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Discovery and chemical composition of the eastmost deep-sea anoxic brine pools in the Eastern Mediterranean Sea

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Deep-sea anoxic brine pools are unique and extreme, yet habitable environments. However, their extent and processes of formation are not fully understood. Using geophysical analysis and seafloor surveying, we discovered the eastmost brine pools known in the ultraoligotrophic Eastern Mediterranean Sea, at the Palmahim Disturbance offshore Israel (~1150 m water depth). These brine pools are located directly above a ~1km wide piece of the Messinian evaporites section, which was up thrusted to ~350 m below the seafloor. We sampled brines and short cores to characterize the chemical composition of several small (up to 5m diameter) anoxic, methanic and warm (21.6°C) brine pools and adjacent seafloor sediments porewater. The maximal salinities measured at the pools and adjacent porewater were 63.9 and 72 PSU, respectively. The brines are characterized by enriched Na and Cl concentrations by a factor of ~1.8 and depleted Mg, SO₄, K and Ca contents by factors of circa 6, 3, 2 and ~1.3, respectively, compared to the ambient seawater. Relations of the major element concentrations reveal a mixing curve between seawater and enriched Na/Cl and depleted Mg/Cl, K/Cl and SO₄/Cl end-members, and do not coincide with relics of fossil residual evaporated seawater. We propose their composition reflects: 1) dissolution of Messinian halite (NaCl) by seawater, supported by their low Br/Cl ratios; 2) additional small rise in Na/Cl ratios due to the impact of clay mineral dehydration or/and dissolution of trace (~1% of the Na) amounts of detrital trona (Na₃H(CO₃) 2•2H₂0), coinciding with the enriched alkalinity concentrations; 3) diagenesis processes depleting Mg, K and SO₄, mainly by the formation of authigenic Krich Mg-smectite, clay mineral dehydration, dolomitization/Mg-calcite precipitation and redox processes. The δ^{18} O and δ D values of the Palmahim brine may reflect the impact of clay mineral dehydration. Comparison to all other East Mediterranean brine lakes shows that the Palmahim brine pool system represents similar provenance of brines as observed for the Eastern Mediterranean Napoli, Nadir and Tyro lakes, while potentially recording additional processes attributed to its proximity to the coastal area.

KEYWORDS

Mediterranean Sea, brine pools, chemical composition, deep-sea, seawater, evaporites, Levant Basin

1 Introduction

Deep-sea brine pools accumulated in seafloor depressions have been discovered in different water bodies, notably in the Gulf of Mexico (Shokes et al., 1977), the Mediterranean (Jongsma et al., 1983; Scientific Staff of Cruise Bannock 1984-12 - Cita et al., 1985) and the Red Seas (Charnock, 1964; Swallow and Crease, 1965; and recently Purkis et al., 2022). The Red Sea occupies the utmost number of brine pools attributed to the dissolution of sub-surface evaporites, which were geochemically categorized into two main types, those situated along the deep axis influenced by seismic/rift spreading and consequent hydrothermal fluid and water/volcanic rock interactions and those tied to sediment alterations (Schmidt et al., 2015; Purkis et al., 2022).

The eastern Mediterranean basin contains several complexes of seafloor brine pools at different sub-basins, in which the Tyro and Bannock were the first brine pools discovered in 1983-4 (Jongsma et al., 1983; Cita et al., 1985; De Lange et al., 1990). The Discovery Basin found in 1993-94 had the highest salinity found in the marine environment (Wallmann et al., 1997b) till the recent discovery of Lake Hephaestus, the youngest athalassohaline deep-sea formation (La Cono et al., 2019). Due to their unique chemical composition, these mostly anoxic brine pools that occupy only a small area of the basin were considered hostile to life. Yet, they were found to host unique macrofauna and microbial biodiversity, being extreme environmental hot spots of productivity (Wallmann et al., 1997a; Aloisi et al., 2002; Van Der Wielen et al., 2005; Daffonchio et al., 2006; Edgcomb et al., 2007; Bernhard et al., 2014; Pachiadaki et al., 2014; Merlino et al., 2018; Steinle et al., 2018).

Brines accumulate at the seabed of collapsed basins in the East Mediterranean, having diverse thicknesses up to a few hundred meters (Cita, 2006). Moreover, high salinity values of interstitial waters (up to 350 g/L) were measured in post-Miocene sediments from different Mediterranean Deep Sea Drilling Project sites (McDuff and Gieskes, 1976; Vengosh and Starinsky, 1993; Vengosh et al., 1994). The creation and variable chemical composition of such deep anoxic brine-filled basins are

related to the distribution of Messinian evaporites and suggest the dissolution of different layers or levels of the Messinian suite (Cita, 2006).

