.	15.6262 15.6288 15.7254 15.6359 15.6523 15.6412 n.d. n.d.	38.054 38.068 38.508 38.641 38.339 38.313 n.d. n.d.	0.70992 0.70983 n.d. n.d. 0.78827 0.76440 0.70717 0.70757	n.d. n.d. 30.84 31.98 n.d. n.d. n.d. n.d. n.d.	n.d. n.d. 9.56 5.23 n.d. n.d. n.d. n.d.	n.d. n.d. 16.59 32.25 n.d. n.d. n.d. n.d.	n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d.

Note: concentrations are - μ g extracted from 1 g of sample but for the IR where the initial weight was not determined. Dom. = dominant phase; cal. = calcite, dol. = dolomite, IR = insoluble residue, *a, b, c, etc. = sub samples, %Calc. = the calculated percent of calcite in the solutions; and (*%) = percent Ca released from the rock. (1) - sand, (2) - Alkali granite, (3) -Shelomo Granite (4) - Quartz-porphyry dike (5) - dolomite. For ²⁰⁸Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb ratios, only significant numbers are shown. 1 σ error for the ⁸⁷Sr/⁸⁶Sr ratio is <0.00003, Errors on the Pb, U and Th concentrations are <5% and <10% above and below 0.5 μ g/g, respectively. n.d. = not determined.

view, all Mn ores (nodules and others) formed solely as a result of Mn enrichment due to extensive dissolution of epigenetic Mn-dolomite.

2.2. Cu mineralization

Despite being hosted by the same formations, the Cu and Mn mineralization exposures in the Timna Valley occur separately. This is attributed to different environmental conditions of formation (pH and redox; Bar-Matthews, 1987; Shlomovitch et al., 1999). Secondary Cu sulfides and malachite occur in both quartz porphyry bodies in the TIC, and in the Early Cretaceous sandstones, and are clearly associated with post-Cambrian impregnating solutions. Copper-mineralization occurs in the dolomitic facies of the Timna Formation as copper sulfide minerals of the chalcocite group. The δ^{34} S and δ^{65} Cu values of these sulfides are consistent with their formation during marine sulfate reduction (Shlomovitch et al., 1999; Asael et al., 2007). The δ^{65} Cu values of oxidized Cu minerals (mainly malachite and paratacamite) in the Cambrian dolomites show a significant positive isotopic fractionation (~1 to 3‰) relative to the copper sulfides, consistent with oxidation reaction (Asael et al., 2007, 2009). In most occurrences, the Cu-sulfide was partially or completely oxidized to Cu-silicate (chrysocolla), Cu-chloride (paratacamite) and Cu-carbonates (malachite). Segev and Sass (1989) argued that the Cu mineralization in the sandy lithofacies formed as a result of selective karstification of the dolomite.

Field features, petrographic and chemical composition of both Mn and Cu mineralization thus indicate several generations of ore mineralization. However, as noted above, the exact timing and genetic relationships between the various stages are still under debate.

3. Methods

3.1. Sampling

The Cambrian sequence and the igneous complex were sampled at key locations in the Timna Valley, at Netafim Pass 20 km south west of Timna Valley, from the Sinaf borehole (Fig. 1), and from Feinan, Jordan. Sample locations, type of host rock and the studied mineral phases are presented in Table 1. The samples represent: (1) Timna Igneous Complex (TIC); (2) Cu and Mn-bearing rocks of the Timna Formation (i.e., dolomites, sandy dolomites, shales and sandstones); (3) Non-mineralized Timna Formation dolomites from the geological section of Netafim Pass, from the Sinaf borehole (Fig. 1), and from Feinan, Jordan; (4) Mn nodules (types A and B) from type localities described in Bar-Matthews (1987). In addition, Mn ores were taken from the Mn Hill south of the Timna Complex (Fig. 1c); (5) Cu minerals separated from different host rocks sampled at type localities described in Segev (1986), Bar-Matthews (1987), Shlomovitch et al. (1999) and Asael et al. (2007, 2009). Details of all sample sites are given in Table 1 and Fig. 1c.

3.2. Selective dissolution of Timna Formation carbonate rocks

Two different selective dissolution methods were applied to carbonate rock powders with the main aim of extracting mono-mineralic solutions of either calcite or dolomite. The residual material from both these extraction methods is the third component (i.e., insoluble residue, IR). which is dominantly composed of detrital alumino-silicate minerals. Each of the two methods involves a two-step sequential dissolution process, where only one type of chemical reagent is used, but for different time periods and acid strengths. Prior to the sequential dissolution, the relative amounts of calcite and dolomite (the main mineral phases) were determined in each rock by X-ray Diffraction (XRD) and chemical analyses. The methods and the scheme describing their use are given in the Supplementary data. In the first method, 0.5 M acetic acid (CH₃COOH) was added to rock powder to extract first calcite and then dolomite. In the second procedure (applied to two samples only), 1N and then 3N HNO3 were added to sequentially dissolve calcite and dolomite, respectively. In both methods, following dissolution and separation of the carbonate phases, the residue was then completely dissolved using 1:5 HF and concentrated HNO3 at 150-200 °C (IR). Concentrations of Ca and Mg along with, Al, K and Mn (not shown) were determined at each stage and the dissolved amounts of calcite, dolomite, and Al-silicates were calculated as a check of the selectiveness of the dissolution. Overall, three types of solutions were produced; calcite, dolomite and IR.

3.3. Selective dissolution of Mn and Cu ores

Selective dissolution was also applied to Mn nodules. Hand-picked Mn nodules were sliced and visible laminas were sampled using a 1 mm diamond drill. An aliquot of approximately 100 mg of sample was dissolved with a mixture of 10 ml dilute (1:5) HNO₃ and 0.5 ml of 30% H_2O_2 at ~80 °C. This allowed the dissolution of the Mn phases while not dissolving the detritus (i.e. IR). The major element contents of the solutions confirmed the selective dissolution of Mn phases.

Copper phases were separated from their host rock either by hand picking or by drilling using the 1 mm diameter diamond drill to yield ca. 50–200 mg of sample. Cu-sulfide samples were dissolved with 1:1 mixture of concentrated HCl and HNO₃, while Cu-carbonate samples were dissolved in 10 ml of 0.1N HNO₃. Finally Cu-silicate samples

were digested in a mixture 1:1 of 40% hydrofluoric acid mixed with 7N HNO₃.

3.4. Mineralogy, elemental and isotopic composition

The mineralogical composition of the rocks along with the Cu and Mn mineral phase identification was performed using XRD of powder samples and scanning electron microscope (SEM) Jeol JSM-840 equipped with EDS (Link 10000 detector). Element concentrations were determined by Optima-3300 ICP-Atomic-Emission-Spectrometer and Optima 6000, Perkin-Elmer ICP-MS. The concentrations of K and Na were measured with a Perkin Elmer 5100-PC atomic absorption spectrometer. The relative standard error was <5% for these elements.

The elemental concentration and the Pb isotopic composition in host rocks and mineralized phases were measured in the solutions produced by all selective dissolution methods described above, and in Mn nodules and Cu ores. Strontium isotopic composition was measured in Mn nodules, Cu ores, and the carbonate fraction of bulk rocks; the latter by using 0.5 M acetic acid as a reagent. Strontium was analyzed in representative sub samples from the first (i.e., calcite) acetic acid extraction and in their final IR digestion (remnants of undissolved dolomite and Al-silicates). The isotopic compositions of Pb and Sr were measured using a Nu Plasma MC-ICP-MS instrument. Mass discriminations were corrected using repeated measurements of the SRM-981 and SRM-987 standard. The long-term precision of isotopic ratio determination (2σ , relative standard error) was ~0.02‰ for both 206 Pb/ 204 Pb and 207 Pb/ 204 Pb ratios, 0.05‰ for the 208 Pb/ 204 Pb, and 0.08‰ for 87 Sr/ 86 Sr ratios.

4. Results

4.1. Carbonate rock and Mn nodule mineral phases

4.1.1. Carbonate rocks

Both selective dissolution methods applied in this study were aimed at discriminating between carbonate mineral phases. However, the elemental concentrations of the extracts indicate that each extract, although dominated by one mineral (ca. 70–90%, Table 2), in fact dissolved more than one phase. For simplicity, we named each extract according to the dominant phase (i.e., calcite, dolomite and IR, Table 2).

The reproducibility of the procedure was examined and the relative standard deviation (RSD) of the amounts of calcite and dolomite released was calculated, and found to be <2% and <7% RSD respectively. No correlation is observed between the whole rock elemental composition and the effectiveness of the methods used. The reproducibility of IR in the rock is within 20%, most probably due to the low content of Al-Si in the carbonate rock (1-10%; Supplementary Table S1). The failure of these methods to produce complete mono-mineralic extracts, in particular the 0.5 M acetic acid method, which are known to be effective in other cases (e.g., Tessier et al., 1979; Han and Banin, 1995), may be a result of the complex history of the samples experienced multiple growth events. These events may have led to various crystal sizes and/or to slight changes in their chemical composition, which in turn could have affected their dissolution properties. Hence the isotopic composition of the solutions should point to the dominant mineral extract, rather than a specific mineral value.

