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The paleoenvironment and the evolution of brines in the Jordan-Dead Sea transform and in adjoining areas

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Abstract One of the most important processes leading to the deterioration of groundwater in Israel is the migration of brines penetrating into fresh groundwater bodies. Such manifestations occur at an ever increasing frequency and in unexpected locations. The hydrochemistry of these processes reveals the possibility of involvement of several types of brines. The distribution and the hydrostratigraphic sequence of the brines is correlated with the evolution of paleoenvironments during the geological history of the region. Several major phases of brine and evaporite formation are discerned: The earliest phase occurred in the Paleozoic–Early Mesozoic (Yam Suf–Ramon–Lower Arad Groups) during which brines were generated by dissolution of evaporites. The second major phase in the evolution of brines occurred during the Mio-Pliocene. In the western areas of the country, the brines were generated mainly by the post-Messinian ingression of seawater which dissolved evaporites and reacted with the invaded rock sequence. In the Rift and in adjoining areas, the dominant brine was the final product of the evaporation of an inland marine lagoon (the Sdom Sea) which penetrated into an environment prevalently built of previously formed rocks and, particularly of clastic beds filling at that time, the nascent rift. From this evaporating lagoon precipitated evaporates, the dissolution of which produced brines. A further step in the hydrochemical evolution in the Rift was the creation of the Lisan Lake, which became progressively saline, probably as the result of dissolution and flushing of salts derived from the previous hypersaline Sdom Sea. The

contemporary phase in the Rift is characterized by an ongoing process of flushing-out of residual brines and dissolution of evaporites by currently recharged fresh water. Throughout the geological history of the area, four major periods of flushing stand out. These occurred between the Triassic and the Jurassic, at the end of the Jurassic, as the result of the Oligocene uplift and as part of the Messinian event. As the result of these processes, the rock-sequences were flushed off previously formed brines and evaporites and were “made ready” for following generations of liquids.

Keywords Structural evolution · Paleogeography · Paleohydrogeology · Jordan-Dead Sea–Red Sea Rift · Brines

Introduction

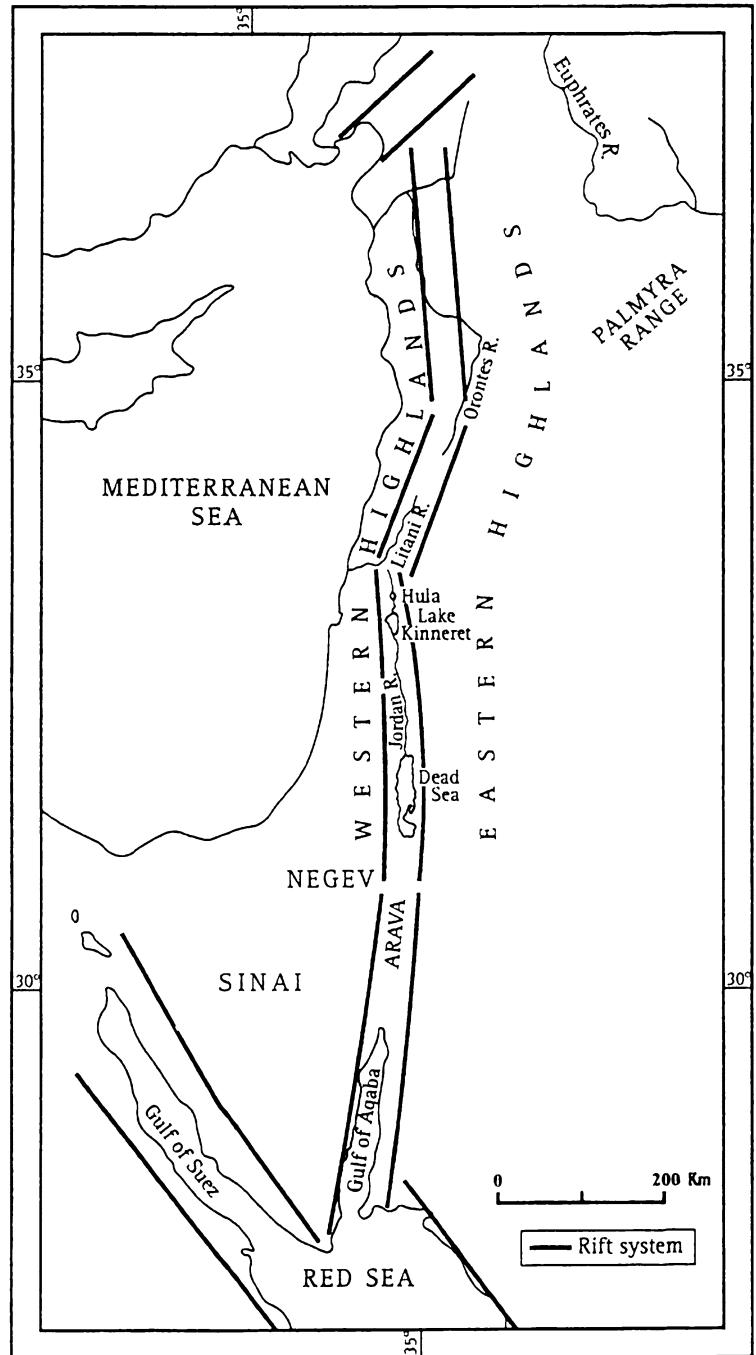
The Syrian–African Rift Valley extends over more than 6,000 km. i.e. almost 1/6 of the earth circumference (Figs. 1, 2). It branches off the northern Red Sea and extends northwards to the edge of the Taurus Mountains in Turkey (Garfunkel 2001). The Jordan Rift Valley is also known as the Jordan–Arava Rift Valley, the Jordan-Dead Sea Rift, the Dead Sea Rift or the Dead Sea Transform. These are terms used by geologists to include almost the entire longitudinal rift system of the Levant. The present study deals with the area between the Gulf of Eilat in the south reaching north of Lake Kinneret.

The Jordan Rift Valley has its peculiar hydrological features. Within the pull-apart basins of the Rift, three lakes were formed: the Hula Lake in the north (now partially dried up), Lake Kinneret and the Dead Sea which stands out by its extreme salinity of 332 g/L total dissolved solids (TDS). Geographically, the Dead Sea is the lowest point in the earth. These elongated depressions within the Rift created suitable local conditions for the drainage of fluids from areas along both sides of the Rift.

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Fig. 1 The Levant, general location map (modified after Horowitz 2001)



In all parts of the Rift, salinisation of fresh groundwater occurs mostly as the result of overexploitation which triggers migration and upflow of Ca-chloride and Ca-Mg-chloride brines. Such brines of different levels of concentrations, are encountered in Israel in most parts of the Rift and in areas adjoining to major structural feature. This type of brines was described by Vengosh and Rosenthal (1994) and grouped under the general term of Rift Group Brines. The overview of numerous hydrochemical investigations carried out during the last half-century (all summarized in Vengosh and Rosenthal 1994) revealed that such general—and mostly

synonymous—terms as Rift Group Brines, Tiberias-Noit and Zohar-Yesha Groups (Mazor and Mero 1969), create “terminological umbrellas” which, due to their attempt to find common hydrochemical denominators and to lead to their regionalisation, often conceal details which could be significant not only for the correct identification of fluids but also for the understanding of their hydrodynamics.

The main target of the present study is to reconstruct the processes and the environments which caused the evolution of fluids in the Rift viewed against the background of the regional geological events which shaped



Fig. 2 Location map of the study area

the whole region and had bearing on its hydrochemistry. The detailed hydrochemistries of water bodies encountered in various rock-formations outside the immediate proximity of the Rift, are discussed in a separate set of papers (Möller et al. 2003, 2005).

