

Review

Exhumation of Messinian evaporites in the deep-sea and creation of deep anoxic brine-filled collapsed basins

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Abstract

The first part of the paper summarizes some basic concepts concerning (a) the distribution of Messinian evaporites in the deepest parts of the Mediterranean Sea and (b) the Mediterranean Ridge accretionary wedge and its peculiar characteristics deriving from the presence of a substantial evaporitic body in the deforming sedimentary prism.

Then five brine-filled anoxic collapsed basins (Tyro, Bannock, Urania, Atalante and Discovery), discovered from 1983 to 1994, are presented and discussed in their physiographic, geologic, hydrologic and geochemical characters. High density brines deriving from submarine dissolution of outcropping or subcropping evaporites accumulate at the bottom of collapsed basins, if they are not swept away by submarine currents. The interface separating normal sea-water from high density brines is sharp with a density contrast of about 20% and lies at 3200–3500 m below sea level. Strong bacterial activity is developing at the interface and living bacteria have been recovered from the anoxic salty brines. Thickness of the brines may be up to 500 m. Thermal stratification has been observed in three brine lakes. Exhumation and dissolution of Messinian evaporites in the Mediterranean Ridge occur in different tectonic settings: pull-apart basin (Tyro), subducting seamount close to the outer deformation front (Bannock Basin), top of a backstop (Urania, Atalante and Discovery Basins).

Chemistry of the brines is strongly variable and suggests dissolution of different layers or levels of the Messinian suite. Discovery brines are the saltiest ever recorded in natural environment. Their saturation in Mg chloride (bischofite), the end product of sea-water evaporation, suggests that the deepest parts of the eastern Mediterranean were close to dryness at the end of the salinity crisis, strongly supporting the deep basin desiccation model.

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Contents

1.	Forward and motivation	358
2.	Introduction	358
2.1.	Messinian evaporites in the deep-sea	358
2.2.	The Mediterranean Ridge accretionary wedge	358
3.	The anoxic brine lakes originated by submarine dissolution of Messinian evaporites (described from W to E)	363
3.1.	Bannock Basin	363
3.2.	Medriff Brine lakes	364
3.3.	Tyro Basin	366

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4.	Discussion.	367
4.1.	Brine lakes versus brine pools.	367
4.2.	Relationships between anoxic basins and mud volcanoes	372
5.	Conclusions	374
	Acknowledgments	375
	References	375

1. Forward and motivation

The Messinian Workshop held in Corte in July 2004 celebrating thirty years of active research on the Messinian salinity crisis (MSC) showed beyond any doubt how successful the integrated approach has been to increase the stratigraphic resolution and to refine the correlation potential of the various proxy data utilized. Nevertheless, a certain dischasy is still noticed between the numerous scientists working on outcrops in the various circum Mediterranean countries, and those who concentrate on the deep-sea record. The latter is very rich nowadays, as a result of five drilling campaigns (DSDP Legs 13 and 42a; ODP Legs 107, 160 and 161) and on a number of important scientific cruises carried out in the last several years on the Mediterranean Ridge, centered on topics of broad geological significance as mud volcanism, fluid flow in a rapidly deforming accretionary prism containing an important evaporitic formation, submarine dissolution of Messinian evaporites.

The MSC in general has been investigated in depth but a final word is still missing. With a few exceptions (see [Blanc, 2000, in press](#)) the passage from the conceptual model to a numerical model is lagging behind (closure of the hermeneutic circle sensu [Miall and Miall, 2004](#)).

My impression was that the geological community gathered in Corsica was largely unaware of some recent findings (which are essential for budgeting the MSC), notwithstanding the numerous publications dedicated to the topic, including three Nature papers, three special issues of *Marine Geology* and one of *Marine Chemistry*. This impression proved to be correct. In other words, the motivation for my presentation in Corsica, jointly with Angelo Camerlenghi, was essentially aimed at communicating to a large group of land geologists some results of several geological, geophysical and geochemical expeditions.

This is not a research article presenting new observational data and their interpretation. Nor is it a complete review of all the findings documenting in detail the geochemical and microbiological aspects of brine lakes and mud volcanoes. A discussion extended to the

interrelationships among mud diapirism and expulsion of high density brines through fluid venting has been added following the suggestion of the reviewers.

2. Introduction

2.1. Messinian evaporites in the deep-sea

The existence of Messinian evaporites in the deepest basins of the Mediterranean Sea was first discovered in 1970, during DSDP Leg 13 ([Ryan et al., 1973](#)). Drilling in the Balearic, Tyrrhenian and Ionian basins allowed to identify the pan-Mediterranean Horizon M (of [Hersey, 1965](#)) as the interface separating evaporites similar to and correlative with the Messinian evaporites outcropping in Sicily ([Decima and Wezel, 1973](#)) from deep-sea hemipelagic “Trubi” facies marls of early Zanclean age ([Hsü et al., 1973; Cita, 1973](#)).

The estimated volume of Messinian evaporites in the deep-sea is of one million cubic kilometres ([Ryan, 1973](#)). Their distribution is indicated in [Fig. 1](#) after [Rouchy and Caruso \(2004\)](#).

[Montadert et al. \(1978\)](#) distinguished several seismic facies characteristic of the Messinian evaporites; “upper evaporites” well layered, calibrated in several deep-sea holes, “salt layer” (couche fluante, well characterized geophysically) and “lower evaporites” well layered, never calibrated so far ([Lofi et al., 2004](#)).

According to [Montadert et al. \(1978\)](#), thicknesses of total evaporitic sequence range from 3500–3600 m (Herodotus Abyssal Plain (AP), north Mediterranean Ridge Basin) to 1600–1200 m (Balearic AP, Ionian AP). Maximum thickness on land (800 m) is recorded in the central-southern Sicilian Basin (see also [Rouchy, 1982](#)).