4.1.2. Mn nodules

The field appearance of the two types of Mn nodules of the Cambrian Timna Formation is shown in Fig. 2a and b. SEM imaging (Fig. 2c) shows that the Mn nodules contain significant amounts of detrital minerals, mainly quartz and feldspars. The selectiveness of the dissolution method with respect to these minerals was confirmed by the low concentrations of Si, Al and other elements in the Mn nodules mineral extracts (not shown here). The chemical compositions of the Mn nodules (Table 3; solution extracts) accord with those given by Bar-Matthews (1987), whereby Type A nodules are enriched in U, and Type B nodules



Fig. 2. Field and petrographic observations of Type A and B manganese nodules. (a) Folded stratiform-laminated sediments around Type A nodules at the upper part of the Timna Fm. (b) The diffuse boundaries of the Type B nodules. (c) Back-scattered SEM image of the two manganese nodules. Type A consists of bright hollandite (Holl.) laminae and gray pyrolusite (Py.) and darker quartz (Qz) grains randomly distributed. The massive Type B nodule consists of mainly of coronadite (Corr.) and the absence of quartz grains. Note the coronadite needles between the two types of nodules.

are enriched in Pb and relatively depleted in U (Supplementary; Table S2). Moreover, Type A nodules are composed of few tens of microns wide laminae of alternating hollandite and pyrolusite (Fig. 2c). The contact between the two phases is sharp and shows no evidence of replacement texture, hence suggesting direct precipitation of both minerals from solution. On the other hand, Type B Mn nodules exhibit diffuse boundaries between the two phases; coronadite and hollandite (Fig. 2c). Although in places Type B has concentric structure like Type A nodules, they generally show a massive structure (Fig. 2c). The textural relationship between the two types indicates alteration of Mn nodule Type A to Type B.

4.2. Isotopic composition

4.2.1. Timna Igneous Complex (TIC)

The bulk Pb and Sr isotopic composition of granites and a quartz porphyry dike from the TIC is presented in Table 2.

4.2.2. Carbonate and bulk rock extracts

The Pb isotopic compositions of the mineralized and non-mineralized calcite and dolomite solution fractions, insoluble residues and bulk rock samples are shown in Fig. 3a on a plot of 208 Pb/ 204 Pb vs. 206 Pb/ 204 Pb ratios. The Pb isotopic composition varies among the solutions produced by the selective extraction methods. Overall, two different trend-lines can be discerned, apparently converging to low isotopic ratios (<38 and <18, respectively). Solutions extracted from non-mineralized rocks define the upper part of trend-line I, while solutions from rocks subjected to Cu- Mn- mineralization define trend-line II. The IR of all rocks shows wide distribution of values across the whole data field.

The ⁸⁷Sr/⁸⁶Sr ratios in the carbonate extracts correlate well with both the 1/Sr ratio and with the calculated percentage of calcite extracted (Fig. 3b; $R^2 = 0.807$ and 0.693, respectively) regardless of the amount of calcite dissolved (30 to 90%). Besides Ca, no correlation was found between ⁸⁷Sr/⁸⁶Sr ratio and any of the major element concentrations (not shown here).

4.2.3. Mn nodules

Chemical composition and SEM imaging of the detritus (IR, not shown) indicate the present of quartz, K-feldspar, barite, illite and/or mica. The two types of Mn nodules differ in their Pb and Sr isotopic composition. On a plot of 208 Pb/ 204 Pb vs. 206 Pb/ 204 Pb (Fig. 4a), the Mn nodules define two orthogonal trends in which Type A nodules have a relatively constant 208 Pb/ 204 Pb ratio and vary significantly in their 206 Pb/ 204 Pb ratios, whereas Type B nodules show significant variation in the 208 Pb/ 204 Pb ratios and little variation in 206 Pb/ 204 Pb ratios. These trends match those found by Ehrlich et al. (2004). Pb isotopic values converge at ca. 206 Pb/ 204 Pb = 18.0 (Type B nodules) and 208 Pb/ 204 Pb = 38.0 (Type A nodules). Additionally, there is a good correlation between 207 / 204 Pb and 206 / 204 Pb ratios (Fig. 4b), with the exception of sample MT-8, which plots below the correlation line. The 208 Pb/ 204 Pb variations among the Mn nodules do not show any correlation with their host rock type (sandy-shale and shale lithofacies).

 87 Sr/ 86 Sr ratios plotted against 206 Pb/ 204 Pb ratios (Fig. 4c) clearly reveal the significant differences in the 87 Sr/ 86 Sr ratios of the two types of Mn nodules. Type A nodules have a relatively constant 87 Sr/ 86 Sr value of 0.7093 \pm 0.005 (note also the relatively constant 208 Pb/ 206 Pb ratios for these samples), whereas Type B nodules range significantly, from 0.709 to 0.716 at low 206 Pb/ 204 Pb ratios (~17.8).

4.2.4. Copper phases

The Pb isotopic compositions of Cu phases separated from the Timna Formation rocks and from the TIC are presented in Table 4 and plotted in Fig. 5. The three main Cu phases; sulfides (mainly covellite), paratacamite, and malachite, mostly fall along the same trend lines found for the carbonate and bulk rock samples (trends I and II, Fig. 3a). In addition, samples from the same locations plot close to each other regardless of their mineralogy. A number of samples from one site (Mt. Michrot; Fig. 1) show deviations to higher ²⁰⁶Pb/²⁰⁴Pb ratios.

5. Discussion

5.1. Pb-U age corrections

The Pb data represent various rocks, soluble extracts, insoluble residua (i.e. detritus) and Mn and Cu ores. Thus it is reasonable to question whether or not the initial Pb isotopes ratios or the initial Pb/U ratio may have changed during and since sediment deposition and through mineral formation. An attempt was made to calculate the μ values and initial ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁷Pb/²⁰⁴Pb ratios for rock extractions, IR, and Mn nodules (Supplementary, Table S2). It was found that samples with current Pb/U ratio lower than 2.7 yield unacceptable low initial ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁷Pb/²⁰⁴Pb ratios and even negative (erroneous) values, regardless of the age assigned which could hint to such case.

5.1.1. Carbonate extracts and IR

A number of problems arise when addressing the age correction for the carbonate extracts and IR of the Timna host rocks and for the Mn nodules: mainly what age should be assigned; the sediment emplacement age or the source rock age? In addition, any solution that undergoes fluid-rock interaction would incorporate elements from the rock according to the solution chemical properties (e.g. Eh, pH, Cl content) and generally will not have the same U/Th and U/Pb ratios as the rock. Later, these ratios would change as a result of diagenetic and epigenetic processes and indeed, the Pb/U ratios vary significantly between 0.1 and 148 (Supplementary, Table S2) for the rock extracts and IR. As for the age assignment, one possibility is to choose the insoluble residue apparent age as the assigned age for initial Pb isotope calculations since it represents the detrital component of these rocks. However, the apparent ²⁰⁶Pb-²⁰⁷Pb age calculated for the insoluble residue of the rocks for samples where the Pb/U ratio is \geq 2.7 is 627 \pm 470 Ma. This age carries an unacceptable error (10 points, MSWD = 4200!). A better age constraint is given by the igneous rocks of the Timna Intrusive Complex whose major events are dated at 610-620 Ma (Beyth, 1987; Beyth et al., 1994; Beyth and Reischmann, 1997; Morag et al., 2012). Consequently an age of 620 Ma is assigned for the host rock and IR age correction calculations (Supplementary, Table S2). In addition, the alternative option, the sediment emplacement age, i.e. the Middle Cambrian (ca. 520 Ma) was also calculated for comparison. Calculations reveal that the difference between these two options is insignificant with the same samples yielding unacceptable low and erroneous initial ratios.

All calculated μ values greater than ca. 28 correspond to Pb/U \leq 2.7 (Supplementary, Table S2). These values are significantly above the expected value for the isotopic evolution of Pb (9.735, Stacey and Kramers, 1975). In addition, there is no evidence for systematic difference between the calculated μ values for the IR and carbonate phases. The calculated initial Pb ratios form a linear array; away from the calculated value for 620 and 520 Ma (Fig. 6a, after Stacey and Kramers, 1975). This indicates that the measured Pb and U content for all samples cannot explain the shift from expected initial Pb ratios or that the assigned age must be older. This may be explained by disturbance of the U-Pb system or by the sample handling where the sequential extraction preferentially extracted U over Pb, resulting in low Pb/U ratio. Similar interpretation was given by Ho et al. (1994) in regard to initial Pb isotopic composition of pyrite.

5.1.2. Mn nodules

The age of 620 Ma was also used to calculate the initial ²⁰⁶Pb/²⁰⁴Pb and ^{207P}b/²⁰⁴Pb ratios for the Mn nodules (Supplementary, Table S2). All Mn nodules with the exception of two samples (MT-23 and 23), gave an acceptable initial ratios though lower than expected. However, μ values are mostly below 9.7 (Supplementary, Table S2), which also suggests that they do not represent reservoir values. Indeed, Ehrlich et al. (2004) calculated a ²⁰⁷Pb-²⁰⁶Pb apparent age for manganese nodules which approaches that of the Cambrian rock (470 ± 160 Ma; MSWD = 22). However, on conventional concordia diagram, Type A nodules form a chord which suggests Pb loss. Although it may indicate that the U-Pb system of Type A nodules is disturbed, this result has no bearing on the Pb isotopic composition since there is no fractionation during Pb loss. The Mn nodules differ on a plot of initial ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁷Pb/²⁰⁴Pb ratios where Type A forms a linear array while Type B forms a tighter group with a constant ²⁰⁷Pb/²⁰⁴Pb ratio (Fig. 6b). Nonetheless, both types fall away from the potential initial Pb isotopic compositions values for 620 and 520 Ma.