The origin of these brines is attributed to two main processes: 1) dissolution of the late Miocene (Messinian) evaporites by seawater; 2) upwards advection of fossil relict brines produced during the Messinian evaporites deposition (Vengosh et al., 1998). The second mechanism was suggested by them to represent relict seawater evaporated to different degrees of concentration and hence different chemical compositions. Several studies infer the brine origin based on the chemical composition of the brines, considering their modification by diagenetic and advection-diffusion processes. Thus, some brine lakes like the Discovery, Kryos and Hephaestus are MgCl₂-dominated systems that were attributed to the dissolution of Mg evaporites, mainly bischofite (La Cono et al., 2019). Other brine lakes like, Urania, Bannock and Tyro were related to either the dissolution of different stages of evaporites precipitated in the Messinian or the consequent relics of fossil evaporated seawater entrapped in the sediments and advected upwards (De Lange et al., 1990; Vengosh et al., 1998; Cita, 2006).

The Levant Basin is underlain by Messinian evaporites, reaching a thickness of about 2 kilometers in the center of the basin and pinching out underneath the basin's margins (Gardosh and Druckman, 2006; Roveri et al., 2014; Gvirtzman et al., 2017; Meilijson et al., 2019; Manzi et al., 2021). The salt had undergone extensive and multiphasic deformation from near syn- to post-depositional (Gvirtzman et al., 2013; Feng et al., 2017). The deformation is controlled by both the marginal loading of the sediments as well as the underlying structure (Reiche et al., 2014; Gvirtzman et al., 2015; Ben Zeev and Gvirtzman, 2020). As the salt deforms, it modifies and shapes the seafloor morphology in the region. The Palmahim Disturbance is a significant (c. 50 x 15 km) submarine slide deforming the continental margin of southern Israel, attributed to gravitational slumping above the Messinian evaporites (Garfunkel et al., 1979). Local evocation of Messinian evaporites and extensive faulting at the base of the Palmahim disturbance form potential conduits that allow fluid seepage to the surface (Eruteya et al., 2018).

Following a geophysical study of the area, we conducted in April and November 2021, remotely operated vehicle (ROV) based visual surveys of the ~1150 m deep seabed in the toe domain of Palmahim Disturbance, 60 km offshore the Israeli Mediterranean coast. During this survey, we discovered a complex of several small brine pools, located geographically at the eastmost part of the basin, east of the other deep anoxic brine pools discovered in the Mediterranean Sea. Here, we report on our discovery and aim to characterize the physical and chemical settings of the brines, assessing the brine origin. Our study is based on unique *in-situ* measurements that were performed with a CTD mounted on an ROV arm, as well as measurements of the chemical composition in samples from the brine pool and porewater from a short sediment core at the edge of one pool.

2 Materials and methods

2.1 Geophysical data and bathymetry

Preliminary site evaluation and site selection were carried out based on an analysis of the Oz 3D seismic volume. These commercial 3D seismic data were acquired by Ion-GTX over an area of 400 km² using ten 8 km long streamers with a cable separation of 100 m. The data were depth migrated to produce a $25 \times 12.5 \times 8$ m resolution 3D volume. Our geophysical analysis was carried at the University of Haifa Applied Marine Exploration Lab. (AMEL) using the AspenTech Subsurface Science & Engineering software suite.

Initial bathymetric mapping of the study area was carried out using a Kongsberg EM302 and by a Knudsen chirp 3260 Sub-Bottom profiler with 3.5 kHz central frequency mounted in a gondola beneath Israel Oceanographic and Limnological (IOLR) R/V Bat Galim (Kanari et al., 2020). In January 5, 2021, a high-resolution seafloor survey was carried out using the University of Haifa ECA robotics A18D Autonomous Underwater Vehicle (AUV, SNAPIR) deployed from R/V Bat Galim. The SNAPIR AUV surveyed the seafloor with a Kraken MINSAS120 Interferometric Synthetic Aperture Sonar (SAS) at 3cm/pixel resolution, Edgetech 2205 Sub-bottom profiler and a NORBIT 400 kHz central frequency WBMS Multibeam Echo sounder. A preliminary analysis of these data, carried at AMEL, was used for the planning of the ROV survey.

