

# Reports

## The Dead Sea: Deepening of the Mixolimnion Signifies the Overture to Overturn of the Water Column

**Abstract.** *Throttling of freshwater inputs into the meromictic Dead Sea weakened the long-term stability of the water column. Between 1975 and 1978 successive deepening of the pycnocline from 70 meters to beyond 200 meters were recorded. Complete overturn finally took place during the winter of 1978–1979. This unique process was accompanied by changes in the geochemistry of several components.*

The Dead Sea, situated at the lowest spot of the Jordan rift valley, is the terminal lake of the Jordan River system and the deepest salt lake on earth (Fig. 1A). The density profiles of the water masses of the Dead Sea from the last century until the 1960's (1) (Fig. 1B) indicate that a stable meromictic structure existed in the northern basin. In 1959 (2) the pycnocline was at a depth of about 40 m and the density difference between the upper and lower water masses [the mixolimnion and monimolimnion, respectively (3)] was considerable: the average density of the surface layer was  $1.205 \text{ g cm}^{-3}$  as compared with an in situ density in the bottom layer of  $1.233 \text{ g cm}^{-3}$ . The level of the Dead Sea has been declining since the mid-1950's as a result of the diversion of freshwater from its major water supply. This decline was accompanied by the shrinkage of the shallow southern basin, which was finally detached in 1976 (4). The excess evaporation over inflow also resulted in the gradual increase of the density of the mixolimnion, and in the years after the 1959 survey of Neev and Emery (2) there were indications of some deepening of the pycnocline layers (5). By 1975, the mean density of the mixolimnion had approached the value of  $1.23 \text{ g cm}^{-3}$  (6). Surface salinities therefore were approaching those of the deeper, supposedly fossil layer, and thus the overturn of the water column of the Dead Sea became a distinct possibility. Because of the uniqueness of such an occurrence, we organized during 1975–1979 a series of hydrographic expeditions (7) to document the impending changes in the lake. We report here on the first phase of events from 1975 until late 1978, which consisted of the deepening of the pycno-

cline while still maintaining the meromixis of the lake. During the winter of 1978–1979, complete overturn of the water masses took place.