To summarize, the U-Pb in the rock extracts and IR indicate a disturbed system either because of the geological history or because of the extraction procedure. However, because each extract is dominated by one phase (i.e. calcite, dolomite and IR) it can be concluded that the Pb isotope ratio represents the major phase. Similarly, the calculated Table 3

Element concentrations and Pb and Sr isotopic composition of Mn nodules, Timna Valley.

Sample	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	⁸⁷ Sr/ ⁸⁶ Sr	MnO ₂ %	Min. phase	Туре	Sr µg/gr	Pb μg/gr	U µg/gr	Th μg/gr
MT 7 (1)	17 00/9	15 6220	28 020	0.71096	22.5	Holl	D	242.2	5691	21.1	5.2
$MT_7(1)$	17.9048	15.6256	38.029	0.71080	23.3	Holl	B	157.2	469	5.0	1.9
$MT_7 (2)a$ $MT_7 (2)b$	17,9200	15 6241	38.045	0.70875	25.7	Holl	B	272.6	3186	62	2.0
MT-7 (2)c	17 9355	15 6254	38.043	0 70848	26.7	Holl	B	460.1	249	3.9	2.8
MT-8 (1)a	17.8661	15.6046	37.956	0.72711	n.d.	Holl Corr.	B	n.d.	85.024	61.1	2.3
MT-8 (1)b	17.8679	15.6079	37.966	0.71997	n.d.	Holl Corr.	B	n.d.	72,720	41.9	2.6
*MT-8 (2)a	17.8764	15.6202	38.008	0.70905	66.9	Holl Py?	А	1150	22,655	31.6	n.d.
*MT-8 (2)b	17.8762	15.6202	38.007	0.70926	44.2	Holl Corr.	В	1696	89,899	58.0	n.d.
*MT-8 (2)d	17.8766	15.6199	38.008	0.70931	45.8	Holl Corr.	A + B	1749	88,690	58.8	n.d.
MT-8 (2`)a	17.8682	15.6063	37.963	0.72575	n.d.	Holl Corr.	В	n.d.	73,257	40.9	2.6
MT-8 (2`)b	17.8675	15.6080	37.970	0.72629	n.d.	n.d.	В	n.d.	n.d.	n.d.	n.d.
MT-8 (3)a	17.8678	15.6082	37.966	0.71929	n.d.	n.d.	В	n.d.	44,480	41.7	2.3
MT-8 (3)b	17.8706	15.6146	37.973	0.72457	n.d.	n.d.	В	n.d	55,807	38.4	1.9
MT-8 (4)a	17.8757	15.6193	38.005	0.70941	41.0	Holl Corr.	В	2245	70,873	43.9	n.d.
MT-9 (1)a	17.9266	15.6204	38.003	0.71189	23.8	Holl.	В	208.8	6562	35.9	0.9
MT-9 (2)a	17.9598	15.6216	37.999	0.70966	37.7	Holl.	A + B	564.5	22,050	702.2	1.4
MT-9 (2)a	17.9222	15.6191	37.997	0.71058	42.7	Holl.	A + B	269.5	23,222	159.0	3.6
MI-I0 (1)a	18.0024	15.6276	38.017	0.70997	45.6	Holl.	A	146.5	14,160	188.5	3.5
MI-IU(I)D	17.9439	15.6244	38.015	0.70973	38.0	H0II.	A	143.7	9020	100.2	1.2
MT 10 (1)C	17.9405	15.0248	38.015	0.70967	49.1	HOII.	A	392.7 61.90	12,454	108.3	1.4
MT = 10 (2)a	17.9921	15.0274	28.010	0.70904	27.4		A	204.5	10.024	08.2	1.5
*MT_10(2)b	17.9525	15.6258	38.010	0.71085	67.6	Holl - Py		1189	30.965	30.2 134.0	1.9 n.d
MT-10(2)c	17.9397	15 6231	38.012	0.70000	333	Holl	B2	105.1	8536	57.1	11
MT-10 (2)d	17 9748	15.6261	38.015	0 70928	68.2	Holl - Pv	A.	208.4	7924	138.1	3.6
*MT-10 (2)d	17.9794	15.6260	38.018	0.70865	70.8	Holl Pv.	A	846.1	8065	133.6	n.d.
MT-10 (2)e	17.9736	15.6262	38.017	0.71181	46.9	Holl.	A	161.2	4666	106.4	3.3
*MT-10 (2)e	17.9757	15.6246	38.014	0.70891	72.0	Holl Py.	А	835.6	8622	151.1	n.d.
MT-10 (2)f	17.9547	15.6243	38.013	0.70939	46.3	Holl.	А	153.5	8121	115.0	2.4
MT-10 (2)g	17.9498	15.6255	38.013	0.70942	38.3	Holl.	А	120.9	6622	86.7	1.5
MT-10 (2)h	17.9599	15.6243	38.012	0.70940	35.6	Holl.	A?	91.11	4089	72.7	1.8
*MT-10 (2)h	17.9516	15.6281	38.022	0.71022	65.7	Holl Py.	A	493.9	13,496	122.2	n.d.
MT-10 (2)i	17.9518	15.6227	38.013	0.71012	40.9	Holl.	A?	214	8495	132.0	2.0
*MT-10 (4)	17.9750	15.6257	38.017	0.70933	70.5	Holl Py.	A	1250	10,320	164.7	n.d.
MT-10 (3)a	17.9517	15.6234	38.009	0.71020	40.7	Holl.	A	382.7	17,371	130.2	1.5
MI-I0 (3)b	17.9510	15.6238	38.013	0.71008	35.0	Holl.	B	259.9	10,369	75.0 76.4	0.9
MT 10 (2)d	17.9360	15.0234	38.010	0.70951	42.0	HOII.	A + B	235.9	12,502	158.0	0.7
$MT_{-10}(3)a$	17.9785	15.6270	38,010	0.70892	24.0 70.0	Holl	Δ	144.0	6847	136.0	2.0
MT-10 (3)f	17,9616	15.6234	38.020	0.70833	513	Holl	A	461.6	9692	0.0	< 0.001
MT-13 (1)	17.9092	15.6212	38.033	0.71090	8.2	n.d.	B?	248	4125	0.0	< 0.001
MT-13 (2)	17.9146	15.6233	38.041	0.70970	6.5	n.d.	B?	153.1	3149	0.0	< 0.001
MT-13 (3)	17.9174	15.6241	38.042	0.70996	6.4	n.d.	B?	147.3	2775	0.0	< 0.001
MT14 (1)a	17.8899	15.6167	37.996	0.71556	4.8	n.d.	B?	27.89	3203	0.0	< 0.001
MT14 (1)b	17.8893	15.6179	38.001	0.71463	4.6	n.d.	B?	41.63	3240	0.0	< 0.001
MT14 (2)a	17.8915	15.6236	38.011	0.71419	51.8	Holl.	В	21.1	3323	577.3	< 0.001
MT14 (2)a`	17.8874	15.6170	37.998	n.d	58.6	Holl.	В	24.4	4276	648.6	< 0.001
MT14 (2)b	17.8724	15.6140	37.983	0.70925	30.1	Holl Py.	A	320.8	38,472	1095	< 0.001
MT14 (3)a	17.8768	15.6157	37.989	0.70927	32.0	Holl.	A	550.3	36,115	0.0	< 0.001
MT14 (3)a	17.8766	15.6158	37.991	0.70959	21.8	Holl.	A	258.4	29,477	0.0	< 0.001
MT 15 (0)a	19.0773	15.6821	38.001	0.70959	50.5	Holl Py. Cryp.	A	186.1	2136	0.0	< 0.001
MT 15 (0)c	20.3041	15,7454	30.003	0.70892	07.0 70.7	гу. Ру	Λ Δ ⊥ Ρ2	207.3	6816	<0.001 <0.001	<0.001 <0.001
MT 15 (0)C	10.7440	15.6836	38.001	0.70868	/9.7	ry. Holl	$A + B^2$	200.0	21/2	<0.001 ####	1.5
MT 15 (1)a MT 15 (1)a	19,7728	15 7232	38.013	0.70861	71.0	Pv	A A	200.5	3271	nd	n d
MT 15 (1)b	20 1488	15 7436	38.017	0 70852	77.8	Pv	A	203.1	1685	n d	n d
MT 15 (1)c	19.2085	15.6890	38.002	0.70947	60.8	Holl Pv.	A	230.7	2547	n.d.	n.d.
MT 15 (2)a	19.2038	15.6937	38.012	0.70862	77.5	Py.	А	271.8	4304	n.d.	n.d.
MT 15 (2)b	20.1096	15.7398	38.013	0.70880	75.3	Py.	А	257.4	2824	n.d.	n.d.
MT 15 (2)c	19.5084	15.7066	38.007	0.70867	85.2	Py.	А	238.6	4440	n.d.	n.d.
MT 15 (2)c	18.9640	15.6855	38.002	0.70834	87.3	Py Corr.	А	269.1	4247	n.d.	n.d.
MT 15 (2)c	18.9640	15.6846	38.018	0.70837	87.3	Py.	А	269.1	4247	n.d.	n.d.
MT 15 (2)d	20.6503	15.7621	38.006	0.70878	69.1	Py.	A	186.6	2034	n.d.	n.d.
MT 15 (2)e	18.9568	15.6812	38.013	0.70860	90.3	Py.	A	243	6940	n.d.	n.d.
MT 15 (2)f	18.1349	15.6322	37.997	0.70984	90.1	Py.	A	422.6	14,837	n.d.	n.d.
MT 15 (2)g	19.0991	15.6885	38.015	0.70856	22.7	Py.	A	70.52	1405	n.d.	n.d.
MT 15 (2)h	19.5431	15./121	38.015	0.70863	/1.6	Py.	A	191.1	1242	n.d.	n.d.
IVII 15 (3)a MT 15 (2)b	18.3922	15.0510	38.014 28.022	0.70993	70.3 74.2	Holl Dy and Cryp.	A	180.4	2864	11.0. n.d	11.0. n.d
MT 15 (3)D	10.4010	15.0595	38.025	0.70090	74.5 82.5	Pv	A	100.1 238 D	2608	1.d. 1 <i>4</i> 77	u. ∠0.001
MT 15 (3)a	18 1305	15.7217	38.007	0.70905	90.7	iy. Pv	A	230.9 262 1	4820	840	< 0.001
MT 15 (3)c	17.9170	15.6217	38.008	0.71559	61.3	Pv.	A	77	10.270	n.d.	n.d.
MT 15 (3)c	18.6311	15.6641	38.014	0.70861	89.3	Py.	A	221.4	2059	n.d.	n.d.
MT 15 (3)a	19.0413	15.6817	38.000	0.70885	89.9	Py.	А	227.8	5578	####	21.2