2.2 ROV-based visual surveying and water and sediment sampling

Two ROV surveys, incorporating visual video and *in situ* measurements and sampling, were carried out in the Palmahim

Disturbance toe site (Figure 1) using the University of Haifa SAAB Seaeye Leopard Yona ROV, deployed off R/V Bat-Galim. The Yona ROV is equipped with a Schilling Orion 7P Manipulator, SubC 1CAM lite Mk6 (4K) main camera as well as 3 additional SD cameras. An exploratory ROV survey of the site was carried out April 19-29, resulting in the discovery of the brine pools. The main sampling and *in-situ* measurement survey at the site were conducted during 15-17 November 2021.

A Sea-Bird SBE16plusV2 CTD system was mounted on the ROV to collect *in-situ* measurements of pressure, temperature, salinity and dissolved oxygen. To enable a precise controlled insitu measurements of the brine we attached a tigon tube to the arm of the ROV (Figure 1) and connected its other end to the CTD pump. Measurements of the brine pools were performed by introducing the arm alone into the pool (Figure 1). The manufacturer reported precision of the SBE16plusV2 CTD is ± 0.004 for salinity (inferred from the ± 0.0005 S/m conductivity precision) and ±0.005°C for temperature. The pressure, conductivity and temperature sensors were calibrated by the manufacturer (as described in Ozer et al., 2020). CTD data was processed using the Sea-Bird data processing software following the manufacturer's recommendations. In addition, water samples for dissolved oxygen were sampled and measured onboard immediately upon retrieval following the modified Winkler method (Carpenter-Winkler titration procedure Carpenter, 1965), using an automated Metrohm Titrando 905 titration system to calibrate the dissolved oxygen of the CTD.

A Niskin bottle was mounted horizontally on the front part of the ROV and was triggered using the ROV arm once inserted into the brine pool. Short push-cores (30 cm long Perspex tubes) were collected adjacent to the pool edge using the ROV. Porewaters for major and minor ions were sampled using Rhizons immediately upon retrieval of the ROV onboard from 5 depth horizons and the sediment overlaying water. Sediment samples (~2 ml) for methane concentrations were collected with edge cut syringe from the perspex corer which contains side holes (1 cm in diameter) and immediately transferred into a flushed argon glass bottle containing 5 ml sodium hydroxide (1.5 N) for headspace measurements of methane concentration (after Nusslein et al., 2003). The bottle was sealed with a crimper.

Ambient seawater samples were collected with the R/V Bat-Galim at parallel depths (\sim 1150 m) using Niskin bottles mounted on a Seabird rosette at about 50 km northward to Palmahim Disturbance for the comparison between the chemical composition of the brine pools and porewater to the ambient seawater.

2.3 Chemical analysis

Onboard, water samples were immediately collected directly from the Niskin bottles. The brine salinity (expressed as



FIGURE 1

Bathymetry and location map of the discovered brine pools at the edge of Palmahim Disturbance, 1100m water depth (A-C). Extracts of video documentation of the brine pools as visualized by the remotely-operated vehicle (ROV) (D-F, scale in panel (D) is approximated) and *in-situ* CTD measurement of the brine by pumping water *via* a tigon tube attached to the arm of the ROV (E, F).

conductivity), pH, and dissolved oxygen concentrations were measured onboard immediately upon sampling using a WTW Multi 3630 IDS sensor. The pH electrode was calibrated against the standard NBS buffers.

2.3.1 Major and minor ions

Chemical analysis of the brine, porewater and seawater samples was performed by standard spectrometric methods: Na, K, Mg, Ca, and Sr were analyzed by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) Optima 5300 Perkin Elmer. Samples dilution was 1:10, an internal standard of Scandium (Sc) was used (final concentration of 5 ppm) and the analytical precision was estimated within $\pm 0.5\%$. Cl and Br were analyzed by Dionex ICS-2000 Ion Chromatography. The analytical precision was within $\pm 3\%$. Ba, Li and Mn were measured by ICP-MS (Inductively coupled Plasma Mass Spectrometry) NexION 300D, Perkin Elmer. The analytical precision was within $\pm 10\%$. Quality control was performed by the run of 3 Standard Reference Samples (SRSs) of the U.S. Geological Survey (USGS).