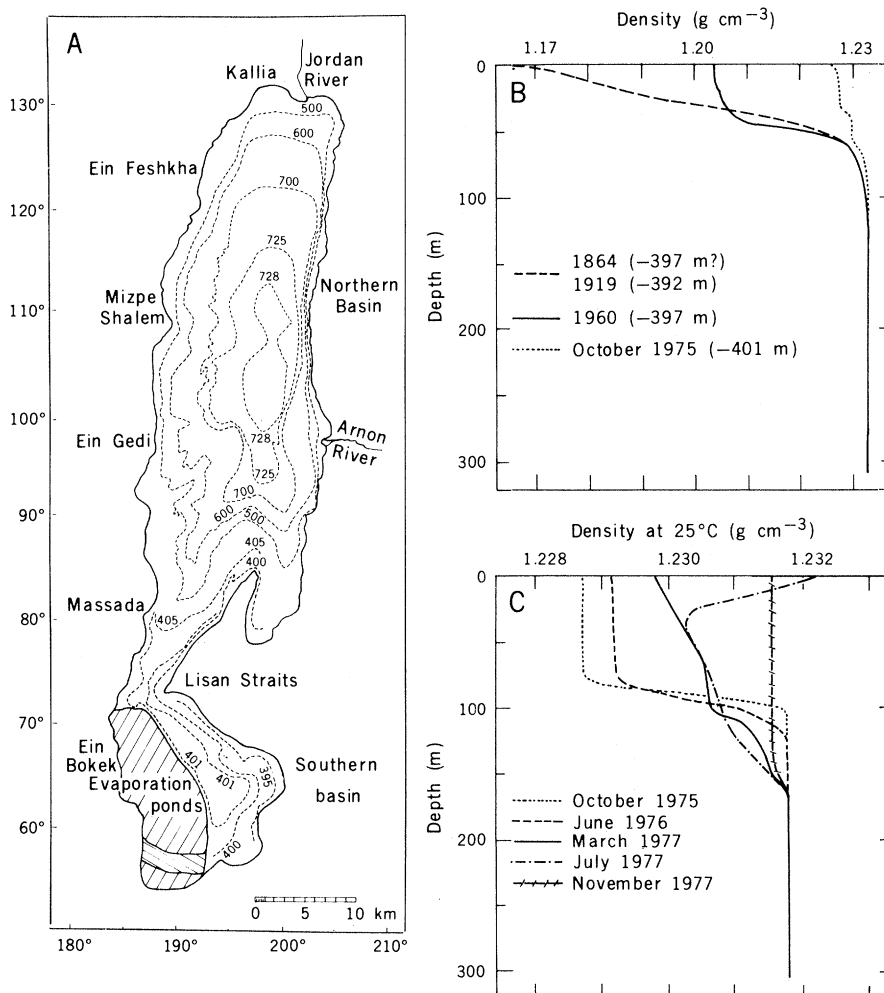


Fig. 1. Data on the Dead Sea. (A) Bathymetric map, with contour lines indicated in meters below mean sea level. (B) In situ density profiles according to literature sources. The Dead Sea levels at the times listed (in meters below mean sea level) are shown in parentheses. (C) Salinity profiles, October 1975 through November 1977, measured in terms of the density at 25°C.

As illustrated in Fig. 1C, the pycnocline (8) descended from a depth of between 70 and 100 m in 1975 to 100 to 120 m in 1976 and 130 to 150 m in 1977 (9). During this period the mixolimnion further increased in salinity both as a result of the continuing evaporation excess and the incorporation of brine from the deep-water masses. Until 1977, however, the pycnocline of the Dead Sea was still essentially maintained by the salinity gradient. After the destruction of the 1977 summer stratification within the mixolimnion, the salinity profile throughout the lake had approached uniformity to the extent of the sensitivity of our density measurements (10). Further weakening of the stability by cooling during the winter of 1977–1978 has resulted in a new positioning of the pycnocline (at this stage probably maintained mainly by a weak temperature gradient) at a depth of approximately 175 m.

The composition of the brine, that is, the concentration ratio of the major ionic constituents, had been uniform within

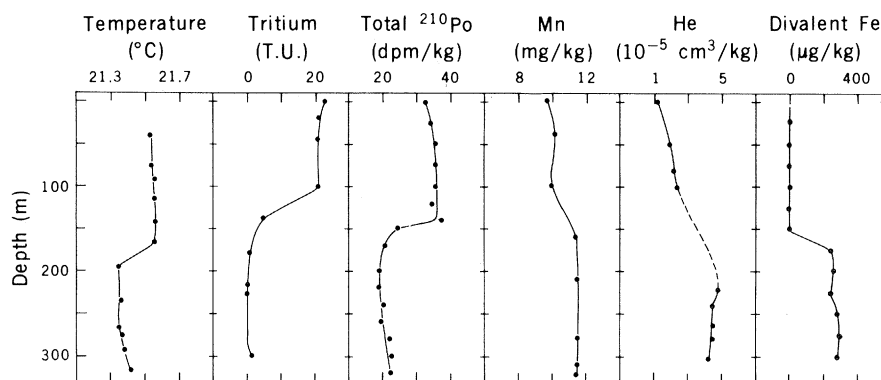


Fig. 2. Depth profiles of temperature and trace components in the Dead Sea for January through February 1978.

the analytical error throughout the lake (11). However, a number of trace metals, gaseous species, and radiotracers showed a marked discontinuity across the pycnocline (Fig. 2). In the case of Fe, S, Pb, and Mn, this was apparently related to the difference in the oxidation-reduction potential between the upper oxygenated layer and the deeper anoxic part of the lake. As an illustration, in February 1978 the pycnocline was sharply outlined by the increase of  $\text{Fe}^{2+}$  concentration across it. A decline in the  $^{210}\text{Pb}$  concentration in the monimolimnion has been explained as due to scavenging on insoluble sulfides (12), whereas the buildup of Mn concentrations in the lower water mass is attributed to the solubilization of Mn under reducing conditions to form a chloridic complex of divalent Mn.

The immediate effect of the volume change associated with the descent of the pycnocline on the concentration of the tracer is obviously one of dilution; the concentration changes that subsequently take place reflect individual geochemical properties, and rates of adjustment range from the almost momentary oxidation of divalent Fe on exposure to oxygen to the slow buildup of the  $^{210}\text{Pb}$  concentration from its parent  $^{226}\text{Ra}$  on a time scale dictated by the radioactive half-lives and scavenging rates. The concentrations of tritium ( $^3\text{H}$ ) are dictated by the exchange rate across the water surface and the rates of internal mixing within the mixolimnion and the transition layer. The complex interplay of these transport rates is reflected in the shape of the tritium profile and that of other gaseous components (Fig. 2).