Geological and structural setting

The narrow, N-S directed morphological depression of the Dead Sea–Jordan Valley Rift is a plate boundary of the transform type which connects the Red Sea (where

sea floor spreading occurs) with the Zagros zone of continental collision (Fig. 1). Since the time of its formation, the movement along the transform has caused a left-lateral relative displacement. The amount of displacement has been estimated to over 100 km (Garfunkel 2001), although other researchers indicated lower figures—especially for northern Israel and Lebanon (Michelson et al. 1987). According to Garfunkel (2001) the tectonic system of the Jordan Rift Valley is that of left stepping, deep seated en-echelon, left lateral faults which define a series of large pull-apart basins and structural swells. Along the pull-apart basins, the lateral motion is combined with vertical offsets reaching more than 10 km (Garfunkel 2001). The main basins along the Rift structure are the Gulf of Aqaba basin (which is in itself composed of three pull-apart basins; Ben Avraham 1985), the Dead Sea basin, the Fazael depression, the Bet Shean Valley, Lake Kinneret and the Hula Valley (Fig. 1). The two lakes, Kinneret and the Dead Sea, fill morphotectonic depressions in the Dead Sea–Jordan Rift Valley (Figs. 1, 2). Lake Kinneret is 20 km long, 12 km at its widest, and has a maximum depth of 46 m. The surface of the lake is at present below -209 m MSL. This low elevation makes it a regional drainage base for rainfall falling on the surrounding hills and percolating through the stepwise downfaulted blocks to the lake. The Dead Sea extends at the lowermost elevation in the world (-410 m MSL). It is the terminal lake for surface and groundwater flow in the area. The basins within the Rift are filled with sedimentary successions attaining thicknesses of 5–10 km and are occasionally intruded by igneous bodies. The sub-bottom structure of the Lake, clearly indicate that it is being affected by active faulting (Saltzman 1964; Michelson et al. 1987).

The brines in the Jordan Rift Valley and the sources of their salts

In the Jordan Rift Valley and particularly in the Dead Sea area, the chemical composition of brines emerging from springs located along the fault-escarpment, is characterized by average Cl concentrations of 128 g/L and by characteristic ionic ratios (Table. 1, 2). In the area of Lake Kinneret, the water quality is constantly endangered by saline springs emerging along its shores and on the bottom of the Lake. The Cl concentrations of these waters—which are mostly thermal up to 60°C —vary within a wide range of 400–18,000 mg/L. These waters are of Ca- and Mg-chloride composition. Considering Mg/Ca ratios, two hydrochemical types of Ca-chloride waters were identified (Rosenthal 1988):

- Confined, pressurized, thermal and saline groundwaters, with $\text{Mg}/\text{Ca} < 1$. Such waters occur mostly along the western margins of the Rift, in the area of Lake Kinneret, in the Jordan Valley and further south along the western shores of the Dead Sea and the Arava (Devora type-Rosenthal 1988),

Table 1 Averages and ranges of chemical and isotopic components in the brines of israel

Group	Age	pH	$\delta^{18}\text{O}$	$\delta^2\text{H}$	Ca, meq/L	Mg, meq/L	Na, meq/L	K, meq/L	Cl, meq/L	SO ₄ , meq/L	HCO ₃ , meq/L
Yam Suf and Negev Ranges	Cambrian-Permian	ND	-1.39	-15.88	864.89	130.70	1011.05	19.01	2018.56	16.55	0.89
Ramon Ranges	Triassic	6.1	-1.66	-35.30	628-1,124	110-164	918-1,064	12.4-35	1,785-2,322	16-19.7	0.75-1
Arad Ranges	Jurassic	7.38	0.98	-8.86	1071.81	232.11	1140.52	17.10	2323.12	15.41	2.18
Kurnub Ranges	Lower Cretaceous	7.51	1.88	?	1,260-1,941	190-360	1,089-1,278	15.4-21.9	2,184-2,615	10.5-17.4	1.0-3.5
Judea Ranges	Upper Cretaceous	7.1-7.7	1.42-2.43	-4.2	286.79	67.05	885.05	24.34	1244.87	16.41	4.04
Ranges	Eocene	8.6	-5.3	-3.66 to -5.18	167-516	23.5-129	629-1,006	19.96-29.7	1,106-1,312	16.41	3.25-6.5
Avdat Ranges	Neogene-Mavkiim Fm.	ND	-5.23	1.14	82.23	39.95	701.84	10.83	856.33	10.44	7.97
Saqiye Ranges	Neogene-Hazeva Fm.	ND	2.76	0.46-1.53	64-111	21.4-59.2	544-922	7.24-19.4	672-1,080	3.48-18.3	3.05-9.
Dead Sea-Hazeva Ranges	Plio-Pleist. Yafo Fm.	8.36	-3.19	-9.2	20.46	24.21	181.80	2.92	219.04	12.11	5.78
Saqiye-Yafo Ranges	Plio-Pleist. Sdom Fm.	ND	3.77	-20.52	6.4-68	5-45.8	45-395	0.97-8.2	147-521	1-40.6	2.84-7.3
Dead Sea-Sdom Fm Ranges	Ocean Water	6.54	4		7.00	9.00	57.00	5.00	70.00	2.00	4.00
Dead Sea Water		8.1	2								
Ocean Water											

Legend meq/L milliequivalent/L

Table 2 Averages and ranges of ionic ratios in the brines of Israel

Group	Age	Cl/Br weight ratio	Na/Cl meq.ratio	Na/K meq.ratio	Mg/Ca meq.ratio	Mg/Cl meq.ratio	Q = rCa/(rSO4 + rHCO ₃) meq.ratio	SO ₄ /HCO ₃ meq.ratio
Yam Suf and Negev Ranges	Cambrian-Permian	98.33	0.50	72.10	0.14	0.064	49.56	18.59
Ranges		96.5-102	0.45-0.62	53-92	0.11-0.28	0.03-0.08	23.3-79.4	11.1-24.3
Ramon Ranges	Triassic	88.62	0.49	66.69	0.21	0.090	60.93	7.06
Ranges		54.9-92.7	0.3-0.56	48.8-83.3	0.2-0.35	0.08-0.13	41-78.6	4.23-10.88
Arad Ranges	Jurassic	197.26	0.71	36.36	0.23	0.005	14.02	4.06
Ranges		165-248	0.62-0.83	64.80	0.12-0.39	0.04-0.08	5.9-37.8	3.5-5.65
Kurnub Ranges	Lower Cretaceous	301.88	0.82	40.67-99.8	0.49	0.040	4.46	1.30
Ranges		234-335	0.78-0.96	114.80	0.35-0.69	0.01-0.08	1.27-6.64	0.07-1.95
Judea Ranges	Upper Cretaceous	283.00	0.84	110-140	1.20	0.200	1.81	4.24
Ranges		246-365	0.78-1.05	127.00	0.8-3.0	0.1-0.3	1.15-4.47	1.29-14.7
Avdat Ranges	Eocene	315.00	0.81	79.96	1.29	0.129	1.16	0.50
SaqiyeMavkiim Ranges	Neogene-Mavkiim	322.00	0.89	53.4-83.2	0.16	0.012	5.10	4.81
Ranges		314-340	0.84-0.99	84.90	0.11-0.21	0.01-0.02	1.47-14.8	1.5-19
Dead Sea-Hazeva Ranges	Neogene-Hazeva	61.45	0.38	68.7-101	0.32	0.150	437.40	4.28
Ranges		55-68	0.38-0.39	48.80	0.17-0.39	0.09-0.17	48.8-653.3	1.54-10.05
Saqiye-Yafo Fm Ranges	Plio-Pleist. Yafo Fm	332.50	0.80	11.7-113	0.17	0.035	21.80	0.51
Ranges		320-345	0.73-0.84	8.86	0.05-0.28	0.01-0.06	10.7-32.9	0.19-0.82
Dead Sea-Sdom Fm Ranges	Plio-Pleist. Sdom Fm.	45.00	0.35	4.5-16.2	0.11	0.060	794.20	0.46
Ranges		34.8-50.3	0.23-0.53	8.86	0.01-0.19	0.00-0.008	228-1,237	0.06-1.39
Dead Sea Water		41.60	0.56	8.86	4.11	0.560	69.50	2.43
Ocean Water		283.60	0.84	45.6	5.48	0.200	0.35	24.22

- Mostly phreatic and non-thermal waters characterized by Mg/Ca > 1 which occur along the eastern shore of Lake Kinneret and in the north-eastern parts of the Jordan Valley (Newe Ur type-op.citt.).