2.3.2 Total alkalinity

was measured by potentiometric titration with a Methrom, 848 Titrino plus system using the Gran method to calculate it from acid volumes and corresponding pH measurements between pH 3.3 and 3.8 (Sass and Ben-Yaakov, 1977). The titration acid was 0.05 M HCl, which was verified and adjusted using certified reference seawater supplied by the Certified Reference Materials Laboratory, Scripps Institution of Oceanography, CA (Dickson et al., 2003). Duplicate measurements were made for each sample and the precision error was $\pm 1 \ \mu mole \cdot kg^{-1}$.

2.3.3 Methane

Was measured from the headspace on a Focus Gas Chromatograph (Thermo) equipped with a flammable ionization detector (FID) at a precision of 2 mmol CH4 L^{-1} (Sela-Adler et al., 2017).

2.3.4 δ^{18} O, δ D measurements

For δ^{18} O measurements clean vacuum vessels were flushed with a gas mixture of He (99.6%) and CO_2 (0.4%) for 10 minutes to remove the original atmosphere. After flushing, 0.7 cm of the sampled water was injected to the vessels and left to equilibrate with the CO₂ gas for at least 48 hours at 25°C. Values of δ^{18} O were measured using a Finnigan Gas Bench II extraction system in continuous flow connection with a ThermoFinnigan Delta V mass-spectrometer, following the CO₂ - H₂O equilibration technique (Epstein and Mayeda, 1953). All oxygen isotopic measurements were made in duplicates and are reported relative to Standard Mean Ocean Water (SMOW). Four wellquantified internal laboratory standards were used for calibration. \deltaD measurements were performed using a Thermo Finnigan High-Temperature Conversion Elemental Analyzer (Flush2000-EA) attached to a Delta V mass-spectrometer at a reaction temperature of 1450°C (Nelson, 2000). \deltaD values are reported relative to SMOW. Analytical reproducibility of duplicates was better than 0.1‰ for $\delta^{18}O$ and 1.0‰ for $\delta D.$

3 Results and discussion

3.1 Geophysical setting at the Palmahim Disturbance brine pools

The study area is located in the northwest part of the Palmahim Disturbance compressional toe domain, as defined by Garfunkel et al. (1979). Our analysis shows that the Messinian to present sedimentary section in this area has undergone complex deformation (Figure 2). This includes folding and combined southeastward up thrusting and left lateral strikeslip displacements along multiple salt-rooted faults. These faults accommodate hundreds of meters of offsets, changing their modes and deformation amplitude along their strike and producing ridges and throughs in the present bathymetry. In particular, an up to ~ 1 km wide and ~3 km long portion of the Messinian evaporites section was up-thrusted by ~1 km, with its top reaching ~350 m below the present seafloor. Directly above the shallowest tip of the up-thrust Messinian sliver, we observe tens of meters wide bathymetric depressions, underlain by high amplitude reflectivity within tens of meters below the seafloor. Similar reflections have been related to active methane seepage farther to the south at the toe domain of Palmahim Disturbance (Rubin-Blum et al., 2014; Eruteya et al., 2018; Tayber et al., 2019). These observations prompted the focused seafloor surveying of this site, leading to the discovery of the Palmahim Disturbance brine pools. We, therefore, suggest that focused seepage of fluids and methane, routed through the subsurface Messinian evaporites sliver, lead to the formation and on-going seepage of the discovered brine pools. The deformation and

faulting of the salt have been suggested as a mechanism that may facilitate the migration of fluids to the seafloor in the Levant basin (Eruteya et al., 2018; Tayber et al., 2019; Oppo et al., 2021).

Seafloor surveying of the site discovered a complex of several small (up to 5 m diameter) brine pools (Figure 1) at 1150 m water depth, in the toe domain of Palmahim Disturbance, 60 km off the Israeli Mediterranean southern coastline. At least 5 brine pools were positively identified. The pools are clustered within an area of ~1,500 m² and visually seem to be inter-connected (in part) by a system of stream channels. All pools have circular shapes probably owning to their mode of development and formation.