Table 3 (continued)

Sample	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	⁸⁷ Sr/ ⁸⁶ Sr	MnO ₂ %	Min. phase	Туре	Sr ug/gr	Pb ug/gr	U ug/gr	Th ug/gr
					,,,			P8/8*	ro/ 81	P8/81	P8/8*
MT 15 (3)b	18.8133	15.6742	38.011	0.70871	91.9	Py.	А	276.6	4711	788.2	11.4
MT 15 (3)c	18.6688	15.6799	38.046	0.70923	76.3	Holl Py.	А	237.2	4415	####	1.9
MT 15 (4)a	17.9147	15.6184	38.008	0.71551	10.1	n.d.	В	34.89	10,508	n.d.	n.d.
MT 15 (4)b	18.2635	15.6443	37.996	0.71343	17.9	Holl.?	В	44.34	7231	n.d.	n.d.
MT 15 (5)a	18.1703	15.6348	37.991	n.d.	23.4	Holl.	В	58.8	10,810	262.0	< 0.001
MT 15 (5)b	18.1703	15.6348	37.991	0.71180	33.2	Holl.	В	245.7	14,640	225.2	< 0.001
MT 15 (5)c	18.0070	15.6237	37.999	0.71144	33.2	Holl.	В	n.d.	n.d.	n.d.	n.d.
MT 22 (1)	17.8979	15.6218	38.004	0.70824	0.1	Mn ore		17.7	90	614.8	0
MT 23 (1)	18.5193	15.6732	38.168	0.71212	29.5	Mn ore		447	12.195	n.d.	n.d.
MT 23 (2)	18.2900	15,7268	38.362	0.70849	1.5	Mn ore		66.11	1594	n.d.	n.d.
MT 23 (3)	18.3383	15.6328	38.051	n.d.	4.2	Mn ore		115.8	74	707.6	6.7

Labelling is as follow: MT-7(1)a = 7 is the sample location, in bracket is the nodule number, a etc. are spots within the nodule. *MT = bulk nodule, MT-13, 22 and 23 are highly enriched Mn sandstones. Errors (1 σ) are: <0.0003 for $^{207}Pb/^{204}Pb$, $^{206}Pb/^{204}Pb$ ratios, <0.005 for the $^{208}Pb/^{204}Pb$ ratio and <0.00003 for the $^{87}Sr/^{86}Sr$ ratio. All Mn was calculated as $%MnO_2$. Mineral phases are as follows: Py. = pyrolusite, Holl. = hollandite, Corr. = coronadite and Crypt. = cryptomelane. Type = Type A or B nodules. BM and SE samples are from Ehrlich et al. (2004). N.d. = not determined.

initial values for the Mn nodules do not form a tight group expected for a single source, but a linear array.

5.2. The isotopic composition of Pb and Sr as tracers of the formation of the different mineralogical phases

As presented in Chapter 2, previous studies (Segev, 1986; Bar-Matthews, 1987; Segev and Sass, 1989; Bar-Matthews and Matthews, 1990; Shlomovitch et al., 1999) have shown that the Cambrian sequence of the Timna Valley underwent a complex diagenetic and epigenetic history, which included dolomitization, dissolution, de-dolomitization and -Cu- Mn- mineralization. The different studies agree that epigenetic Cu- Mn- mineralization occurred, but disagree on the primary processes leading to this mineralization. An indication toward these processes is given by the distinct difference between rock samples not subjected to Cu- Mn- mineralization, and those subjected, as reflected by their Pb isotopic composition, (Fig. 3a). The data plotted on the ²⁰⁸Pb/²⁰⁴Pb vs. ²⁰⁶Pb/²⁰⁴Pb diagram suggest in general, two mixing lines with three end- members. Trend line I consists in its upper part of non-mineralized samples and in its lower part of calcite of mineralized samples, and trend line II consists of mineralized samples. The common low ratio end-member $({}^{208}Pb/{}^{204}Pb = 37.63 \text{ and } {}^{206}Pb/{}^{204}Pb =$ 17.50, ${}^{207}\text{Pb}/{}^{204}\text{Pb} = 15.60$) of the two trend-lines is represented by the calcite fractions of the non-mineralized samples, which may point toward the initial Pb isotopic values of the Cambrian Sea or that of the very first solution (Fig. 3a).

Since the high ratio end-member of trend-line I is bulk dolomite (MT-19), which consists of ca. 93.3% dolomite (Supplement, Table S2), it is suggested that this value most closely represents the dolomitizing solution. In turn, the high end-member of trend-line II (mineralized rocks), largely points toward the detrital minerals (IR) such as biotite and possibly heavy minerals with high U/Pb and Th/Pb ratios (e.g., apatite, sphene and epidote), which are expected to yield high ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb ratios. Samples that lie between these two mixing lines may suggest a transition between the two. The IR of mineralized and non-mineralized rocks shows a wide distribution of values across the whole data field. This wide dispersion suggests that the IR Pb isotope ratios reflect the varying mineral assemblage of the detritus, rather than processes that occurred later to deposition. For example, high content of feldspars will result in low Pb isotope ratios because of the initial low Pb/U and Pb/Th ratios incorporated in their lattice (e.g. Harlavan et al., 2009).

Since ²⁰⁸Pb and ²⁰⁶Pb are the decay products in the decay chain of ²³²Th and ²³⁸U respectively, the trend lines shown in Fig. 3a correspond to the Th/Pb and U/Pb ratios of the solutions that interacted with the primary sediment to form the present rock. Thus, the good distinction between the two groups of samples suggests that two different types of

solution were involved, i.e., dolomitizing and mineralizing solutions. The Pb isotopic composition suggests that while the non-mineralized samples largely retain the dolomitizing solution signature, the mineralized samples interacted with a later and different type of solution, one that had isotopic composition close to that of the detritus. Since the detritus originated from the igneous complex, the latter solution is indeed expected to have high Pb isotope ratios, due to relatively high U/Pb and Th/Pb ratios in the TIC rocks and their age. It is notable though, that neither the bulk granite value nor the bulk quartz porphyry dike values from the TIC lie on either of the trend-lines. This observation implies that the solutions are a result of minerals-solution interaction rather than bulk rock-solution interaction (i.e., a consequence of incongruent dissolution; Harlavan et al., 2009). While spatial observations indicate that Cambrian Cu- Mn- mineralization primarily affected the Timna Formation rocks, the dolomitization process was a regional event and affected even remote areas such as the Netafim crossing, the Sinaf borehole and Feinan in Jordan (Fig. 1). Samples from these latter localities lie on the trend-line I (Fig. 3a). Most important is the understanding that the dolomitization and mineralization solutions are different which suggest a different timing most probably as suggested by Segev and Sass (1989). Mn- mineralization post-dated dolomitization.

