

The Geochemical Evolution of the Dead Sea

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ABSTRACT

The Dead Sea brine, essentially of carnallitic, Ca-chloridic composition, is produced mainly from evaporated residual seawater brine, through modifying processes which include: a) $\text{Ca} \rightleftharpoons \text{Mg}$ exchange between the brine and calcite and aragonite in the infiltrated porous rock (diagenesis); b) dissolution and incongruent alteration of carnallite to sylvite at depth (metamorphism), and c) mixing with cyclic, seawater-type saline waters, under d) multiple progressive-regressive evaporation cycles, with occasional desiccation.

INTRODUCTION

The Dead Sea is a body of brine, characterized by its Ca-chloridic and carnallitic composition. It is located within the Dead Sea Rift, where an evaporating marine gulf, followed by lakes, deposited up to 10 km of Plio-Pleistocene to Recent evaporites and elastics, known as the Dead Sea Group (Zak, 1967; 1974).

The origin of the salts and evolution of the brines of the Dead Sea basin have been discussed by various investigators (Bentor, 1961; Lerman, 1967; Loewengart, 1962; Mazor, 1968; Neev and Emery, 1967; Nissenbaum, 1969; Starinsky, 1974; Zak, 1960, 1967, 1974).

Loewengart (1962) suggested an airborne sea salts origin for the Dead Sea salts. Loewengart also proposed the still-accepted basic mechanism for changing the marine-type, sulfatic-chloridic solution into a Ca-chloridic type of brine, through $\text{Ca} \rightleftharpoons \text{Mg}$ exchange between the solution and the carbonate host rock (Loewengart, 1962; also cited in Braitsch, 1962; Loewengart and Zak, 1972; Starinsky, 1974). Zak (1960, 1967, 1974) accepted the basic approach of Loewengart, but showed that besides airborne sea salts, seawater had entered the ancestral Dead Sea basin through a Plio-Pleistocene gulf. Zak also concluded that brines of the various periods and stages exist in the subsurface, under the Dead Sea and within the surrounding older formations.

The various studies of the geochemical evolution of the Dead Sea raise questions such as its carnallitic characteristics, potassium depletion and bromine enrichment. In the following, a model of evolution is presented and an attempt is made to answer these questions on the basis of the inter-relationships between geochemical and field evidence.

FIELD RELATIONSHIPS OF THE EVAPORITES AND BRINES

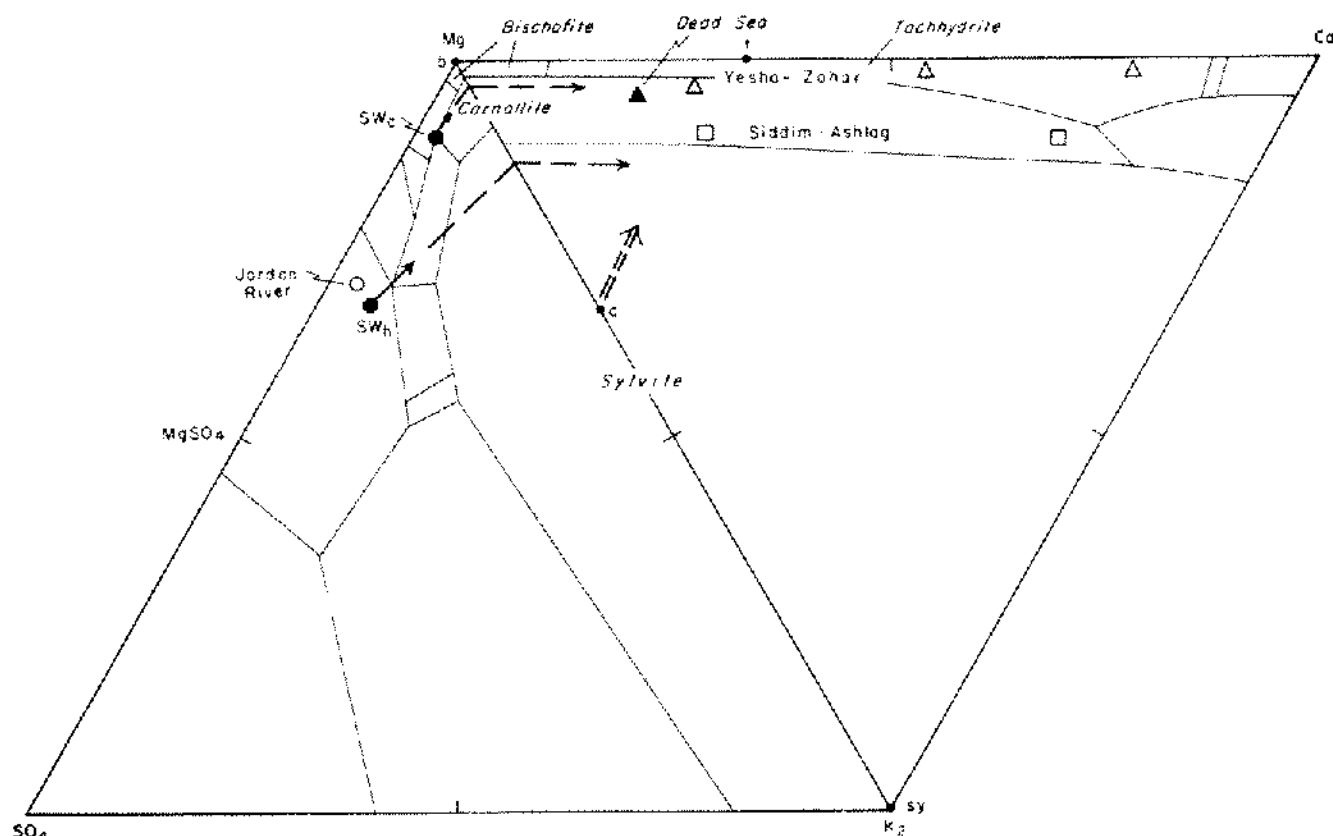
Evaporites of the Dead Sea Group are composed mainly of halite, some gypsum, anhydrite and dolomite, of marine origin. The upper part of the section contains aragonite and subsidiary, partly recycled, gypsum and halite of inland basin origin. Beds and pockets of carnallite and sylvite, formed during desiccation, also occur. The presence of Ca-chloride minerals, possibly tachhydrite, formed by diagenesis, can be inferred from the chemical composition.