3.2 Geochemistry of the Palmahim Disturbance small brine pools

We mapped the distribution patterns of salinity, temperature and dissolved oxygen in selected brine pools and their vicinity, based on the *in-situ* CTD measurements, which were segmental, as the CTD pump was not enabled constantly to avoid damage by sediment particles (Figure 3). The maximal recorded salinity and temperature were 63 PSU and 21.6°C, whereas all measurements adjacent and above the pool complex or brine-seawater interface, were higher than the ambient background levels (Figure 3). Our observations suggest that regardless of the sharp interface between the brine and bottom seawater, the latter exhibits minor enrichment of salinity and temperature probably attributed to certain diffusion or advection caused by the bubbling out or upwards of methane bubbles, as

FIGURE 2 Seismic imaging of the subsurface near the brine pools. Two intersecting depth migrated profiles across the location or the brine pools (star in A, arrow in B-E), one along an NNW-SSE trend (B, C) and one along a WSW-ENE (D, E) show the Messinian salt being segmented by faults and up thrusted towards the surface, reaching to shallowest levels beneath the discovered brine pools.







visualized by the ROV survey. We also consider disturbance by biota, mainly by the shark *Galeus melastomus*, which occurred in large numbers in the brine pools area, and was often observed swimming next to the brine pools. *In-situ* dissolved oxygen measurements indicate anoxic conditions (<0.1% saturation) within the brine pools. This coincides with the onboard measurements showing values of 0.04-0.7 mg L⁻¹ (decreasing), likely representing both the limited mixing with the bottom seawater and the substantial respiration at the interface. We measured high concentrations of dissolved Mn (up to 10.1 μ M) in the brine pools and porewater (Figure 4; Tables 1, 2), which are typical below oxic-anoxic interfaces, including anoxic brines (De Lange et al., 1990).

We collected 3 samples from two distinct brine pools with a horizontal Niskin bottle mounted and triggered by the ROV. While it was technically impossible to set the Niskin vertically, the replacement of water *via* the horizontal Niskin was limited in the smaller and shallower brine pool (samples BP3 and BP5, Table 1) and thus the collected water represents the brine and some "contamination" of bottom seawater. Therefore, the chemical composition of those samples represents a mixture between the brine end-member and the ambient seawater. We additionally analyzed the porewater chemical composition of a short (\sim 12 cm) push core collected by the ROV at the edge of one of the pools (Figure 1). The chemical composition of the most saline brine and porewater samples at Palmahim Disturbance, ambient seawater and other brine lakes in the Eastern Mediterranean Sea were compared to assess their origin (Table 2). In the Palmahim Disturbance brine, Na, Cl, Li and Sr are enriched, while Mg, K, SO₄, Br are depleted compared to the ambient seawater (Figure 4). Compared to other Mediterranean brine pools, our results exhibited the lowest Mg concentrations and similar Na/Cl and Mg/Cl ratios as Napoli, Nadir and Tyro brine pools (Table 2).

The chemical composition of all the samples collected here, 3 brine pools and 6 porewater samples, are presented in Table 1, and were used to assess their provenance (end-members) by comparison to the expected seawater evaporation composition,



dissolution of Messinian evaporites and potential diagenetic processes.

Cross-plotting relationships of the major element concentrations reveal a mixing curve between seawater and enriched Na or Cl and depleted Mg, K, SO₄ end-member (Figure 4). The linear increasing trend line for Na, Li and Sr vs. Cl, and the linear decreasing trend line for Mg and SO₄ vs. Cl (Figure 4) suggests an enriched NaCl and depleted Mg and SO₄ end member impacting the brine pool and top porewater composition. The potential enrichment of Na and Cl *via* the dissolution of subsurface evaporitic halite attributed to the Late Miocene (Messinian) crisis by seawater cannot explain the observed relatively high Na/Cl ratios to the full extent (Figure 4). These ratios are much higher than the expected ratios attributed to relics of seawater evaporation path or modified/residual brines after the precipitation of evaporites, starting with halite at a degree of evaporation >10 or Na concentration of ~5500 mM (McCaffrey et al., 1987; Shalev et al., 2018).

A recent study suggests that porewater from the Napoli mud volcano may be affected by clay mineral dehydration hence a decreasing chlorinity and thus increasing Na/Cl ratios (Behrendt et al., 2022). Such a process may explain an enriched Na/Cl endmember which consists of halite dissolution by seawater and additional diagenetic removal of Cl. The relatively low Br/Cl ratios also support the dissolution of early-stage halite evaporites containing low crystalized Br (Shalev et al., 2018).