The source of salts in the Jordan Rift Valley has been investigated by numerous authors (Goldschmidt et al. 1967; Mazor and Mero 1969; Starinsky 1974; Rosenthal 1988; Arad and Bein 1986; Simon and Mero 1992; Flexer et al. 2000). Starinsky (1974) suggested that the brines found in the subsurface of the Rift represent a residual product of evaporated Pliocene seawater which precipitated halite during the course of its evolution and attained Ca-chloride composition by subsequent dolomitisation. Subsequently, these brines became (in an unexplained manner) confined and pressurized. However, the downward percolation (and subsequent pressurization) of such concentrated residual fluids through hundreds of meters of undisturbed and partly impermeable rock-sequences (some of them containing thick formations of evaporites), is geologically unfeasible (Flexer et al. 2000). Starinsky (1974) also suggested that the Mg-rich brines emerging from the saline springs along the western shores of the Dead Sea, represent a residual product of evaporated Pliocene seawater which was trapped in the primordial Sdom depression within the Rift. During the course of its evolution, this evaporating brine precipitated halite. The brines could have been the main sources of the contemporary Dead Sea water (Starinsky 1974; Vengosh et al. 1991). According to Gvirtzman et al. (1997) the outflow of these saline waters is nowadays controlled by the head and the flow of fresh groundwater and possibly by thermal convective flow. However, the very high hydraulic pressures (hundreds of atmospheres) characterizing Ca-chloride brines in the deep boreholes around Lake Kinneret such as Devora 2A, Jordan 1 and Rosh Pina 1 (Rosenthal 1988) and Zemah 1 (U. Baida and N. Nevo, personal communications), clearly indicate deep confinement of these brines and contradicts the model of Starinsky (1974) for brine formation because during the Pliocene, no geological processes occurred which could have generated such deep confinement (Rosenthal 1988; Ilani et al. 1986). These divergent facts may actually indicate the possible existence of several generations of Ca-chloride brines. Flexer et al. (2000) proposed an alternative model for the formation of the brines in the Jordan Rift Valley. It is based on evidence from the wildcat borehole Zemah-1 and relates the formation of the brine by dissolution of sulphates, halite and of K-Mg rich and Na-poor post-halite evaporites which were identified in the rock-sequence penetrated by borehole Zemah 1 and eventually from similar salt-structures in the Rift. The ablation of the evaporites would obviously create a Mg-rich brine such as has been encountered along the eastern and southern shore of Lake Kinneret. The Ca-rich brines encountered along the western littoral of the lake and elsewhere in the Rift, could be the result of further massive Mg-removal by dolomitisation (Bergelson et al. 1999).

Hydrogeological evolution of the area

The hydrogeological evolution of the area was reconstructed by examining, analyzing and synthesizing the geological and structural evidence which accumulated during the last century. The hydrochemical scheme relies on a data-base containing over 26 complete (major ions and stable isotopes) analyses of fluids from oil wildcats, exploratory boreholes and water wells. The reliability of these analyses has been repeatedly and critically checked by Bentor (1969), Starinsky (1974), Fleischer et al. (1977), Greitzer (1980), Menashe (1991) and by the present authors. Having ascertained that the water samples were extracted by reliable methods from definite rock units, it was possible to define representative hydrochemical end-members occurring in different stratigraphic units. The average chemical composition and ranges of concentrations of saline waters along the western margins of the Jordan Rift Valley are given in Table. 1 and 2.

The possible evolution of the regional geological and hydrogeological environment

The formation and the emplacement of brines in the Jordan Rift Valley, should be regarded as part of the regional geological and hydrogeological evolution i.e. two processes which seem to be closely connected. However, following major tectonic events, the different hydrogeological regimes which evolved throughout the geological times, were partly or completely disarranged by interaquifer flow. Nevertheless, there seems to be considerable evidence to outline—in broad lines—the possible sequences of hydrogeological and hydrochemical events and to relate them to the structural evolution of the area.

The initiation of the present-day Rift dates back to Late Eocene–Oligocene. However, certain authors such as Bender (1974) and Hussein and Hussein (1990) suggested that since the Precambrian, the Rift was eventually a N-S longitudinal zone of crustal weakness and of rifting. These authors suggested that the distribution and the orientation of Precambrian dikes, the structure and petrography of Precambrian rocks and to the isopach maps of Phanerozoic stratigraphic units (Horowitz 2001) coincide with the ancient lineaments. The present authors believe that the geological history of the whole area as it was before the formation of the Rift (i.e. preceding the Late Eocene–Oligocene), is relevant and pertinent to the formation and evolution of brines and to the hydrogeology of the Jordan Valley which evolved after the Oligocene. Therefore, the regional geological and hydrogeological evolution during the Precambrian–Oligocene time span is presented in broad lines as a necessary background for later events in the Rift. Figure 3 portrays the relevant time- and lithostratigraphic units. Figure 4

schematizes the tectonic-sedimentary evolution of the region.

The time span between the end of the Precambrian and until the Cretaceous, was dominated by the slow emergence of the Arabo-Nubian massif (Husseini and Hussein 1990). Continental conditions prevailed over most of the massif and the drainage of both groundwater and surface flow must have been north-westwards to the primeval ocean. During this long period, along the margins of the massif occurred repeated marine inland incursions of variable intensity and depths (Alshaharan and Nairn 1997). The ongoing struggle between land and sea created coastal lagoons in some of which sea water evaporated creating brines (Table. 1, 2). The only water hosted in the Precambrian Zenifim Formation [Shelomo Group (Ramon 1 borehole, 2,188 m)] has a Cl concentration of 66 g/L with a very low content of sulphate with a SO_4/Cl equiv. ratio of 0.006 and has a typical Ca-Cl composition.

The rock units of the Carboniferous-Permian Negev Group are built of sandstones, of slightly gypsiferous limestones and dolomites with pyrite. The Cl concentrations are in the 62–135 mg/L range, increasing upwards towards the overlying Ramon Group (Triassic) (Table. 1, 2). Sulphate concentrations although generally low, behave in a similar manner. The ionic ratios in the three formations are similar and of typical Ca-Cl brines. Cl/Br weight ratios are low (97) possibly indicating seawater evaporation. These are relatively “light” waters with $\delta^{18}O$ values in the -0.26 to -2.8% range which probably indicate subsequent flushing by fresh water (see further).

According to Bentor (1969), the brines in the deep Paleozoic beds in southern Israel evolved as the result of early Paleozoic sea water evaporation which have been later modified by various diagenetic processes. The main evaporation phase occurred all over the Middle East in Late Proterozoic and/or Early Cambrian (Stoecklin 1968; Hussein and Hussein 1990). Though no evaporites of this type occur in the ancient and deep-seated beds in Israel, the early Cambrian sediments in the southern Negev carry abundant salt casts (Bentor 1969). According to Abu Jaber et al. (1989), in the study region, marginal marine basins apparently began forming during the Triassic and Jurassic and reached their apex during the Cretaceous.

The Triassic Ramon Group (Zak 1963) was characterized by large-scale marine oscillations which are the response to a regression of global extent. Due to alternations of normal shelf and intertidal hypersaline to brackish environments, in the Upper Triassic sequence occur thick beds of gypsum (the Mohilla Formation and the Abu Ruweis Fm. in Jordan (Zak 1963, Bandel and Khoury 1981 respectively). In Israel, the thickness of gypsum beds increases from the central Negev, northwards. Moreover, in borehole Ramallah 1 (Fig. 2) this formation contains also halite. In central-northern Israel, evidence from borehole Devora 2A reveals the massive occurrence of evaporites alternating with