The⁸⁷Sr/⁸⁶Sr ratios of both the carbonate extract (0.5 M acetic acid) and the bulk IR do not correlate with the concentration of any of the major elements. Hence we suggest that the ⁸⁷Sr/⁸⁶Sr ratios of the extracts are primarily sited within the carbonate phases, with no significant contribution from detrital phases. The ⁸⁷Sr/⁸⁶Sr ratio of the carbonate extracts is positively correlated with 1/Sr (Fig. 3b), indicating a mixing line between two components. Moreover, this ratio is also positively correlated with the percent of Ca released from the rock by acetic acid (44 to 92%, Table 2). Hence, the ⁸⁷Sr/⁸⁶Sr ratio, Sr content and mineral calculations indicate two end members. One is highly enriched with Sr (119 $\mu g/g$ Sr) and has a low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, (0.70707, Table 2) and is the calcite (93% calcite, Table 2). The second end-member has low Sr content (15 μ g/g) and high 87 Sr/ 86 Sr ratio (0.71121, Table 2). Although both end-members are dominated by calcite, the amount of carbonate released by the extraction is significantly different (92 vs. 44%, Table 2, Fig. 3b). A probable source of the solution for this second end member is K-rich Al-silicate minerals, such as mica and alkali-feldspars, as evident by the high K and Fe concentrations in the IR fraction. No correlation was found between the Sr isotopic ratio and the major element concentrations, which may suggest the presence of the varying amounts of detritus in the rocks, whereas only high amounts of detritus contribute Sr with high isotopic ratio.

The 87 Sr/ 86 Sr ratios obtained for two calcite extracts (MT-5e and MT-25a, 0.70875 and 0.70898, respectively; Table 2) are close to the values expected for the Cambrian sea (0.709 \pm 0.001; see later a discussion of this

value in Section 5.4). However, since the calcite in carbonate rocks of the Timna Formation is known to be secondary (Segev and Sass, 1989), these values do not reflect primary calcite which was deposited during the Cambrian, but rather a mixing value of secondary calcite and dolomite.

The IR fraction includes some calcite and dolomite in addition to Alsilicates (i.e. not all calcite and dolomite were removed by the prior acetic acid sequential extraction), but no correlation was found between 87 Sr/ 86 Sr ratios and the relative proportions of calcite and dolomite in the carbonate fraction, nor with total carbonate, suggesting that the 87 Sr/ 86 Sr ratio in IR is predominantly derived from the Al-silicate phase. It is notable that the lowest 87 Sr/ 86 Sr ratio measured in the IR extracts is still higher than the IR values obtained for the acetic acid calcite extract (0.7167 compared with 0.7112). The lack of correlation observed between 87 Sr/ 86 Sr and 1/Sr ratio in the IR fractions (not



Fig. 3. (a) ²⁰⁸Pb/²⁰⁴Pb vs. ²⁰⁶Pb/²⁰⁴Pb ratios in the calcite and dolomite dominated fraction, and in the insoluble residue (IR). Solid symbols are samples which show evidence for Cu or Mn Cu-Mn-mineralization (Min), whereas open symbols represent samples in which no Cu-Mn-mineralization was observed (non-min). Trend lines I, and II, are referred to in the text. (b) A plot of ⁸⁷Sr/⁸⁶Sr ratios vs. 1/Sr (bottom x-axis) and % Ca extracted (upper x-axis).

shown) implies a different Al-silicate mineral assemblage in each of the samples. A strong correlation is found between 87 Sr/ 86 Sr and Al/Sr and K/Sr ratios and between Mn and Sr concentrations (not shown here), consistent with a variable Al mineral assemblage.

In conclusion, the Pb isotopic composition allows the distinction between rocks that were subjected to Cu- Mn- mineralization processes and those that were not affected it. Moreover, it is also clearly shown that different solutions were involved in a regional dolomitization event and the Cu- Mn- mineralization event that affected the Cambrian Timna Formation rocks. The Sr isotopic compositions are primarily controlled by mixing relations between various end members, but mainly between secondary calcite, dolomite, and detrital minerals.

5.3. Pb and Sr isotopic evolution of Mn nodules

The major question regarding the Mn mineralization is the source of Mn in the solutions that deposited the Mn nodules in the sandy-shaly lithofacies. This, in turn, reflects the timing of events; whether or not Mn- mineralization took place in a single or in multiple events? This question is addressed using both Pb and Sr isotopes. Field and mineralogical evidence suggests that Type A nodules were formed at the sediments-water interface while the sediments were still saturated, and under oxidizing conditions (Bar-Matthews, 1987; Fig. 2a this study). Moreover, the presence of intact detritus guartz and feldspars with no signs of dissolution or alteration texture suggests that this type of nodule, originated in the Cambrian Sea. These observations may allow determination of the ocean water Pb and Sr isotopic composition, which can be related to modern Mn nodules. Type B Mn nodules on the other hand, show clear signs of dissolution fronts when found coexisting with Type A nodule material (Bar-Matthews, 1987; Fig. 2c, this study). In addition, its massive form suggests a single event of precipitation. The isotopic composition is discussed in light of the above observations.

5.3.1. Pb isotopes

On a ²⁰⁶Pb/²⁰⁴Pb vs. ²⁰⁷Pb/²⁰⁴Pb plot, the two types of Mn nodules form two distinct groups (Fig. 3a), suggesting their formation from two significantly different solutions. Type A solution is depleted in Th (no significant differences in the ²⁰⁸Pb/²⁰⁴Pb ratio) and enriched in U thus has a constant ²⁰⁸Pb/²⁰⁴Pb ratio. Single source of U is reflected by the correlation of ²⁰⁶Pb/²⁰⁴Pb vs. ²⁰⁷Pb/²⁰⁴Pb. The second solution (Type B solution) has relatively higher Th and lower U concentrations, thus the ²⁰⁸Pb/²⁰⁴Pb ratio varies significantly whereas the ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁷Pb/²⁰⁴Pb ratios remain relatively constant (Fig. 4).

Although, the two types are clearly distinguishable based on the Pb isotopic ratios, a priori it is difficult to determine whether Type B evolved from Type A, or vice versa. Nevertheless, given the strong field, SEM mineralogical and petrographic evidence (Bar-Matthews, 1987, Fig. 2, this study), it is clear that type A Mn nodule preceded that of Type B and hence these isotopic differences reflect this paragenetic transformation. Additionally, since Type A nodules are enriched in U which is more soluble than Pb it is reasonable to deduce that the later process, forming Type B solution would have leached U and precipitated Pb and not vice versa.

The alternative interpretation of Mn nodule formation (Segev et al., 1995) is that post-depositional processes, related to the adjacent Tertiary Dead Sea rifting, resulted in sub-surface dissolution of Mn-dolomite of the Timna Formation, Mn remobilization, and nodule formation. This suggests a single much later epigenetic process. This idea is examined by comparing the Pb isotope data of this study with isotope data of Erel et al. (2006). They studied the source of the brine solutions in the Dead Sea region, which brought about Oligocene to Miocene dolomitization and iron mineralization at Menuha Ridge, 60 km north of Timna Valley. Erel et al. (2006) found that the dolomitizing brine had distinct Pb ratios (207 Pb/ 204 Pb = 16.3 and 206 Pb/ 204 Pb = 31.6) that significantly differed from solutions associated with weathering of igneous

and clastic rocks (15.6 and 18.5, respectively). Moreover, the 208 Pb/ 204 Pb ratios in the dolomites studied by Erel et al. (2006) are remarkably uniform at 38.7 \pm 0.2. Their dolomite trend-line is plotted in Fig. 4b showing the two Pb end-members. This trend line significantly differs from the Mn-nodules trend, though the high end-member of the two lines may converge hence suggesting a common source. In addition, dolomitization of the carbonate rocks of the Timna Formation occurred



Fig. 4. The isotopic composition of Pb and Sr in the two types of Mn nodules and that of Mn Hill; (a) ²⁰⁸Pb/²⁰⁴Pb vs. ²⁰⁶/Pb/²⁰⁴Pb, (b) ²⁰⁷Pb/²⁰⁴Pb vs. ²⁰⁶Pb/²⁰⁴Pb and (c) ⁸⁷Sr/⁸⁶Sr vs. ²⁰⁶Pb/²⁰⁴Pb ratios. Also shown are the dolomite trend line and the Ashosh plug values (Erel et al., 2006). Solid symbols represent Type B Mn nodules while open symbols represent Type A Mn nodules.

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Table 4

The isotopic composition of Pb and Sr in Cu phases, Timna Valley.

TIC Nt. Tima Djur./cov. 18.206 15.621 38.307 TICS 10 Mt. Timna Djur./cov. 18.215 15.645 38.357 TICS 13 Mt. Timna Djur./cov. 18.215 15.641 38.307 TICO 3 Mt. Timna Malach./parata. 18.235 15.614 38.359 TICO 10 Mt. Timna Malach./parata. 18.223 15.645 38.359 TICO 12 Mt. Timna Malach./parata. 18.223 15.645 38.359 TICO 14 Mt. Timna Malach./parata. 18.563 15.583 38.571 Dolmite 18.661 15.666 38.177 CMDS 2 Plant Djur./cov. 18.747 15.598 38.043 CMDS 9 Har Michrot Djur./cov. 18.781 15.666 38.177 CMDS 15d Har Michrot Djur./cov. 18.781 15.666 38.107 CMDS 17C Har Michrot Djur./cov. 18.765 38.186 0.70714
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+†Published in Asael et al. (2012). TIC – Timna Igneous Complex, Djur./cov. – dejurite and some covalite, malach./parata. – malachite and paratacamite, *malachite – mostly malachite, parata. – paratacamite, chryso. – chrysocolla and some plancheite. For site location see Fig. 1. n.s. – not specified includes several locations within Timna Valley. Errors are (1 σ), <0.0003 for ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁷Pb/²⁰⁴Pb ratios and <0.005 for the ²⁰⁸Pb/²⁰⁴Pb ratio. 1 σ errors for the ⁸⁷Sr/⁸⁶Sr ratio are <0.0003.

early on when the sediment was saturated. Thus, these Oligocene-Miocene brine solutions cannot be responsible for the Cu- Mn- mineralization as suggested by Segev et al. (1995). Another potential source for Mn enriched solution is the emplacement of a labradorite-andesine basalt plug (Ashosh plug), 100 km north of Timna at ca. 21 Ma (Levite, 1966; Steinitz and Bartov, 1991). As can be seen in Fig. 4b, the Pb isotopic composition of the Ashosh plug does not represent a potential source for the Mn-mineralizing solutions. It is clear that the Pb isotopic compositions of both types of the Mn nodules indicate solutions that existed prior to the initiation of the Oligocene-Miocene processes associated with initiation of the Dead Sea rifting.