Considering the linear decreasing relationships between Mg and SO₄ vs. Na or Cl (Figure 4) and assuming a Na end-member at complete removal of Mg and SO₄, a value of 1034-1056 mM Na is calculated. This range represents a contribution of approximately 35% additional Na due to halite dissolution and removal of ~8% of Cl by dehydration. An alternative process that may explain Na/Cl ratios higher than expected by seawater

Parameter Water Type	Na mM	K mM	Ca mM	Mg mM	Sr mM	Cl mM	SO4 mM	Br mM	Li µM	Ba µM	Mn μM	δ ¹⁸ O ‰	δD ‰	pН
Ambient seawater* 1100m	528	12.9	11.3	58.6	0.094	624	31.3	1.047	32.41	0.09	0.01	1.5	7.0	8.01
brine pool-3	578	12.8	13.6	53.2	0.196	661	29.3	0.880	33.33	4.15	0.46	1.5	3.9	7.31
brine pool-4	831	6.8	14.7	28.9	0.641	859	15.2	0.838	58.70	4.88	1.91	2.0	-6.5	7.03
brine pool-5	575	11.2	12.9	55.2	0.170	653	29.3	0.864	31.88	3.28	10.11	1.5	4.8	7.26
porewater-1	857	5.9	10.3	19.7	0.803	920	11.0	0.849	80.43	45.16	4.28	na	na	na
porewater-2	928	5.3	9.2	12.1	0.884	978	8.5	0.831	90.58	63.73	1.28	na	na	na
porewater-3	828	11.4	10.9	23.6	0.700	877	13.4	0.853	75.36	10.71	3.19	na	na	na
porewater-4	746	11.3	10.5	32.3	0.554	817	16.2	0.868	64.49	9.47	2.82	na	na	na
porewater-2T	722	8.1	11.8	40.1	0.440	772	22.7	0.878	51.45	10.92	3.90	na	na	na
porewater-4T	617	11.0	14.0	54.6	0.215	680	28.0	0.895	36.23	4.73	0.73	na	na	na

TABLE 1 Chemical composition of the Palmahim Disturbance brine pools and porewater.

na, not analysed.

*the ambient seawater isotopic composition from Sisma-Ventura et al. (2016).

dissolution of halite is the addition of Na *via* dissolution of trace amounts (~1% Na) of detrital trona (Na₃H(CO₃)₂•2H₂0) and/or thenardite (Na₂SO₄), which were observed in sediment cores off the Nile delta (Stanley and Sheng, 1979). The most dominant alkalinity-producing reactions are anaerobic oxidation of methane and carbonate dissolution, followed by sulfate reduction and denitrification processes (Aloisi et al., 2002; Brenner et al., 2016). While the anaerobic oxidation of methane results in a very alkaline environment which promotes carbonate precipitation, sulfide oxidation results in a highly corrosive environment due to the production of sulfuric acid. In addition, at the brine-seawater interface the organic matter mineralization and release of CO_2 may also have a small corrosive impact (Sisma-Ventura et al., 2021). The increased alkalinity in the anoxic brine pools, may thus reflect the latter reactions. However, given that the change in alkalinity is not

TABLE 2 Chemical composition of the Palmahim brine pool (Pal 4) and porewater (Pal PC), ambient seawater and brine pools in the Eastern Mediterranean seafloor.

Reference	Ambient	Pal 4	Pal	Discovery	Urania	L'Atalante	Bannock	Tyro	vro Medee	Thetis	Kryos	Hephaestus	Napoli	Nadir
	seawater PC This study			Benhard et al., 2014				*De Lange et al., 1990	Yakimov et al., 2013	La Cono et al., 2011	#La Cono et al., 2019		&Charlou et al., 2003	
	mM	mМ	mМ	mM	mМ	mМ	mM	mМ	mM	mМ	mmol/ kg	mmol/ kg	mМ	mM
Na	528	799	928	68	3503	4674	4235	5300	4178	4760	125	93	1347	1884
Mg	58.6	27.9	12.12	4995	316	410	650	71.1	788	604	4380	4720	33.9	27.9
Ca	11.3	14.2	9.22	2.6	32	7.3	17	35.4	2.8	9	1	2	8.4	22.2
K	12.92	6.59	5.30	19.6	122	369	127	19.2	471	230	80	28	8.1	7.2
Cl	624	829	978	9491	3729	5289	5360	5350	5269	5300	9043	9120	1380	1979
SO ₄	31.3	15.2	8.46	96	107	397	137	52.7	201	265	320	203	28.4	37.8
Br	1.05	0.81	0.83	110#			9.02*	1.28	65.3	6	70	78	0.69	0.44
Li	0.032	0.057	0.091				0.28*	0.075	0.163	0.09			0.057	0.04
Sr	0.09	0.62	0.88				0.17*	0.33					0.04	0.17
CH4	nd	0.9	13	0.031	5.56	0.52	0.45		0.07		4**		0.06	5.94
Na/Cl	0.85	0.96	0.95	0.01	0.94	0.88	0.79	0.99	0.79	0.90	0.01	0.01	0.98	0.95
Mg/Cl	0.094	0.034	0.012	0.526	0.085	0.078	0.121	0.013	0.150	0.114	0.484	0.518	0.025	0.014
K/Cl	0.021	0.008	0.005	0.002	0.033	0.070	0.024	0.004	0.089	0.043	0.009	0.003	0.006	0.004
SO ₄ /Cl	0.050	0.018	0.009	0.010	0.029	0.075	0.026	0.010	0.038	0.050	0.035	0.022	0.021	0.019
$\delta^{18}O$	1.5	2.0	na	-2.39#	2.54&							-3.06	2.23	2.06
δD	7.0	-6.5	na	-17.9#								-16.5		