At a time when salinity profiles were approaching uniformity, we found the chemical tracers to be reliable indicators of the vertical structure of the lake. According to these indicators, mixing evidently had not proceeded extensively be-

low 175 m by February 1978 (Fig. 2). Partial analysis of data at the end of the summer of 1978 indicated a possible further deepening to beyond 200 m.

During the 1960's when the stratification in the northern basin was still based on a large salinity gradient, the bottom water mass was considered to be essentially fossil. Investigators differed, however, with respect to their estimate of its age (13). At that time dense brines from the shallow southern basin spilled down into the northern part of the lake, fanning out at the pycnocline layer and stabilizing the whole system (1, 14). Whether on occasions a dense parcel of brine descended into the lower water mass remains a moot point. An excess of tritium was consistently found near the floor of the basin (15) and can be interpreted to be the result of such a process. The influx of submarine springs, which is suggested by the excess of terrigenous helium (16) in the monimolimnion, could also contribute to this tritium anomaly.

By November 1978, the water column of the Dead Sea was still not uniform and its meromictic condition was apparently determined by a delicate interplay between salinity buildup through evaporation, dilution by floods, and the annual temperature cycle. However, it appears that at this stage the waters below the pycnocline had not remained as isolated as before. We observed, for example, that samples brought up from the deep layers during 1978 did not smell of  $\text{H}_2\text{S}$ , whereas all deepwater samples obtained prior to this period had been characterized by a conspicuous odor of  $\text{H}_2\text{S}$ .

During our latest cruise (4 to 10 February 1979), we found evidence for complete overturn of the Dead Sea water masses: the temperature was uniform throughout the 320-m water column (with the exception of the top 10 m) at a level somewhat warmer than the pre-

viously recorded temperature of the monimolimnion; divalent Fe was absent all the way down to the bottom of the lake, and the Mn profile was also uniform.

It is especially interesting, from the point of view of the mixing dynamics, that the final overturn was preceded by a lengthy process of erosion of the monimolimnion and deepening of the mixolimnion. In the final stages, however, changes within the lower water mass occurred in parallel with the further deepening of the pycnocline layer. The overturn of the Dead Sea water masses terminates the centuries-long meromictic state of this unique lake.

I. STEINHORN, G. ASSAF

J. R. GAT, A. NISHRY

A. NISSENBAUM, M. STILLER

Weizmann Institute of Science,  
Rehovot, Israel

M. BEYTH, D. NEEV

Israel Geological Survey, Jerusalem

R. GARBER, G. M. FRIEDMAN

Rensselaer Polytechnic Institute,  
Troy, New York 12181

W. WEISS

University of Heidelberg,  
Heidelberg, Germany

#### References and Notes

1. G. Assaf and A. Nissenbaum, in *Desertic Terminal Lakes*, G. D. Greer, Ed. (Utah State Univ., Logan, 1977), pp. 61-72.
2. D. Neev and K. O. Emery, *Isr. Geol. Surv. Bull.* 41 (1967), p. 147.
3. As defined in G. E. Hutchinson, Ed., *A Treatise on Limnology* (Wiley, New York, 1957).
4. Dead Sea brines continue to be pumped by the Dead Sea Potash Works into a ponded part of the southern basin, which serves as an evaporation pond (Fig. 1A); highly concentrated "end-brines" then spill back into the northern basin.
5. D. Neev (unpublished data) found the transition layer at 65 m.
6. M. Beyth, in *Hypersaline Brines and Evaporitic Environments*, A. Nissenbaum, Ed. (Elsevier, New York, in press).
7. Logistic support was provided by the Dead Sea Potash Works Ltd.
8. For the purpose of discussing the dynamics of the deepening of the mixolimnion, it makes sense to locate the position of the pycnocline as the lowest point of the transition layer, at a depth where the properties of the deep fossil layer just are undisturbed. Referring to other depths leads to ambiguities in the case of the Dead Sea with its multistage structure of the transition layer and especially when one is comparing the depth profiles of a variety of geochemical parameters (Fig. 2).
9. I. Steinhorn and G. Assaf, in *Hypersaline Brines and Evaporitic Environments*, A. Nissenbaum, Ed. (Elsevier, New York, in press).
10. The density ( $25^\circ\text{C}$ ) was determined pycnometrically to  $\pm 0.0001 \text{ g cm}^{-3}$ .
11. Average composition of the Dead Sea brines (in grams per liter) in March 1977 was as follows:  $\text{Mg}^{2+}$ , 44.0;  $\text{Ca}^{2+}$ , 17.2;  $\text{Na}^+$ , 40.1;  $\text{K}^+$ , 7.65;  $\text{Cl}^-$ , 224.9;  $\text{Br}^-$ , 5.3;  $\text{SO}_4^{2-}$ , 0.45; and  $\text{HCO}_3^-$ , 0.2. The total dissolved salt content was 339.6 g/liter. Local changes in the  $\text{Mg}^{2+}/\text{Ca}^{2+}$  ratio occur as a result of introduction of "end-brines" from the evaporation ponds (6).
12. M. Stiller, in an unpublished progress report on the Binational Science Foundation Project 936, "The mixing regime and geochemistry of water masses of the Dead Sea," J. R. Gat and D. Neev, principal investigators (1978), p. 10.
13. Neev and Emery (2) estimated an age of more than 1000 years; Assaf and Nissenbaum (1) considered the upper water mass to have been formed some 160 years ago. These estimates are