Mn- mineralization is found within the sands and shales of the Timna Formation in the Mn Hill, south of the Timna Complex (Fig. 1c). In this mineralization type, the Mn is dispersed in the rock and is enriched in Fe, in contrast to Type A and B nodules. This Mnmineralization is characterized by high 207 Pb/ 204 Pb and 206 Pb/ 204 ratios (Fig. 4b) suggesting a third formation event of Mn-Fe ore, not connected with the Mn nodules.

5.3.2. Sr isotopes

Similarly to the Pb isotope ratios, the ⁸⁷Sr/⁸⁶Sr ratios are distinct for each type of the Mn nodules. Type A nodules have a relatively constant low ⁸⁷Sr/⁸⁶Sr value of 0.7093 \pm 0.0005, whereas Type B nodules significantly vary, ranging from 0.709 to 0.716 (Fig. 4c). Hence, the distinction between the two types of Mn nodules is clearly reflected in both the ⁸⁷Sr/⁸⁶Sr and ²⁰⁶Pb/²⁰⁴Pb ratios inconsistent with a single event. Furthermore, if the model suggested by Bar-Matthews (1987) that Type A Mn nodules formed during early diagenesis under oxidizing conditions at the sediment-water interface in the Cambrian Sea is correct, the ⁸⁷Sr/⁸⁶Sr ratios of the Type A nodules should reflect the Sr isotopic



Fig. 5. A plot of ²⁰⁷Pb/²⁰⁴Pb vs. ²⁰⁶Pb/²⁰⁴Pb of Cu phases. The linear trend is of paratacamite separated from the dolomites. TIC = Timna Igneous Complex, Dol. = dolomite, sand = sandstone, Dejur./cov. = dejurite/covalite, malch. = malachite, parata. = paratacamite, cry. = chrysocolla, (2 etc.) = location.

composition of the contemporaneous Cambrian seawater. Determination of the isotopic composition of Sr of the Cambrian Sea is challenging since carbonate rocks from this period are not common, and in general have a complex geological history. Typically, rigorous criteria are applied on samples in order to minimize the effects of diagenetic alteration and contamination from non-carbonate phases (e.g. Burke et al., 1982; Montanez et al., 1996). The isotopic composition of Sr in seawater is thought to reflect erosion rates, as in the case of the rapid increase in isotope ratios during the Cenozoic era. Enhanced erosion of the continental crust exposes fresh surfaces and contributes radiogenic Sr to the oceans via weathering (e.g. Blum and Erel, 2003 and reference therein). The maximum Sr isotope ratio in sea water, observed for the Cambrian, is attributed to the onset of weathering of the Pan-African orogeny belt of southern Africa (e.g. Halverson et al., 2007). Numerous studies have shown that the ⁸⁷Sr/⁸⁶Sr ratios rose rapidly before and during the Cambrian from ca. 0.707 in the Vendian period (650-543 Ma) to near 0.709 or slightly higher in the Cambrian (e.g. Derry et al., 1989; Asmerom et al., 1991; Kaufman et al., 1993; Burns et al., 1994; Derry et al., 1994; Montanez et al., 1996). Comparison of the data of this study with a composite seawater Sr isotope curve for the late Neoproterozoic to Ordovician (Nicholas, 1996,) places the Type A Mn nodules average Sr isotope ratio of 0.7093 \pm 0.0005 in the Early Cambrian era, at ca. 550 to 540 Ma. This observation reinforces the view of their formation during marine Cambrian sedimentation. In contrast, the highly radiogenic and the high range of ⁸⁷Sr/⁸⁶Sr values of Type B Mn nodules indicate late circulating sub-surface solutions, which probably interacted with detritus.

Doe et al. (1999) studied two Mn deposits and found that in one case (Imini, Morocco), Mn deposits are a result of early diagenetic process, whereas in the second case (Molango, Mexico), diagenetic process had much less influence on the Mn deposits. Nevertheless, in the above two cases, the Sr isotopic ratios were higher than the expected ocean water of the relevant periods. In the current study, Type A nodules retained the ocean values (Fig. 4c) because their values are similar to the Cambrian Sea values (0.709, Ebneth et al., 2001).

5.4. Copper ores

The source of Cu in the Timna basin is thought to be intense weathering of Cu porphyry granites and quartz-porphyry dikes of the similar ANS rocks as the TIC, during the Late Precambrian and Early Cambrian (e.g. Wurzburger, 1970; Beyth, 1987, Asael et al., 2007). The Cu mineral assemblage indicates an evolution from reducing conditions (sulfide-forming) to progressively oxidizing conditions (Shlomovitch et al., 1999). The first diagenetic process to form sulfide in marine conditions was the reduction of marine sulfate. The diagenetic Cu-sulfide minerals ($Cu_{<2}S$) were subsequently partially replaced by malachite $(Cu_2 (OH)_2CO_3)$, paratacamite $(Cu_2(OH)_3CI)$ and by chrysocolla $(Cu_2H_2Si_2O_5(OH)_4)$, which subsequently evolved into plancheite $(Cu_8Si_8O_{22}(OH))$. While the replacement of sulfides by malachite requires a change to oxidizing conditions, the formation of paratacamite requires chloride solutions with slightly lower pH. The formation of Cu-silicate minerals occurs during dissolution of detrital minerals such as quartz, feldspar and clays (Shlomovitch et al., 1999).

Although the above alteration sequence is well documented, the Pb isotopic composition of the different Cu phases separated from the Timna Formation and from TIC shows no correlation with the Cu mineral type (Fig. 5). A close examination of Fig. 5 reveals that the different Cu mineral separates better group according to their location within the Timna Valley, rather than their mineralogical type (i.e. dejurite/covellite, paratacamite, malachite, paratacamite/malachite and Cu silicate). This implies that the shift in the Pb isotopic ratios also reflects the distance that the solutions travelled and the interaction with host rock, rather than just formation process. Indeed, the above interpretation is supported when comparing adjacent Cu phases. For example, malachite which occurs as an envelope around the sulfide minerals (Shlomovitch et al., 1999) indicates local replacement due to reaction with the host dolomite under oxidizing conditions. This is also reflected in the Pb isotopic composition of the malachite, which is only slightly different from that of the adjacent CuS, indicating that Pb in the solutions was inherited from the CuS. A second example is paratacamite, which



Fig. 6. Calculated initial $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ ratios of extracts, IR (a) and Mn nodules (b).

formed at lower pH from Cl-rich solutions and occurs both as rims around the sulfides, and as veins within the dolomite (Shlomovitch et al., 1999). This observation implies that the solutions from which it was deposited potentially could migrate a longer distance, which is in accordance with Pb being more soluble under lower pH environment in the presence of Cl ions (Stumm and Morgan, 1981). Indeed, the Pb isotopic ratio of paratacamite found in the laminar dolomite varies systematically with distance (Fig. 5). Moreover, the linear trend for the paratacamite of the dolomite host rock ($r^2 = 0.989$) can represent migration of solution from the southern parts of the Timna Valley to the northern parts and indeed other Cu phases are in close proximity to this trend line (Fig. 5).

The Cu minerals found in the sandstone facies of the Timna formation are mainly Cu-silicates, chrysocolla and plancheite. Since chrysocolla replaces the major silicates in the sandstone (clays, K-feldspar and quartz; Shlomovitch et al., 1999), it is reasonable to assume that its Pb isotopic composition should reflect the isotopic composition of the replaced minerals. Indeed, the lowest Pb isotopes values are those of the chrysocolla in the sandstones which, in this case probably replace feldspars. Moreover, Pb isotopes ratios of the dejurite/paratacamite separated from the TIC rocks are slightly radiogenic to be considered as the common Pb values for the whole system. This is with agreement with Asael et al. (2007) that concluded that the CuS in the dikes was also altered after formation. The ⁸⁷Sr/⁸⁶Sr ratios determined for Cu phases separated from the sandstones and shales cluster around 0.7078, whereas those of Cu phases separated from dolomite have a wide range from 0.7066 to 0.7086. Most interesting is the single CuS sample (Table 4) separated from dolomite that has a Sr isotopic composition closes to Type A Mn nodules, and potentially representing the Cambrian Sea Sr values. However, since primary CuS precipitation in the Cambrian sea is unlikely, this value most likely reflects the primary Cu-sulfide formation process which occurred during early diagenesis of the dolomites, where sulfide produced by bacterial reduction of sulfate meets Cu(II) solutions derived from the continental weathering source. This process was also inferred by Asael et al. (2007) on the basis of the Cu isotope composition of the Cu sulfides.