**Steinle et al., 2018 - µmol/kg; na, not analysed.

conservative, and that it does not correlate to a change in Ca concentration, another mechanism may also contribute. This might be the dissolution of trona which would contribute bicarbonate. Indeed, the enriched alkalinity concentrations in the 3 pool samples (Table 1; up to 15,363 μ mol kg⁻¹) show much higher values than ~ 2610 μ M of the ambient seawater (Sisma-Ventura et al., 2016), similar to the corresponding dissolution of trona, assuming an addition of approximately 1% Na.

The lower Mg, K and SO₄ contents support interaction with sediments during early-to-late diagenesis (Boschetti et al., 2011) and redox processes (Van Der Weijden, 1992). A depletion of SO₄ is attributed to sulfate reduction and the anaerobic oxidation of methane. The Palmahim Disturbance porewater show clear methane enrichment ranging from 4 to 13.8 mmol $CH_4 L^{-1}$. Methane emission may be related to compressed sediments or gas hydrate destabilization, which may occur at mud volcanoes, seeps and vents related to fault systems (Charlou et al., 2003). We note that considering the anoxic conditions in the brine pools and porewater, it is likely that a certain portion was originally presented as H_2S and thus the SO₄ versus Cl would have been different.

The depletion of K and Mg from porewater may be attributed to the formation of authigenic K-rich Mg-smectite in marine evaporative environments (Hover, 1999) and dolomitization. In addition, subsurface processes of burial diagenesis of the transformation of smectite to illite clay mineral fixes K from porewater even under relatively low temperatures (Hover et al., 2002; Ijiri et al., 2018)

The δ^{18} O and δ D values of the most saline brine pool at Palmahim Disturbance are 2.0% and -6.5%, respectively. Slightly enriched in ¹⁸O but heavily depleted in ²H (D) compared to mean values of 1.5% and 7.0 % of the EMS deep water (Sisma-Ventura et al., 2016), respectively (Figure 5). Messinian halite fluid inclusions may carry depleted or enriched, positively correlated δ^{18} O and δ D values (Rigaudier et al., 2011; Evans et al., 2015), yet counting for only ~0.2% wt, their dissolution results with minimal isotopic impact during mixing with the seawater end-member. The $\delta^{18}O$ and δD values of the most saline brine pool may therefore reflect the impact of clay mineral dehydration (Dählmann and de Lange, 2003) as for the isotopic composition of pore and fluid water from sediment cores at the Napoli and Milano mud volcanoes dome sites, yet slightly depleted in the δ^{18} O. They indicate a deep end-member typified by enriched δ^{18} O and depleted δ D values related mainly to the smectite-illite transformation process and estimated that this reaction efficiently removes Cl. The latter may explain both, the isotopic composition and the excessively high Na/Cl ratios in the Palmahim Disturbance brines. In addition, the δ^{18} O values in Palmahim Disturbance are somewhat lower than the expected levels of evaporated seawater to the salinity of 63 PSU, reinforcing that its brine isotopic composition is not solely sourced from evaporated seawater. Yet, the slightly enriched δ^{18} O but much depleted in δD compared to the EMS deep water indicates that clay mineral dehydration is likely affecting the brine pool isotopic composition.