Brines and saline waters of the Dead Sea basin may be classified into three main groups, according to their genetic and chemical characteristics (Fig. 1): the Yesha'-Zohar 'diagenetic' brine, the Siddim-Ashlag 'metamorphic' brine, and the Jordan-seawater type 'cyclic' saline waters.

Diagenetic brine. The Yesha'-Zohar 'diagenetic' brine, with up to several hundred g/l salt content, is Ca-chloridic ($\text{Ca}^{2+} > \text{HCO}_3^- + \text{SO}_4^{2-}$). It is found in the subsurface around the Dead Sea.

This brine is thought to have originated in the residual chloridic-sulfatic, Plio-Pleistocene marine brines, which infiltrated the subsurface of the rift and its vicinity. There it was modified into Ca-chloridic brine through $\text{Ca} \rightleftharpoons \text{Mg}$ exchange with Ca-carbonates of the enclosing rock. Calcium, which is replaced by magnesium and taken into solution, precipitates with available sulfate, and the excess remains in solution (Loewengart, 1962, and in Braitsch, 1962; Loewengart and Zak, 1972; Starinsky, 1974).

Metamorphic brine. The Siddim-Ashlag 'metamorphic' brines, with over 300 g/l salts, mainly Mg-Ca-K-Na-chlorides, are generally at halite, sylvite and also carnallite saturation, though with a relatively low Br/Cl ratio.



Figur 1. Jänecke ternary diagrams at halite saturation, for the systems: left $\text{NaCl} - \text{KCl} - \text{MgCl}_2 - \text{Na}_2\text{SO}_4 - \text{H}_2\text{O}$ (at 25°C); right $(\text{NaCl}) - \text{KCl} - \text{MgCl}_2 - \text{CaCl}_2 - \text{H}_2\text{O}$ (at 93°C), (mineral stability fields after Braitsch, 1962). Solid triangle: Dead Sea brine (Neev and Emery, 1967); Open triangle: Yesha'-Zohar 'diagenetic' brine (Zak, 1960); Square: Siddim-Ashlag 'metamorphic' brine (Zak, 1960); Open circle: Jordan River (Bentor, 1961); Solid circle: Seawater (after Braitsch, 1962); SW_h —at halite saturation point; SW_c at carnallite saturation point; Broken arrow: Diagenesis pathways: left diagram— Mg^{2+} and SO_4^{2-} loss (through $\text{Ca} \rightleftharpoons \text{Mg}$ exchange and Ca -sulfate precipitation); right diagram: Mg^{2+} loss against Ca^{2+} gain; and double arrow: Metamorphism pathways: dissolution and incongruent alteration of carnallite to sylvite by Ca-chloridic brines.

These brines are assumed to evolve through dissolution and partly incongruent alteration of carnallite (and possibly other minerals) by Ca-chloridic brines, at depth.

Cyclic saline waters. The Jordan-seawater type, 'cyclic' saline waters, mostly of runoff and phreatic origin, are sulfatic-bicarbonatic ($\text{Ca}^{2+} < \text{HCO}_3^- + \text{SO}_4^{2-}$) and chloridic, of modified seawater composition.

The Dead Sea water, with a salt content of about 300 g/l, is at carbonate, sulfate and close to halite saturation. Carnallite is the next mineral to precipitate, when the water is evaporated to half its volume.