- based on the assumption of very small mass exchange across the pycnocline, possibly limited to the rate of molecular diffusion [A. Lerman, *Geochim. Cosmochim. Acta* **31**, 2309 (1967)].
14. It is obvious that this circulation was curtailed since the mid-1970's with the gradual throttling of the Lisan Straits and the final disconnection of the southern basin in 1976; the Dead Sea has since become horizontally more homogeneous as indicated by temperature measurements.
  15. W. F. Libby in 1960 found an excess of 1 tritium unit (T.U.) in bottom waters; J. Houtermans in 1965 gave a value of  $2.5 \pm 0.2$  T.U. at 300 m (off Ein Gedi) compared to 1.6 T.U. at a depth of 200 m (the latter sample was probably slightly con-

taminated during sampling). A profile taken off Massada in shallower water gave  $5.08 \pm 0.3$  T.U. at 155 m (bottom); the surface tritium content at that time was 175 T.U. A similar trend can be observed in the 1978 profile in Fig. 2: bottom waters (at 300 m), 1.5 T.U.; waters at 240 m, 0.25 T.U.; and surface waters, around 20 T.U.

16. Measurements by H. Craig (1978).
17. Financial support was provided by the Israel-United States Binational Science Foundation (Project 936), the National Geographic Society, and the Minerva Science Foundation.

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## Catalytic Production of High-Grade Fuel (Gasoline) from Biomass Compounds by Shape-Selective Catalysis

**Abstract.** Shape-selective hydrocarbon catalysis, such as the conversion capability of zeolite catalysts of the ZSM-5 type to produce high-grade gasoline from methanol, can be extended to produce a similar gasoline or aromatics from plant extracts. Examples are rubber latex, corn oil, and peanut oil. Novel mechanisms for shape-selective reaction sequences are demonstrated.

We have explored the use of molecular shape-selective catalysts (1) for direct and efficient conversion of high-molecular-weight biomass constituents to high-quality chemical components or fuel (gasoline).

The most talked-about biomass-to-liquid fuel scheme, and the only scheme

that is of major national commercial significance, is that for converting grain carbohydrates to ethanol. There is growing interest in such a process for displacing nonrenewable resources (petroleum and natural gas) by biomass crops. As described in greater detail elsewhere (2), the true productivity and true cost of the

net high-grade fuel in that case depends on the agricultural energy proficiency (that is, by how much the amount of high-grade fuel input initially invested in the agricultural effort is "amplified" by solar energy addition), and the efficiency of the conversion process (that is, the subsequent "attenuation" of the biomass energy in converting it to the high-grade fuel product). We are therefore interested in exploring highly efficient conversion technology.

It is common experience in the catalytic conversion of fossil fuel constituents (for example, petroleum crude fractions, coal liquids, and coals) that the efficiency of conversion to hydrocarbon fuels increases for organic compounds with higher hydrogen-to-carbon ratios and lower heteroatom contents. For this reason, biomaterials that are hydrocarbons or hydrocarbon-like are particularly interesting candidates for conversion to low-molecular-weight fuels or chemical raw materials. Calvin and co-workers (3) have proposed a search for plant species that generate a high proportion of hydrocarbon-like constituents. Buchanan and co-workers (4) have summarized a number of plant species that contain this class of material.