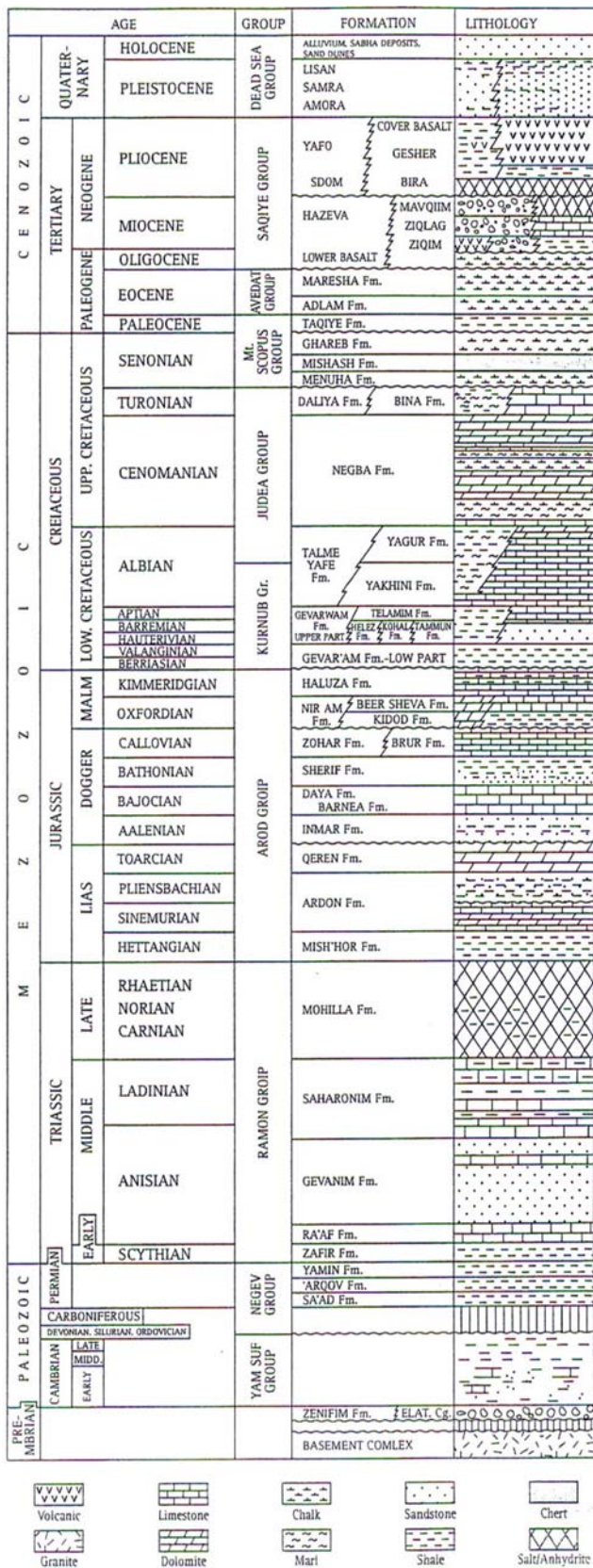
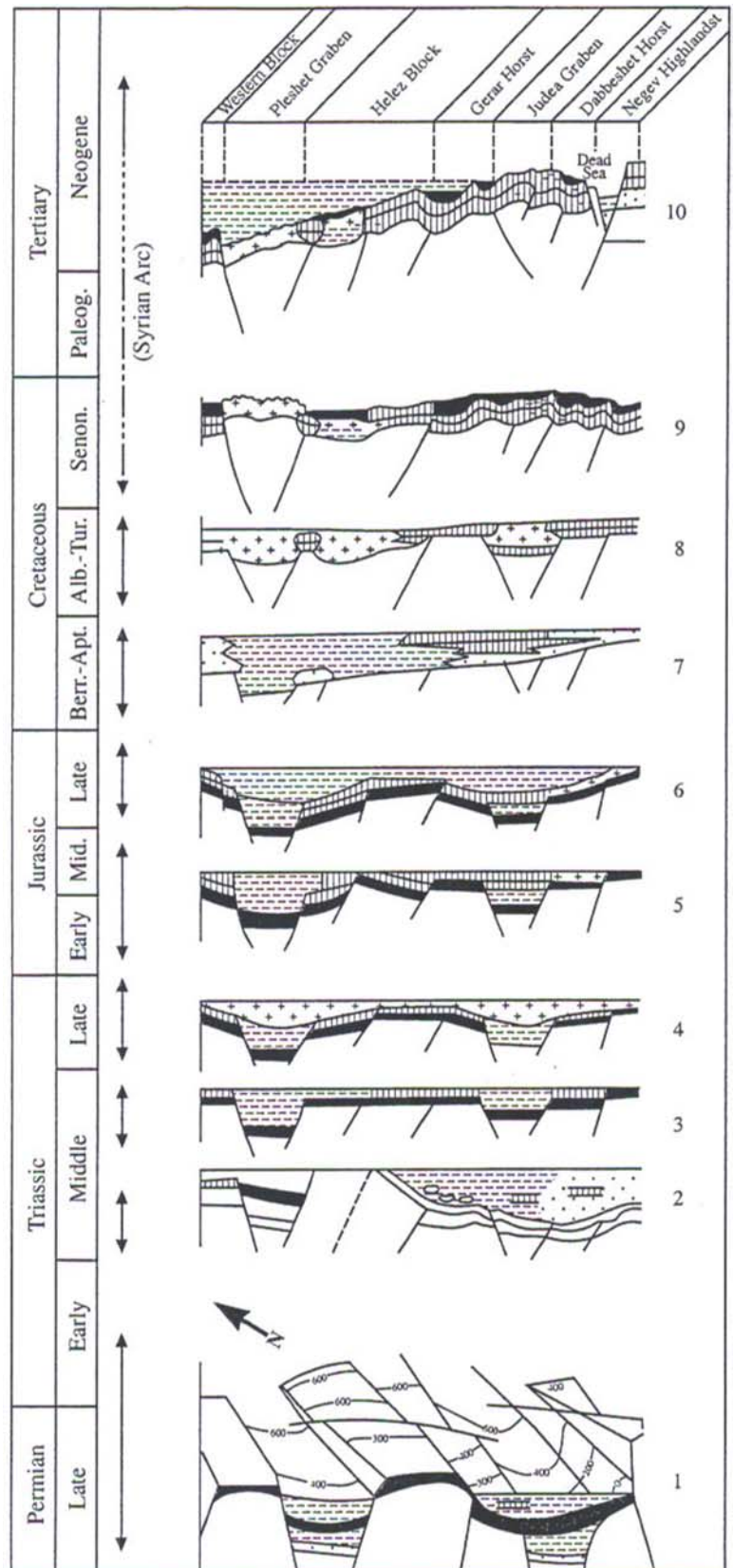


Fig. 3 Columnar section

limestone and dolomites (3,195–3,940 m). These beds are underlain and overlain by volcanic material (4,203–4,217 m; 3,974–3,996 m; and 3,062–2,790 m). The brines encountered in the Ramon Group have Cl concentrations in the 55–140 g/L range. Sulphate concentrations are in the range of 190–1,550 mg/L. All fluids are of the Ca chloride type with high Ca-excess factors ($Q = \text{Ca}/(\text{SO}_4 + \text{HCO}_3^-)$ (equiv.) of up to 245. In borehole Devora 2A these brines are pressurized (480 bars) and thermal (162°C; Rosenthal 1988). The distribution of $\delta^{18}\text{O}$ also indicates a northeastern trend. The lightest waters (-5.05 to -2.01‰) occur in the southern part of the country, whereas heavier waters (up to 2.81‰) evolve progressively northwards. Considering indicative ionic ratios [$\text{Ca}/(\text{SO}_4 + \text{HCO}_3^-)$, Na/Cl , Mg/Ca and Cl/Br weight ratio] Rosenthal (1988) suggested that these brines were relict fluids of the evaporative processes which underwent further diagenesis by dolomitisation. The formation of such brines could have also been chemically linked to the very intensive Triassic volcanic activity in Northern Israel (as evidenced from boreholes Asher, Yagur, Haifa, Atlit and Devora 2A—Fig. 2). According to Möller et al. (2005), these brines were formed by massive ablation of halite and gypsum/anhydrite with significant influence of igneous processes. Generally, the salinity of brines in the Negev and Ramon Groups increases north-eastwards in the general direction of the contemporary Rift and of the Dead Sea (Greitzer 1980). This is consistent with the views expressed by Bentor (1969) by which the ongoing gradual emergence of the Arabo-Nubian massif throughout the Paleozoic–Lower Cretaceous time span must have created a regional hydrological gradient facilitating northward flow of these brines from the areas of their formation in Sinai and southern Israel to structurally lower lying areas.