To conclude, the data suggests that the solutions that were involved in the Cu reduction/oxidation reactions were localized and hence, the newly formed minerals inherited the isotopic composition of the dissolved precursor minerals or host rocks.

Fig. 7 summarizes the Cambrian sequence of the Timna Valley underwent a complex diagenetic and epigenetic history, which included dolomitization, dissolution, de-dolomitization and Mn- Cu- mineralization. During these events, complex mobilization processes affected the isotopic systems of Pb and Sr, which allows them to be effective tracers of the Cu- Mn- mineralization.

6. Conclusions

Conclusions that can be drawn from the Pb and Sr systematics are summarized in the following points:

- 1. Pb isotopic composition suggests that the non-mineralized rocks largely retain the dolomitizing fluid signature. The mineralized rocks, however, interacted with fluid that had isotopic composition close to that of the detritus with high Pb isotope ratios.
- 2. The geochemistry of the Mn and ores in the shales and dolomites in the upper part of the Timna shows that Type A Mn nodules have ${}^{87}\text{Sr}{}^{86}\text{Sr} = \text{of } 0.7093 \pm 0.005$, supporting their formation from the Cambrian sea at the sediment-water interface, under oxidizing conditions. Their formation and subsequent mobilization processes for both Mn and Cu are schematically illustrated in.
- The primary pyrolusite-hollandite minerals comprising Type A nodules, together with high U and low Th concentrations from pore water, resulted in variable ²⁰⁶Pb-²⁰⁷Pb ratios due to the evolution of these ratios with time.
- 4. Variable ⁸⁷Sr/⁸⁶Sr and constant Pb isotope ratios in type B Mn nodules, which are mainly composed of the Pb bearing mineral coronadite, support their formation during epigenetic process as a result of alteration of Type A Mn nodules.
- 5. The timing of the main epigenetic processes is not clear, but the solutions involved in forming Type B Mn nodules significantly differ in their Pb and Sr isotope compositions from the Oligocene-Miocene brines that affected carbonate bedrocks adjacent to the Dead Sea Transform.
- 6. The Pb isotopic compositions of the different Cu phases in the Timna Formation and the Timna Intrusive Complex show no correlation with the Cu mineral type, but show grouping according to their location within the Timna Valley implying that Pb isotopic ratios reflect processes such as migration distance and interaction with host rock. This is strongly shown malachite which occurs as an envelope around the sulfide minerals (Fig. 7). On the other hand, Pb isotopic ratios in the paratacamite, which formed at lower pH from Cl-rich



Fig. 7. Schematic illustration of the geochemical evolution of the Cu and Mn nodules and their Sr and Pb isotopic composition in the dolomite and shales of the upper part of the Timna Formation. Petrographic description of the Mn and Cu ores is after Bar-Matthews (1987) and Shlomovitch et al. (1999) respectively. The source for Mn, Cu, U, Pb and Sr is the weathering of the Arabian Nubian Shield complex. Mn enriched in the Cambrian Sea (as solutant or as fine particles), is incorporated in the lattice of syngenetic-diagenetic dolomite. Type A Mn nodules were formed at the water-sediment-interface, under oxidizing conditions, along with U^{+6} from the pore water. These Mn nodules incorporate Sr with the Cambrian maine water isotope ratio ($^{87}Sr/^{86}Sr = 0.709$). Pb and U are mainly incorporated in the pyrolusite lamina, resulting in the evolution of $^{206}Pb^{-207}Pb$ ratios with time. During epigenetic process, some of the Type A Mn nodules are altered, U is leached out and Type B Mn nodule is formed with variable $^{87}Sr/^{86}Sr$ and constant Pb isotopic compositions mostly reflect local solution. Widespread alteration of Cu_xS to paratacamite in the laminar dolomite resulted in varying $^{206}Pb^{-207}Pb$ ratios reflecting mixing processes.

solutions and occur both as rims around the sulfides, and as veins within the dolomite, show variation in ²⁰⁶Pb-²⁰⁷Pb ratios that reflect mixing processes along a linear trend due to regional rather than local solution migration.

7. ⁸⁷Sr/⁸⁶Sr ratios determined for Cu phases in sandstones and shales cluster around 0.7078, whereas those of Cu phases separated from dolomite have a wide range from 0.7066 to 0.7086. A single CuS sample separated from dolomite has a Sr isotopic composition closes to Type A Mn nodules, and potentially representing the Cambrian Sea Sr values.

In conclusion, it is evident from this work that careful, petrographically well controlled, application of the Pb and Sr isotope systems to complex Cu- Mn- mineralization systems provides new avenues for resolving primary sedimentary ore formation processes from the later epigenetic processes. Particularly, it becomes possible to discriminate the Cu- Mn- mineralization signature of marine processes from those of later terrestrial processes in older terrains where plate tectonics has considerably modified the original paleogeographic setting.

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Appendix A. Supplementary data

Supplementary material.

References

- Arribas, A.J.R., Tosdal, R.M., 1994. Isotopic composition of Pb in ore deposits of the Betic Cordillera, Spain: origin and relationship to other European deposits. Econ. Geol. 89, 1074–1093.
- Asael, D., Matthews, A., Bar-Matthews, M., Halicz, L., 2007. Copper isotope fractionation in sedimentary copper mineralization (Timna Valley, Israel). Chem. Geol. 243, 238–254.
- Asael, D., Matthews, A., Oszczepalski, S., Bar-Matthews, M., Halicz, L., 2009. Fluid speciation controls of low temperature copper isotope fractionation applied to the Kupferschiefer and Timna ore deposits. Chemical Geology: Chemical Geology 262, 147–158.
- Asael, D., Matthews, A., Bar-Matthews, M., Harlavan, Y., Segal, I., 2012. Tracking redox controls and sources of sedimentary mineralization using copper and lead isotopes. Chem. Geol. 310–311, 23–35. http://dx.doi.org/10.1016/j.chemgeo.2012.03.021.
- Asmerom, Y., Jacobsen, S.B., Knoll, A.H., Butterfield, N.L., Swett, K., 1991. Strontium isotopic variations of Neoproterozoic seawater: implications for crustal evolution. Geochim. Cosmochim. Acta 55, 2883–2894.
- Bar-Matthews, M., 1987. The genesis of uranium in Mn phosphorite assemblages, Timna Basin, Israel. Geol. Mag. 124, 211–229.
- Bar-Matthews, M., Matthews, A., 1990. Chemical and stable isotope fractionation in Mn oxide-phosphorite mineralization, Timna Valley, Israel. Geol. Mag. 127, 1–12.
- Bartura, Y., Wurzburger, U., 1974. The Timna copper deposit. Gisements Stratiformes et Provinces Cupriferes. Liege, Soc. Geol. Belgique, pp. 277–285.
- Bentor, Y.K., 1952. Report on the Copper and Mn Deposits in Wadi Menayeh. Israel Geol. Surv. Rep. (34pp).
- Bentor, Y.K., 1956. The manganese occurrences at Timna (southern Israel), a lagoonal deposit. 20th Int. Geol. Congress, Symposium Sobre Yacimientos de Mno 2, pp. 157–172.
- Beyth, M., 1987. The Precambrian magmatic rocks of the Timna Valley, southern Israel. Precambrian Res. 36, 21–38.
- Beyth, M., Reischmann, T., 1997. The age of quartz monzodiorite, the youngest plutonic intrusion in the Timna igneous complex. Isr. J. Earth Sci. 45, 223–226.
- Beyth, M., Stern, R.J., Alter, R., Kroner, A., 1994. The Late Precambrian Timna igneous complex, Southern Israel: evidence for comagmatic-type sanukitoid monzodiorite and alkali granite magma. Lithos 31, 103–124.