 δ^{18} O and δ D values of Palmahim Disturbance brine samples (circles), ambient seawater (star) and the Discovery and Hephaestus brine lakes (diamonds). From Dählmann and de Lange (2003): the distribution range of pore fluids from 2 ODP sites (970 and 971) at Milano and Napoli mud volcanoes (gray squares and mixing line); GH - gas hydrate (δ^{18} O +3‰, δ D +20‰); MD - clay mineral dehydration (trend leading towards δ^{18} O +20‰, δ D -70‰). MMWL - Mediterranean meteoric water line (δ D =8 δ^{18} O +22‰) with meteoric water that corresponds to the SW value. Messinian halite inclusions fall on the line (δ D =3.82 δ^{18} O -26.41‰) (Rigaudier et al., 2011).



3.3 Comparison to other Eastern Mediterranean brine pools

The major ion ratios, mainly cross plotting of ion/chloride ratios (Figure 6) assist in revealing the characteristics and origin of the Palmahim Disturbance brine/porewater as compared to other East Mediterranean brines (Table 2 and references therein). Two main mechanisms were suggested as a source of the East Mediterranean brine pools: 1) dissolution of Messinian, mainly late-stage evaporites, precipitated along different degrees of seawater evaporation. The following main minerals were experimentally identified at different degrees of evaporation: gypsum (CaSO₄.2H₂O), halite (NaCl), epsomite (MgSO₄•7H₂O), kainite (KMgClSO₄•3H₂O), carnallite (MgKCl₃•6H₂O), kieserite (MgSO₄•H₂O) and bischofite (MgCl₂•6H₂O) (McCaffrey et al., 1980; Shalev et al., 2018); 2) relics of fossil residual evaporated seawater representing different degrees of evaporation/salinity. During the evaporation path of seawater, the composition or ions ratios of the relict brine change and they become relatively enriched in Li, Br and B (Vengosh et al., 1998; Vengosh et al., 2000; Shalev et al., 2018) attributed to salts precipitation (McCaffrey et al., 1980; Shalev et al., 2018). The latter two processes may interact and are followed by diagenetic processes mainly water-rock interactions, which further changes their composition, mainly regarding Mg, Ca, K and SO₄.

The Na/Cl and Mg/Cl ratios vs. Cl (Figure 6) show brine pools attributed to halite dissolution (e.g. Lakes Napoli, Tyro), dissolution of Mg salts under late-stage evaporation, mainly bischofite, for example, lakes Hephaestus, Discovery and Kryos (La Cono et al., 2019) and of relics evaporated brines, such as Urania and Bannock (Vengosh et al., 1998; Charlou et al., 2003). The Palmahim Disturbance brine represents the lowest Mg/Cl ratios and a Na/Cl ratio beyond the maximum that can be attributed to the dissolution of halite based on its Na or Cl enrichments from the ambient seawater concentration. Nonetheless, the Palmahim Disturbance brine show Na/Cl, Mg/Cl and K/Cl ratios similar to the Napoli and Nadir lakes, as well as to Tyro lake, except Mg/Cl (Figure 6).

The Palmahim Disturbance brine/porewater represents separate characteristics from other East Mediterranean brines in terms of its relatively high and low Na/Cl and Mg/Cl ratios, respectively. While most other brine lakes are located at the deep basin (bathyal depths), the Palmichim Disturbance site is at the toe of the continental slope (relatively close to the coastline), potentially exposed to coastal shelf sabkhas in the past (Lugli et al., 2013). These coastal features would also be connected to the base of the slope through an extensive canyon system that excavated the Levant margin prior and during the salt emplacement (Buchbinder and Zilberman, 1997; Reolid et al., 2022).

4 Summary

We report here for the first time the chemical characteristics of the eastmost brine pools discovered in the eastern Mediterranean basin. Based on their chemical composition it is suggested that this small brine pools system represent similar provenance of brines as observed in the Napoli lake while recording additional process attributed to water-rock interactions, redox processes and potential impacts of its proximity to the past coast and evaporative sabkhas. Its physical-chemical characteristics and methane-degassing environment create a unique biological oasis in contrast to its barren, ultra-oligotrophic surroundings.

Data availability statement

The original contributions presented in the study are included in the article/supplementary material. Further inquiries can be directed to the corresponding authors.

Author contributions

Conceptualization: MY, R-BM and HB; Data acquiring: HB, S-VG, OT, KM, AG, GA, JY, BO, MY, R-BM; Formal analysis: HB, S-VG, BO, LM, MY; Project administration: R-BM, MY; Writing original draft: HB, S-VG, BO, R-BM, MY with the help of authors. All authors approved the submitted version.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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