The transition from the Triassic to the Jurassic is defined by a major unconformity of twofold nature: (1) tectonic—generating the angular unconformity, and (2) regressional—causing the progressive erosional truncation and karstification of the underlying Triassic substratum. The accompanying regional exposure and laterisation are manifested by karstic pockets filled with bauxite, penetrating deeply into the Upper Triassic. The Mishhor Formation evolved as the result of leaching by intensive groundwater movement penecontemporaneous to and after the burial of the clastic lateritic suite (Goldbery 1982; Valetton et al. 1983). In northern Israel, the laterites (and the Ardon carbonates) are replaced by a very thick sequence of volcanics. The intensive surface and groundwater flow which caused mature karstification and lateritisation in the Mishhor Formation probably also flushed and displaced the previously formed brines which were either carried away westwards to the sea (which was at that time the only drainage base) or were flushed downwards to deeper stratigraphic levels in the subsurface. Hence, pre-Jurassic brines could have been preserved only in few natural reservoirs (locally

Fig. 4 Tectono-sedimentary development of grabens and horsts, sag basins, tilting and vertical inversions in Israel (modified from Cohen et al. 1990): 1 interblock "passive" sags overlying NNE trending grabens (isopachs in meters), 2 landward tilt, sedimentary wedge, 3 horsts and grabens, 4 interblock "passive" sags, 5 horsts and grabens, 6 interblock "passive" sags, 7 step-faulted basinward tilt, sedimentary wedge, 8 mild horst and graben influence, 9 inversion and intense folding, intrablock "active" fault-fold Senonian sags with local anoxic sedimentation, 10 westward tilt of entire basin, sedimentary wedge, formation of Jordan Rift Valley



protected by geological conditions) from flushing and from total evacuation. If such brines were generated in areas located (nowadays) to the east of the Rift (i.e. in Jordan), they may have been flushed out because of the (subsequent) much higher structural position of the eastern side of the Rift and more so of the Triassic beds.

The Jurassic Arad Group (Coates et al. 1963) is characterized by two marine transgressions separated by a period of regression represented by large amounts of anhydrite (Nevo 1963). The Jurassic period stands also out by important basaltic and ultrabasic igneous activity. Evidence for such activity is from boreholes Devora 2A (1,025–1,192 m). The Arad Group hosts at present two types of brines. In its lower part the Cl content is in the 39–105 g/L range with low concentrations of sulphate (380–1,000 mg/L). These are typical Ca chloride brines with Ca excesses of 37–134, Na/Cl of 0.49–0.68 and low Cl/Br weight ratios (60–127) which could have been formed as the result of the evaporation of sea water and also by ablation of halite and gypsum/anhydrite. In the upper half of the Arad Group, the brines are of an entirely different type. These are Na-chloride brines with Na/Cl ratios in the 0.78–1.18 range and much higher Cl/Br weight ratios (111–248). The Ca-excess factors are much lower than in the lower part of the Group, i.e. in the 0.81–38 range. These brines could originate from seawater which might have undergone a certain degree of evaporation without reaching the point of halite precipitation. The brines in the lower part of the Arad Group are characterized by “light” $\delta^{18}\text{O}$ (–1.92 to –2.41 ‰). In the upper half of the Group the brines have $\delta^{18}\text{O}$ values in the 0.51–1.66 ‰ range.

At the transition between the Jurassic and the Lower Cretaceous (Kurnub Group) the tectonic and erosive activities continue and the whole area is uplifted causing a truncation of up to 1,000 m (Bender 1974; Bartov 1983). By considering evidence from Upper Middle Jurassic carbonate formations, Buchbinder (1981) and Buchbinder et al. (1983) reported the occurrence of a paleokarst surface developed along an unconformity surface in the Upper Jurassic section. Considering the lithostratigraphy and the paleogeographic evidence, it stands to reason that the Jurassic rock-sequence was prevalently permeated by seawater. Local pockets of brine may have been left behind by evaporative processes in lagoonal and deltaic areas. The intensive volcanic activity must have generated not only thermomineral springs but also Ca-rich brines resulting from interaction of seawater with basic lavas. However, the massive erosion and denudation involved enormous volumes of waters which on one hand flowed to the drainage base in the west and on the other hand penetrated the subsurface, partly flushing out previously formed brines. The process of flushing could have been enhanced by the intensive faulting which facilitated interaquifer flow. Here again connate Jurassic waters may have been preserved in pockets isolated by local geological conditions.

Following the infraCretaceous uplift of the Arabian massif and the subsequent erosion and truncation (Abu Jaber et al. 1989; Alshaharan and Nairn 1997), the margins of the massif were covered by thick sequences of sands, sandstones and conglomerates (Lower Cretaceous Kurnub Group), representing prevalently continental conditions and surface flow was mainly directed north-westwards; further westwards and closer to the sea coastal and shallow marine conditions prevailed. This was not a period of volcanic quiescence. Basalts and tuffs were encountered in Lower Cretaceous sequences in the Negev, in Samaria, in the Galilee and in the Golan (Bartov 1983). Gradually, the marine transgression penetrated deeper inland east- and south-eastwards covering large, previously denudated areas and covering the flanks of the Arabian massif. Most samples of brines which occur at present within the Kurnub Group were extracted from the oil-bearing Heletz Formation composed mainly of sands occurring at the base of the Kurnub Group sequence as well as from calcareous beds in the overlying Lower Cretaceous Telamim and Yakhini Formations and from sandy horizons in the Gevar-Am shales and in the Talme Yafe formation. As shown in Table 1 and 2, the chemical composition of the liquids derived from different formations, is very similar. The Cl content reach as high as 36 g/L and sulphates are in the 144–2,190 mg/L range. Gavrieli et al. (1995) proved the dependence between the sulphate content and presence of oil in the source-formations. The Na/Cl equiv.—and Cl/Br weight ratios of these brines (0.87–0.98 and 250–477) indicate that they could have evolved respectively from seawater which did not reach the point of halite precipitation. The Ca-excess factor which does not exceed $Q = 13.3$ may have been the result both of chemical reduction of sulphates and of dolomitisation (Gavrieli et al. 1995). $\delta^{18}\text{O}$ is in the range of 1.37–2.85‰ though in the Telamim Formation light values of –1.46 ‰ were also encountered.

The Mid-Cretaceous–Eocene marine carbonate regime

During the Middle Cretaceous (Judea Group) (Cenomanian), wide parts of the Middle East were covered by sea. Marine conditions prevailed in the study area and a thick sequence of carbonate sediments was laid down. This was also a period of volcanic activity—mostly in the eastern part and in the western part of the country. Such conditions prevailed until the end of the Turonian during which began the folding of the Syrian Arc causing tectonic re-adjustment, i.e. formation of basins and of highs (Abu Jaber et al. 1989; Alshaharan and Nairn 1997). The previous monotonous and flat platform sedimentation disappeared and was replaced by morphological highs and lows. The slow emergence and the evolution of uplifted land areas is also accompanied by the progressive supply of sand (from the massif), by its deposition in the emerging

basins and also by precipitation of anhydrite in the shallow lagoons (Bartov 1983). The fluids that permeated the sediments during the Cretaceous-Palaeocene were probably residual seawater which may have locally undergone chemical changes due to input of fluids and gases derived from volcanic activity and to interaction with host rocks. One may however assume that as the result of subsequent folding and emergence during the Oligocene, these fluids drained and were flushed out from the Cretaceous-Oligocene rock-sequence. The fluids which occur at present in the Judea Group sequence are characterized by Cl^- concentrations which do not exceed 21 g/L (Zilberbrand et al. 2003). The values of the equiv Na/Cl and Cl/Br weight ratios resemble those of seawater (0.86 and 286, respectively). Q values are low and do not exceed 3. Considering the values of the Mg/Ca ratio, two groups are discerned, i.e. one group of water with Mg/Ca < 1 and another with values > 1. Brackish and saline water related to the latter group occur beneath the Coastal Plain (between Gaash and Cesarea in the north and Sahaf-Beerli in the south—Fig. 2) and in the western inland valleys, in the Zevulun and Yizrael Valleys. Apart of Mg/Ca > 1 these waters are characterized by equiv. Na/Cl of ~ 0.86 and Cl/Br weight ratio close to the marine value. These fluids could be relics of ancient or even sub-recent (Pleistocene) seawater. The other group, with Mg/Ca < 1 could be of similar origin but may have undergone alteration involving ion exchange with the surrounding calcareous rocks (Bar 1983). The survey of stable isotopes was not systematic. The available results indicate a wide spectrum of $\delta^{18}\text{O}$ between -5.67 and $+3.2\text{‰}$.