- Beyth, M., Longstaffe, F., Ayalon, A., Matthews, A., 1997. Epigenetic alteration of the Precambrian igneous complex at Mount Timna, southern Israel: oxygen-isotope studies. Isr. J. Earth Sci. 46, 1–11.
- Bigot, M., 1981. Quelques donnees sur lwenvironmrnt geologique et la gitologie des occurrences cupro-manganesiferes du Wadi Araba (Royaume Hashemite de Jordaine). Fr. Bur. Rech. Geol. Minieres Bull. II. 1-2, 153–163.
- Blum, J.D., Erel, Y., 2003. Radiogenic isotopes in weathering and hydrology. In: Drever, J.I., Holland, H.D., Turekian, K.K. (Eds.), Surface and Ground Water, Weathering and Soils. Treatise on Geochemistry Vol. 5. Elsevier-Pergamon, Oxford, pp. 365–392.
- Brevart, O., Dupr, B., Allgre, J.C., 1982. Metallogenic provinces and the remobilization process studied by lead isotopes: lead-zinc ore deposits from the southern Massif Central, France. Econ. Geol. 77, 564–575.
- Burke, W.H., Denison, R.E., Hetherington, E.A., Koepnick, R.B., Nelson, H.F., Orro, J.B., 1982. Variation of seawater 87Sr86Sr throughout Phanerozoic time. Geology 10, 516–519.
- Burns, S.J., Haudenschild, U., Matter, A., 1994. The strontium isotopic composition of carbonates from the late Precambrian (~560-540 Ma) Huqf Group of Oman. Chem. Geol. Isot. Geosci. 111, 269–282.
- Cooper, G.A., 1976. Lower Cambrian brachiopods from the Rift Valley (Israel and Jordan). J. Paleontol. 50, 269–289.
- Derry, L.A., Jacobsen, S.B., Knoll, A.H., Swett, K., 1989. Sr isotopic variations in Upper Proterozoic carbonates from Svalbard and East Greenland. Geochim. Cosmochim. Acta 53, 2331–2339.
- Derry, L.A., Brasier, M.D., Corfield, R.M., Rozanov, A.Yu., Zhuravlev, A.Yu., 1994. Sr and C isotopes in lower Cambrian carbonates from the Siberian carton: a paleoenvironmental record during the 'Cambrian explosion'. Earth Planet. Sci. Lett. 128, 671–681.
- Dixon, P.R., Danny, M.R., 1991. Fluid flow connections to basement rocks below sedimentary basins: evidence from the base metal deposits in Ireland. Geophys. Res. Lett. 18, 943–946.
- Doe, B.R., Deleveaux, M.H., 1972. Source of lead in southeast Missouri galena ores. Econ. Geol. 67, 409–425.
- Doe, B.R., Ayuso, R.A., Futa, K., Peterman, Z.E., 1996. Evaluation of the sedimentary manganese deposits of Mexico and Morocco for determining lead and strontium isotopes in ancient seawater. American Geophysical Union, Geophysical Monograph 96.
- Doe, B.R., Ayuso, R.A., Futa, K., Peterman, Z.E., 1999. Evaluation of sedimentary manganese deposits of Mexico and Morocco for determining lead and strontium isotopes in ancient seawater. Earth Processes: Reading the Isotopic Code. Geophysical Monograph 95. AGU.
- Ebneth, S., Shields, G.A., Veizer, J., Miller, J.F., Shergold, J.H., 2001. High-resolution strontium isotope stratigraphy across the Cambrian-Ordovician transition. Geochim. Cosmochim. Acta 65, 2273–2292.
- Ehrlich, S., Harlavan, Y., Bar-Matthews, M., Halicz, L., 2004. Isotope ratio measurements of uranium and lead in manganese nodules by multiple-collector inductively coupled plasma mass spectrometry. Appl. Geochem. 19, 1927–1936.
- Erel, Y., Listovsky, N., Matthews, A., Ilani, S., Avni, Y., 2006. Tracing end member fluid sources in sub-surface iron mineralization and dolomitization along a proximal fault to the Dead Sea transform. Geochim. Cosmochim. Acta 70, 5552–5570.
- Geyer, G., Landing, E., 2004. A unified Lower Middle Cambrian chronostratigraphy for West Gondwana. Acta Geol. Pol. 54, 179–218.
- Gross, S., Bartura, Y., 1984. Mottra, ite-Pb (Cu, Zn)(VO)4OH from the Timna massif (south Israel). Isr. J. Earth Sci. 33, 43–47.
- Halverson, G.P., Dudás, F.Ö., Maloof, A.C., Bowring, S.A., 2007. Evolution of the 87Sr/86Sr composition of Neoproterozoic seawater. Palaeogeogr. Palaeoclimatol. Palaeoecol. 256, 103–129.
- Han, F.X., Banin, A., 1995. Selective sequential dissolution techniques for trace metals in arid-zone soils: the carbonate dissolution step. Commun. Soil Sci. Plant Anal. 26, 553–576.
- Harlavan, Y., Erel, Y., Blum, J.D., 2009. The coupled release of REE and Pb to the soil labile pool with time by relative weathering of accessory phases, Wind River Mountains, WY. Geochim. Cosmochim. Acta 73, 320–336.
- Ho, S.E., McNaughton, N.J., Groves, D.I., 1994. Criteria for determining initial lead isotopic compositions of pyrite in Archaean load-gold deposits: a case study at Victory, Kambalda, Western Australia. Chem. Geol. 111, 57–84.

- James, E.W., Christopher, D.H., 1993. Pb isotopes of ore deposits in Trans-Pecos Texas and northeastern Chihuahua Mexico: basement, igneous and sedimentary sources of metals. Econ. Geol. 88, 934–947.
- Kaufman, A.J., Jacobsen, S.B., Knoll, A.H., 1993. The Vendian record of Sr and C isotopic variations in seawater: implications for tectonics and paleoclimate. Earth Planet. Sci. Lett. 120, 409–430.
- Kiippel, V., Schroll, E., 1988. Pb-isotope evidence for the origin of lead in strata-bound Pb-Zn deposits in triassic carbonates of the Eastern and Southern Alps. Mineral. Deposita vol. 23, 96–103.
- LeHuray, A., Caulfield, J.B.D., Rye, D.M., Dixon, P.R., 1987. Basement controls on sedimenthosted Zn-Pb deposits: a Pb isotope study of Carboniferous mineralization in central Ireland. Econ. Geol. 82, 1695–1709.
- Levite, D., 1966. Magmatic Phenomena in the Arava Valley, Israel. Msc thesis. The Hebrew University of Jerusalem, Israel (in Hebrew).
- Montanez, I.P., Banner, J.L., Osleger, D.A., Borg, L.E., Bosserman, P.J., 1996. Integrated Sr isotope variations and sea-level history of Middle to Upper Cambrian platform carbonates: implication for the evolution of Cambrian seawater 87Sr/86Sr. Geology 24, 917–920.
- Morag, N., Avigad, D., Gerdes, A., Harlavan, Y., 2012. 1000 to 580 Ma crustal evolution in the northern Arabian-Nubian Shield revealed by U-Pb-Hf of detrital zircons from late Neoproterozoic sediments (Elat area, Israel). Precambrian Res. 186, 101–116.
- Nakai, S.I., Halliday, A., Kesler, S., Johns, H.D., Kyle, J.R., Lanes, T.E., 1993. Rb-Sr dating of sphalerites from Mississippi Valley-type (MVT) ore deposits. Geochim. Cosmochim. Acta 57, 417–427.
- Nicholas, C.J., 1996. The Sr isotope evolution of ocean during the 'Cambrian Explosion'. J. Geol. Soc. 153, 243–254.
- Parnes, A., 1971. Later lower Cambrian trilobites from the Timna area and Har 'Amram (Southern Negev, Israel). Isr. J. Earth Sci. 20, 179–205.
- Rothenberg, B., Shaw, C.T., 1990. The discovery of a copper mine and smelter from the end of the Early Bronze Age in the Timna Valley. Institute for Archaeo-Metallurgical Studies Newsletter 15–16, 1–8.
- Rushton, A.W.A., Powell, J.H., 1989. A review of stratigraphy and trilobite faunas from the Cambrian Burj Formation in Jordan. Bull. Nat. His. Mus. Lond. (Geolo.) 54, 131–146.
- Segev, A., 1986. Lithofacies Relationships and Cu-Mn- Mineralization Occurrences in the Timna Formation, Timna Valley. Ph.D. thesis. The Hebrew University of Jerusalem (115 pp., Hebrew).
- Segev, A., 1992. Remobilization of uranium and associated metals through karstification process: a case study from Timna Formation (Cambrian), Southern Israel. Ore Geol. Rev. 7, 135–148.
- Segev, A., Sass, E., 1989. Lithofacies and thickness control by epigenetic dissolution-the
- dolomitic Timna Formation, Cambrian, southern Israel. Sediment. Geol. 63, 109–126.Segev, A., Halicz, L., Steinitz, G., Lang, B., 1995. Post depositional processes on a buried Cambrian sequence in southern Israel, north Arabian MASSIF: evidence from new K-Ar dating on Mn-nodules. Geol. Mag. 132, 375–385.
- Shlomovitch, N., Bar-Matthews, M., Segev, A., Matthews, A., 1999. Sedimentary and epigenetic copper mineral assemblage in the Cambrian Timna Formation, southern Israel. Isr. J. Earth Sci. 48, 195–208.
- Sneh, A., Bartov, Y., Weissbrod, T., Rosensaft, M., 1998. The Geological map of Israel, 1: 200,000, Sheet 3. Isr. Geol. Surv., Jerusalem.
- Soudry, D., Weissbrod, T., 1995. Morphogenesis and facies relationships of thrombolites and siliciclastic stromatolites in a Cambrian tidal sequence (Elat area, southern Israel). Palaeogeogr. Palaeoclimatol. Palaeoecol. vol. 114, 339–355.
- Stacey, J.S., Kramers, J.D., 1975. Approximation of terrestrial lead isotope evolution by a 2stage model. Earth Planet. Sci. Lett. vol. 26, 207–221.
- Steinitz, G., Bartov, Y., 1991. The Miocene-Pliocene history of the Dead Sea segment of the Rift in light of K-Ar ages of basalt. Isr. J. Earth Sci. 40, 199–208.
- Strum, E., 1953. Possible origins of Mn ores in the Negev. Israel Research Council Bull. vol. 3, 177–191.

Stumm, W., Morgan, J.J., 1981. Aquatic Chemistry. Wiley Interscience, New York (583 pp). Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51, 844–851.

Wurzburger, Û., 1970. Copper silicates in the Timna ore deposits. Isr. J. Chem. 8, 443-457.