In its chemical composition, the Dead Sea brine resembles the Yesha'-Zohar brine, with which it has a common origin. Each is modified by differentiating processes, and slow hydrostatic and density-induced infiltration and re-flushing cause the mixing of the two masses. In the hydro-chemical sense, the 150 km³ brine body of the Dead Sea may thus be regarded as an outcrop of the surrounding, bigger, Yesha'-Zohar brine mass.

A MODEL OF MIXING AND INTERACTION PROCESSES

The dynamic relationships of the brines described, are illustrated on a contiguous set of two Jänecke ternary diagrams (Fig. 1) of the system $(\text{NaCl}) - \text{KCl} - \text{MgCl}_2 - \text{CaCl}_2 - \text{H}_2\text{O}$, for the Ca-chloride brines, and of the system $\text{NaCl} - \text{KCl} - \text{MgCl}_2 - \text{Na}_2\text{SO}_4 - \text{H}_2\text{O}$, for the sulfatic-chloridic Jordan-type waters and seawater at various evaporation stages.

Both observed and theoretical paths of evolution may thus be projected in relation to the stability fields of the minerals known (and assumed) to be present. The tachhydrite-carnallite paragenesis, which is temperature-dependent, becomes apparent.

The Dead Sea brine falls well within the carnallite stability field, though at present diluted and modified through regressive evaporation, by the input of Jordan-type waters (sulfatic; higher Na/Cl ratio), Siddim brines (sylvite stage and close to carnallite stage) and Yesha' brines (carnallite

field, more Ca-chloridic). Chemical and sedimentological characteristics indicate a major subrecent progressive-regressive evaporation cycle in the Dead Sea, which has lately regressed from a carnallite stage.

The multiple cyclic nature of such progressive-regressive evaporation events is indicated by the very high Br/Cl ratio in the Dead Sea and by the presence of carnallite and sylvite deposits in the basin, as well as by sedimentological evidence of desiccation.

The evolution of the Ca-chloridic-carnallitic Yesha'-Zohar-Dead Sea group of brines from concentrated seawater, through modifying processes that include diagenetic exchange, incongruent alteration, evaporation, dilution and mixing, is demonstrated by comparing their compositions when at carnallite saturation (Fig. 1).

This geochemical evolution becomes even more meaningful when comparing it with the Ca-chloride evaporites of the proto-Atlantic Brazil and Congo-Gabon basins (Wardlaw, 1972) and with the recent brine pools of the Red Sea (Brewer and Spencer, 1969).

DISCUSSION

D. Carvalho.

Question. In your exposition you didn't mention temperature effects. So, I would like to ask you if there is a regular distribution of temperatures along the Dead Sea or are there anomalous zones that could be correlated with the "metamorphic field" of your diagram?

Answer. There is usually a temperature gradient within the Dead Sea, changing seasonally. However, the density gradient and stratification due to salinity seem to be sufficiently contrasted to be able to support an irregular, even inverted, thermal gradient which often develops, more often within the transition water layer (for more detail see Neev and Emery, 1967).

The "metamorphic" brines mentioned (Fig. 1) refer to brines believed to form through incongruent dissolution of carnallite deposits at depth, and precipitation of sylvite. No geothermal anomalies are distinguished in connection with these brines.

Positive geothermal anomalies up to 60–70°C are displayed in the Dead Sea Rift, especially by sulfatic, seawater type saline waters; some (up to 30–40°C) are displayed by the "diagenetic" brine type, in seepages at the foot of the fault escarpment bordering the Rift. Altogether the geothermal anomalies, found in the Dead Sea Rift, are weak and of rare occurrence.

I. A. Kunasz.

Questions. 1) You suggest two origins for Dead Sea brine. What about geothermal contribution? 2) You propose $\text{Ca} + \text{SO}_4$ reaction in the mix zone. Is there evidence of CaSO_4 secondary cement in the mix zone?

Answers. 1) No evidence is known favoring a quantitative geothermal contribution (see answer to D. Carvalho). 2) Where the Dead Sea type of water, which contains a very small concentration of sulfate, enters into the diagenesis zone, the gain of Ca^{2+} (replaced by Mg^{2+} , in the carbonate rock) could cause only a neg-

ligible Ca-sulfate precipitation, at most. Even at a continuous, long-term process, the precipitating Ca-sulfate would not amount to more than an indistinguishable quantity.

J.D. Martinez:

Question. Please describe the nature of the caprock at the "Lot's Wife" location.

Answer. The caprock is composed of the insoluble residue within the rock salt beds as well as of interbedded insoluble units, meters thick. It consists of anhydrite and gypsum, dolomite, clay, silt and quartz sand. The sulfates are mostly elongated in a horizontal orientation, parallel to the strike of the underlying rock salt beds.

ACKNOWLEDGEMENTS

I thank my colleagues, S. Loewengart, M.R. Bloch, L. Heller-Kallai and A. Starinsky for the many discussions and also I. Perath, whose critical review and editorial suggestions are greatly appreciated. The study was supported by the Hebrew University, Faculty of Science, Grant No. 015.0475.

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