During the Senonian and Paleocene (Mt. Scopus Group) occurred a radical change of the sedimentary regime which became that of basins and of synclinal channels. The paleotopography of anticlines and synclines formed by the folding of the Syrian Arc, controls facies and thicknesses of the predominantly chalky formations of this Group (Flexer 1971; Abu Jaber et al. 1989; Alshaharan and Nairn 1997). The Senonian was a period during which most of the area was covered by seawater which replaced any fresh water which might have been trapped in the underlying strata following the Turonian events. Senonian paleodolines are found in central and northern Israel but are missing from the southern Negev and Sinai. This is attributed to the emergence of northern Israel during the lowermost Senonian (Coniacian) stage while southern Israel was submerged. The main lithological components of the Mt. Scopus sequence are phosphorites and shales rich in bituminous material. These components could have chemical impact on the chemical composition of groundwater and particularly on the enrichment of Br in groundwater. At present, due to its chalky and marly composition, the Mt. Scopus Group plays an important hydrogeological role, mostly as a regional aquiclude.

The Eocene (Avdat Group) is characterized by a regional marine transgression reaching as far as the slopes of the Arabo-Nubian massif in the south and southeast.

The Tethys covered the previous morphology of basins and of uplifted sills, precipitating chalks in the basins and nummulite-bearing limestones on the elevated structures. Seawater penetrated into all underlying rock-formations causing their flushing. The only information on the chemistry of saline waters in the Avdat Group is from the well Nir Am Gas 1 borehole. The chemical composition of this water (2,482 mg/L TDS) resembles in all details the previously described saline waters occurring in the Judea Group with Mg/Ca ratio of 1.29 which may be relics of the (Pleistocene) sea.

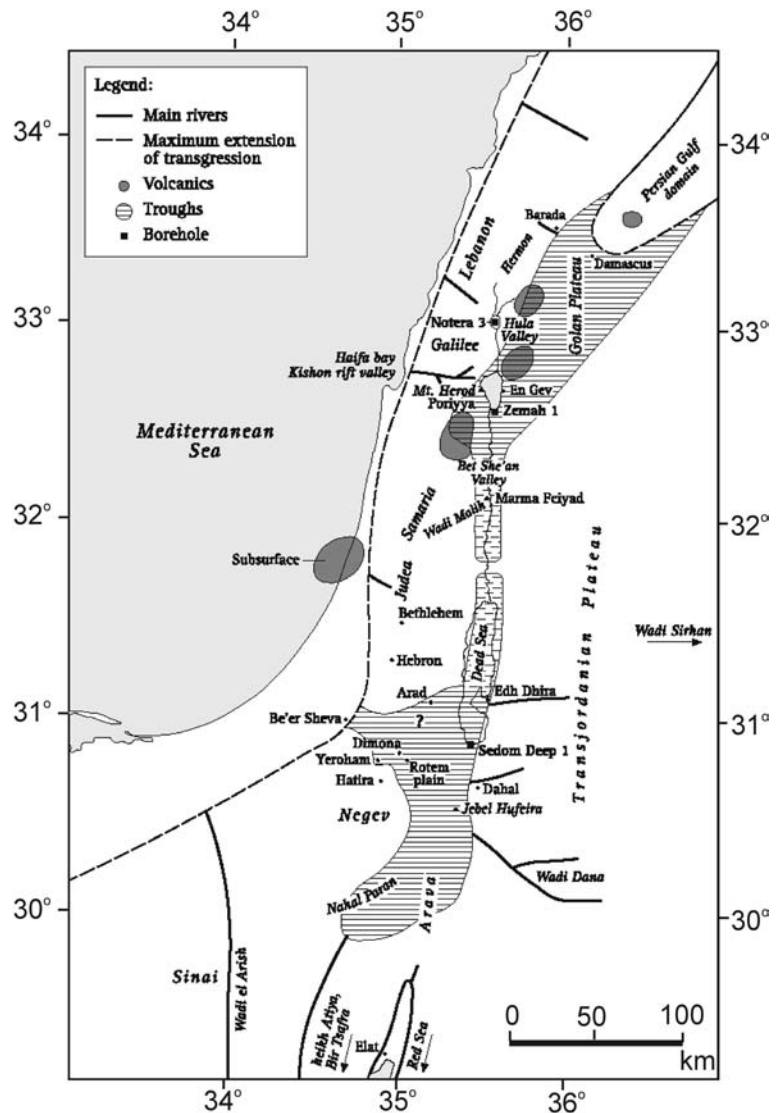
The formation of the proto-Rift during the Oligocene

At the transition from the Eocene to the Oligocene, the whole paleogeographic picture of the area changed. The Tethys retreated and land emerged, shaped by the Levantine folding (the Syrian arc). A major structural event, i.e. the embryonic subsidence of the Rift Valley also occurred during this period (Horowitz 2001). The marine as well as the continental Oligocene accumulations located along a N-S trace, indicate quite convincingly the formation of a proto-Rift suture during the Oligocene (Fig. 4). This could be a tectonic rejuvenation of an old (Precambrian) geosuture or a line of weakness as suggested by Bender (1974) and by Hussein and Hussein (1990). During this period, a marine seaway invaded the proto-Rift from the Indian Ocean (Michelson and Lipson-Benitah 1986), encircled most probably the Arabo-Nubian dome (Fig. 5) and penetrated into the proto-Rift from the east (through Wadi Sirhan in Jordan) towards the area of Lake Kinneret. This marine branch has also migrated southwards to the present day Dead Sea area (Khalil 1992). One should however not overlook the possibility of the existence of another seaway through the Gulf of Suez. A possible marine ingress into the southern Arava Valley was reported by Horowitz (2001). Due to the structural evolution, a generally NE-SW striking mountainous backbone emerged and a watershed, separating between drainage to the retreating Tethys and to the evolving proto-Rift, was created. The new orographic system, facilitated both drainage and evacuation of erosion products not only westwards to the sea but also to the proto-Rift.

The transition from the Miocene to the Pliocene

During the Middle-to-Late Miocene the (presumably) Tortonian marine ingress found its way through the Yizreel Valley into the northern part of the nascent Rift, filling the freshly formed rhomb-shaped depressions within the Rift south of Lake Kinneret, with lacustrine deposits and evaporates as represented by the Bira Formation and by the thick sequence of salts encountered in borehole Zemah 1. This marine inundation of the proto-Rift is regarded as the first major marine transgression.

Fig. 5 Middle Miocene paleogeography (after Horowitz 2001)



The following transition from the Miocene to the Pliocene is indicated by the Messinian event in which the Mediterranean Sea and the marine lagoon which penetrated into the proto-Rift, dried up leaving behind thick accumulations of evaporites (Vengosh et al. 1993). The westward retreat of the sea during the Messinian time should have left a stratigraphic lacuna in the Jordan Valley. However, its geological impact is not clear to the present day.