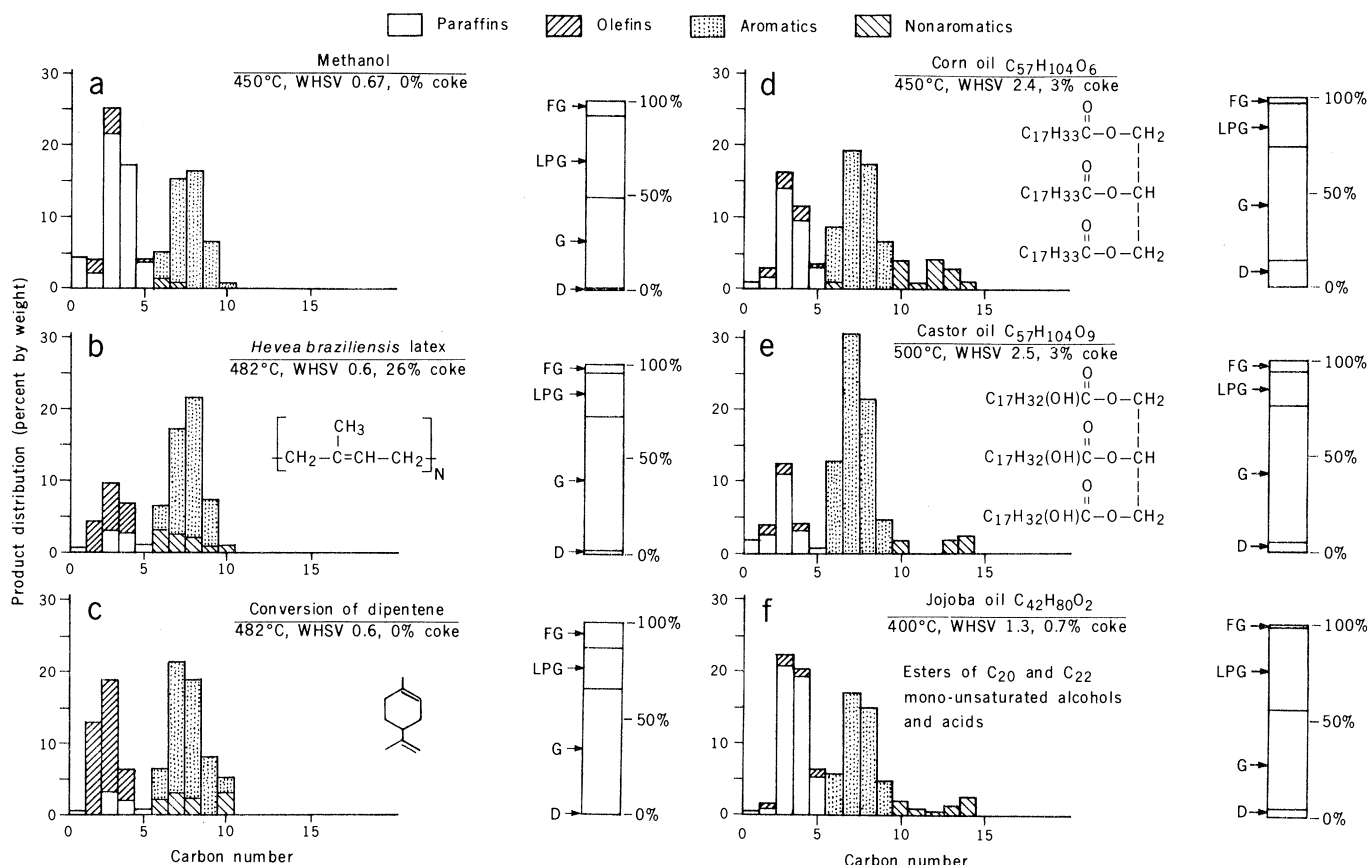


Fig. 1. Product spectra from catalytic conversion of methanol, and of various biomass constituents. The abbreviations FG, LPG, G, and D are for fuel gas, liquid petroleum gas, gasoline, and light distillate, respectively; WHSV is for weight-hourly space velocity.