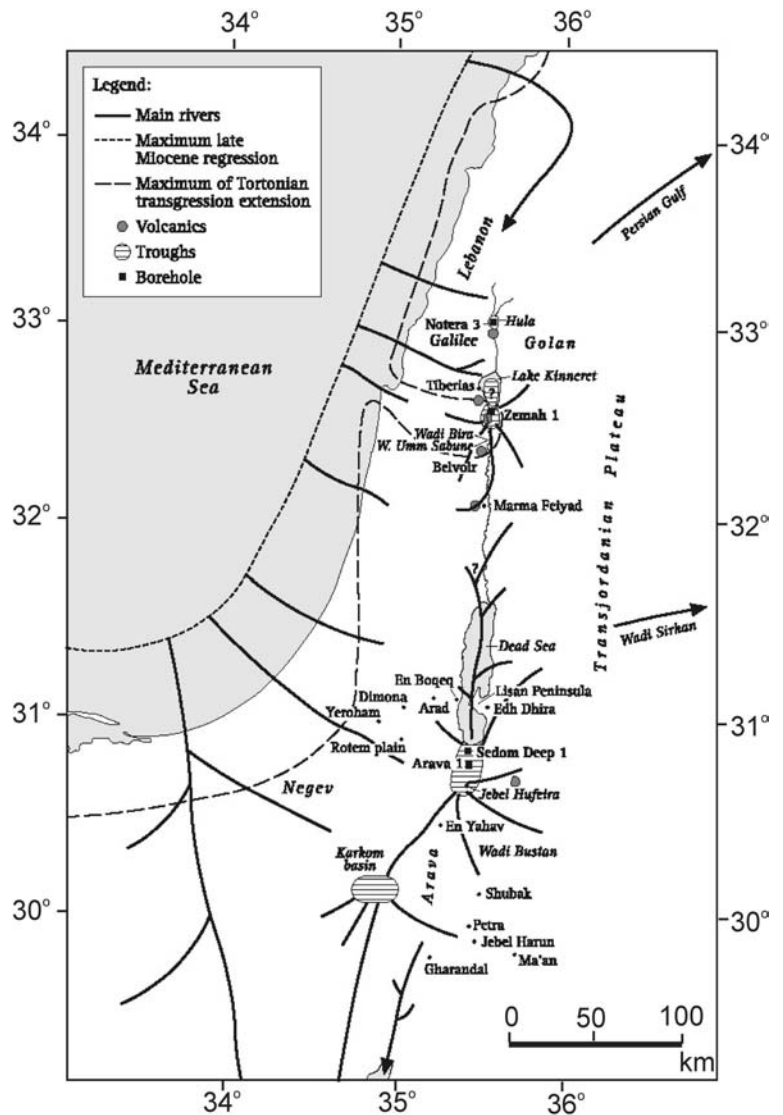
Pliocene

Another transgressionary pulse occurred at the beginning of the Pliocene with the opening of the Straits of Gibraltar and the inundation of the Mediterranean Sea. This second major marine transgression reached as far northwards as to the area of Lake Kinneret and southwards to the region of the present-day Dead Sea. All geological evidence indicates that the second (Pliocene)

transgression into the Rift generally followed the same paths and reached the same areas as the previous Upper Miocene transgressive pulse which deposited the Bira Formation and the Zema salts.

The Pliocene paleogeography (Fig. 6) was dominated by deep inland incursions creating fjord-like marine estuaries, the longitudinal shape of which was controlled by the morphotectonics of the evolving Rift. The large inland estuary which covered the (present-day) area of Lake Kinneret, Jordan Valley, Dead Sea and the Arava (hence defined as the Sdom Sea) was connected to the proto-Mediterranean Sea by the Kishon-Yizre'el Valley in the north and probably by the Beer Sheva channel in the south (Horowitz 2001). The Sdom Sea became the drainage base for the western margins of the Transjordanian Plateau and for the eastern slopes of the mountain backbone of (present-day) Israel, i.e. of the Negev, Eastern Judea and Samaria. The tectonic evolution leading to the evolution of the marine estuaries was associated with major faulting and intensive volcanism

Fig. 6 Late Miocene–Early Pliocene paleogeography (after Horowitz 2001)



which were manifested both inside and on the bordering areas of the Rift. On both sides of the Rift, massive flows of lava (the Cover Basalt Formation) covered large areas. The sinking and deepening of the Dead Sea Rift echoed by the uplifted Transjordan plateau, and the disconnection of the marine estuaries (“the Sdom Sea”) from the open sea in the west, caused wide-scale evaporation of the residual seawater bodies which remained in the Rift. These tectonic events were further accompanied by volcanism in Eastern Galilee and on the Golan Heights and in various parts of the Rift. Thick sequences of evaporites (gypsum, halite and probably of post halite salts) accumulated in the deeper parts of the Rift such as the upper part of the Sdom Formation in Mt. Sdom, the salt diapir on the Lisan peninsula and parts of the thick sequence discovered in borehole Zema 1. These salts and the residual Mg- and Ca-rich brines endanger nowadays the fresh regional fresh water resources.

The marine paleoenvironment of the Bira Formation was replaced by fresh water environments of the Geshar Formation (Schulman 1962). By and large, the two basins of the Jordan Valley show mixed lacustrine, fluvial and lagoonal environments. The paleohydrological implications of these events are that the fresh water masses of the Geshar environment flushed—to an unknown extent—the brines which were residual to the evaporative process of the preceding period during which the Bira Formation was laid down. One may assume that only those brine bodies which were trapped in isolated “pockets” and were eventually protected by the marls of the Bira Formation, could have escaped flushing-out by the fresh waters of the Geshar period.

Concurrently with the deep marine ingress into the Rift during the Pliocene, in the western parts of the area (coinciding with the present-day Coastal Plain), the sea rose and advanced through the deep canyons which were created previously during the Messinian regression,

dissolving the evaporites which were deposited there during the desiccation phase. The resultant brine permeated the permeable rock sequence into which canyons incised. According to Rosenthal et al. (1999), these brines penetrated into the permeable calcareous Arad (upper part), Kurnub and Judea Groups from which previously formed fluids were drained and flushed out during the major Oligocene uplift and the following Miocene structural events. The western parts of the country were progressively covered by the transgressing sea depositing the argillaceous Yafo Formation. This marine transgression continued into the Pleistocene.

Pleistocene

During the Middle–Upper Pleistocene prior to 60,000 years ago, the Rift area was again dominated by fluvio-lacustrine conditions (Picard 1943), which generated considerable surface flow to the Rift finally forming a fresh water lake in the Jordan Valley (the Samra Lake). These particular conditions also facilitated dissolution of the evaporite salts accumulated during the earlier parts of the Pliocene and their flushing towards the lower parts of the Rift. Between 60,000 to about 18,000 BP, this lake denoted as the Lisan Lake, (Begin et al. 1974) became progressively saline and covered an elongated narrow depression within the Dead Sea Rift Valley. Two basins (a southern and a northern one) were discerned in the Lake (Fig. 7). The southern basin which was wide and deep, extended from Nahal Amaziahu south of the Dead Sea to Wadi Malih (south of Bet Shean), whereas the northern basin—shallow and narrow—extended between Wadi Malih and Lake Kinneret. The two basins were interconnected by a narrow winding passage near W. Malih (Begin et al. 1974). At its highest levels, the Lisan Lake reached to -180 m MSL (Ettinger and Langotzky 1967). The stratigraphic section of the Lisan Formation contains two members, the Laminated Member at the base and the White Cliff Member above. The detailed analysis of the lithological and mineralogical sequence reveals increase in salinity from the littoral zone (where streams poured into the lake) to the central part of the lake and from the northern to the southern basin. The Laminated Member is composed mainly of alternating aragonitic and detrital varvae, whereas the overlying White Cliff Member has a higher chemical/detrital sediment ratio and contains aragonite, gypsum and halite. According to Stein et al. (1997), the evolution of Lake Lisan took place between two distinct modes. The first was characterized by an extensive supply of freshwater and resulted in a rise of the lake's level, a density layered structure and by precipitation of aragonite. The second mode was marked by a diminishing input of freshwater resulting in mixing or complete overturn of its water and precipitation of gypsum. The two modes reflect the climatic evolution of the region in the late Pleistocene which fluctuated between drier and wetter periods. The transition to the

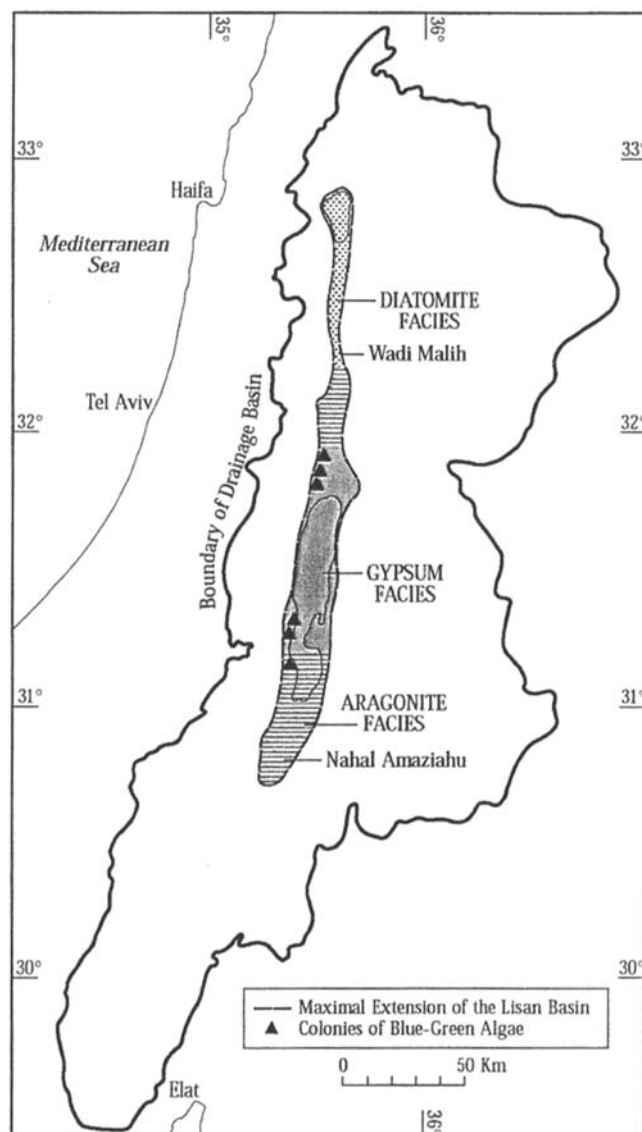
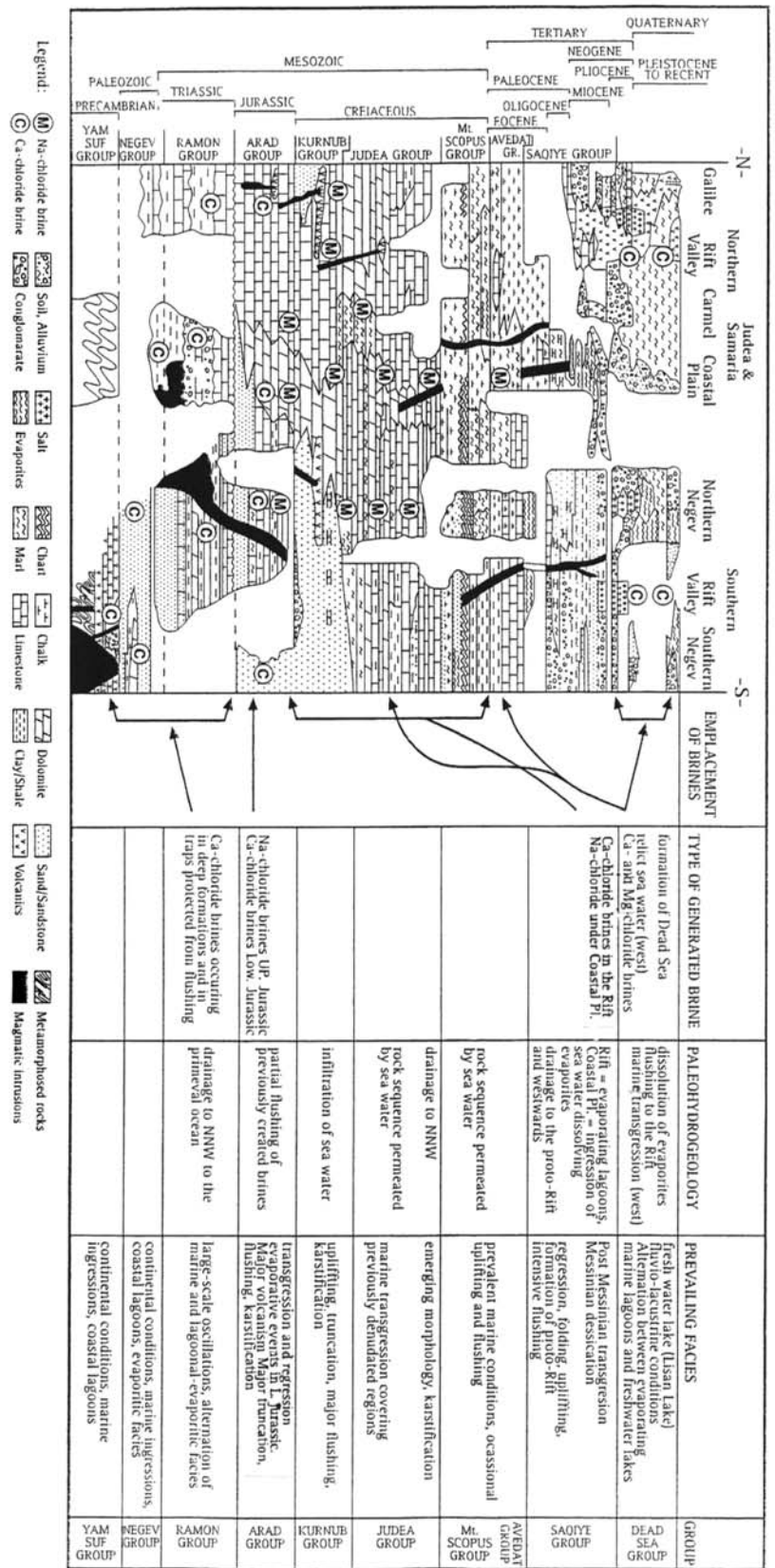


Fig. 7 The extension of the Lisan Lake and the distribution of facies during the Late Pleistocene (after Begin et al. 1980; Begin 1986)

Holocene was accompanied by the drying of Lake Lisan and its contraction to the present Dead Sea (Stein et al. 1997). According to Katz and Kolodny (1989) the early Lisan brine was similar in its chemical composition and total salinity to that of the present Dead Sea as the result of the strong subsidence of the Rift Valley particularly during the Plio-Pleistocene (Bentor 1969), the older formations (even including the Precambrian basement rocks) became exposed along the Rift Valley borders. These events led to a drastic change in the hydrodynamic regime and the old Paleozoic brines hitherto imprisoned in the mountain area, penetrated at depth into down-sunken blocks or into the overlying permeable fill of the subsiding Rift Valley (Bentor 1969). Seepages from the brines contributed effectively to the salt content of various Plio-Pleistocene Rift Valley lakes

Fig. 8 Conceptual model for the structural evolution of the area and the formation of brines



such as the Sdom, Amora and Lisan Lakes which preceded the present Dead Sea. According to Bentor's calculations (1969), these brines supplied about two thirds of the salts now present in the Dead Sea. Similar views were expressed by Starinsky (1974).

In the western parts of the country, the marine transgression which started during the Pliocene and deposited the Yafo Formation, continued into the Pleistocene. This transgression reached eastwards to the foothills of the Judea and Samaria Mts. Rosenthal et al. (1999) and Livshitz (1999) suggested that the saline groundwaters, nowadays irregularly distributed in the Judea and Avdat beds in the subsurface of these areas, could be relicts of this marine transgression. The Cl content of these waters does not exceed 21 g/L and the relevant equivalent ratios (Mg/Ca, Na/Cl and Cl/Br weight ratio) are typical of sea water.

Conclusions

Throughout the geological history of the area, four major hydrochemical phases could be discerned (Fig. 8):

The Paleozoic–Early Mesozoic Phase (Yam Suf and Ramon Groups). During this time span, major marine evaporative processes occurred in the region. The continental evaporative environments which characterized the Paleozoic–early Mesozoic, changed during the Late Mesozoic (Arad, Kurnub and Judea Groups) with prevalently marine conditions. There is chemical evidence for mixing of fluids of marine origin with the deeper brines formed during the preceding phase. The third phase in the evolution of brines was during the Mio-Pliocene. Different conditions prevailed in the areas separated by the emergent water divide. To the west of the water divide, the brines are of the marine type and could be attributed to the Post-Messinian ingression of seawater which dissolved along its flowpath halite and gypsum from the Mavkiim Formation deposited in the deep erosional channels of the Coastal Plain. East of the water divide, i.e. in the Rift and in adjoining areas, the chemical composition of the brine in the clastic Hazeva Formation seems to indicate the presence of the diluted product of the “mother brine” possibly generated by the evaporation of the Sdom Sea. Another step in the hydrochemical evolution in the Rift was the creation of Lake Lisan which became progressively saline, probably as the result of dissolution and flushing of salts deriving from the previous hypersaline Sdom Sea. The high Mg-content characterizing the waters in the Lisan beds (and in the Dead Sea) may have originated from the dissolution of post-halite salts of the Sdom Formation. The question whether the Mg-high saline groundwaters along the eastern shores of Lake Kinneret relate to the Lisan stage or are directly related to the salt diapir of Zemah, is still an open question, though the two possibilities are not contradictory.

We are nowadays witnessing another hydrochemical phase in the Rift. It is characterized by an ongoing

process of flushing out of the brines by currently recharged fresh water. There are numerous indications that man-induced changes in the hydrological regimes (i.e. groundwater exploitation) reduced the pressure of fresh groundwater counteracting that of the brines thus facilitating their upflow and the resulting contamination of fresh water-resources.

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