2.2. The Mediterranean Ridge accretionary wedge

The Mediterranean Ridge is nowadays universally interpreted as an accretionary prism developed above a subduction plane, but at a time when the basic seismic and geologic exploration was carried out (see [Hersey, 1965; Rabinowitz and Ryan, 1970; Ryan et al., 1970; Finetti and Morelli, 1973; Ryan et al., 1973](#)) the conceptual models of accreted terrains were not developed yet. Further research

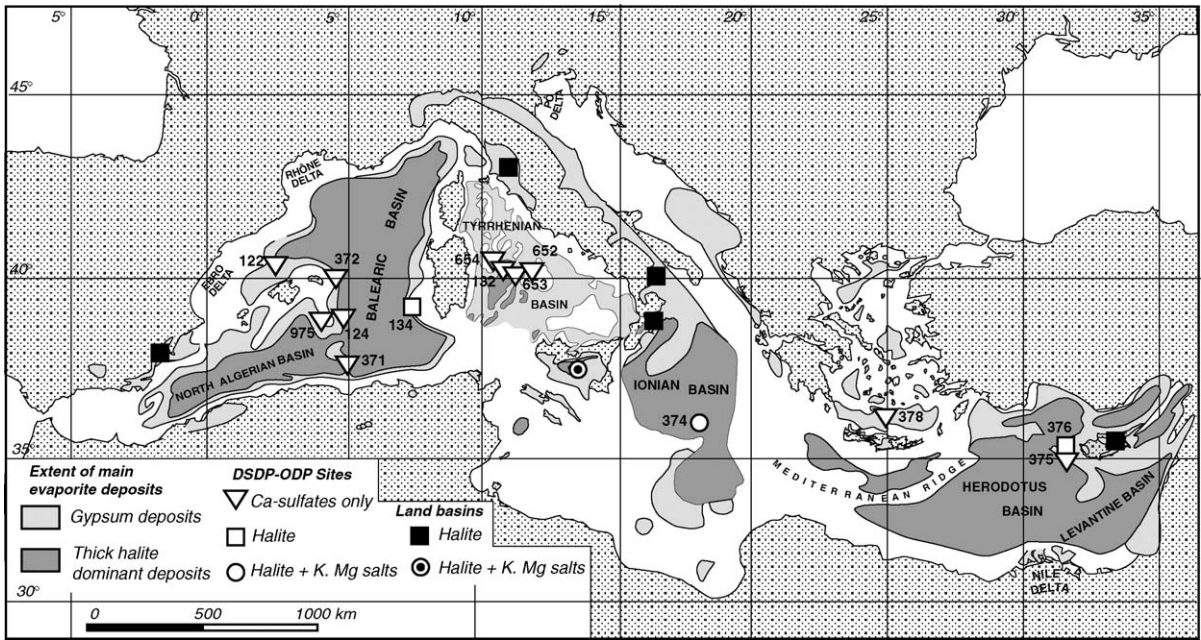
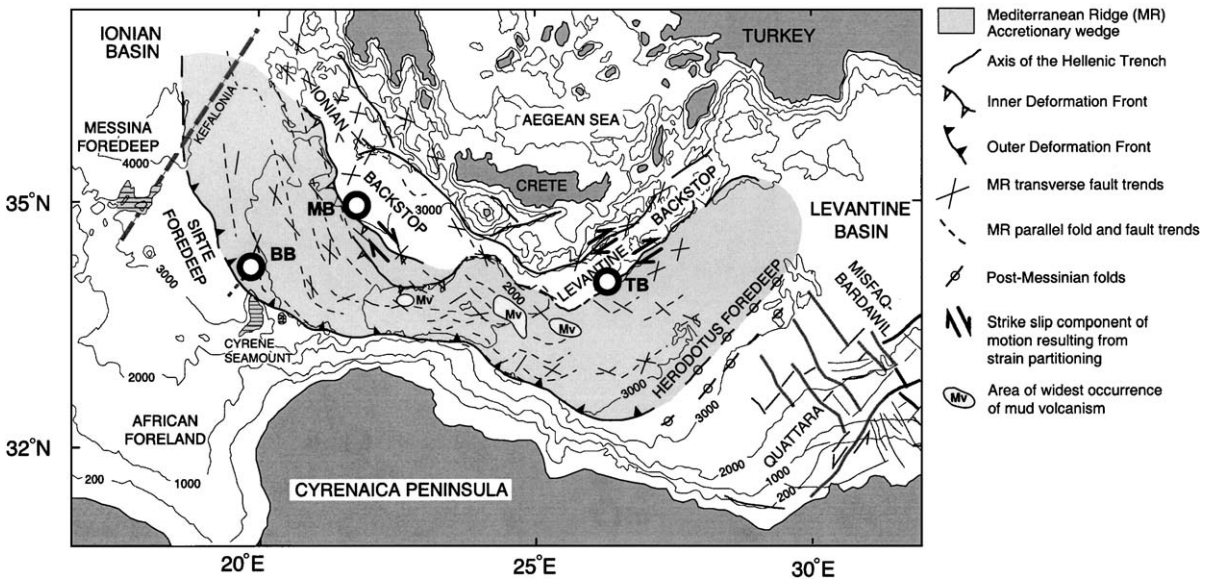


Fig. 1. Distribution of Messinian evaporites beneath the floor of the Mediterranean Sea (after seismic reflection profiles and well calibration) and on surrounding land (after Rouchy and Caruso, 2004).

using modern technologies allowed a better understanding of the ridge (Finetti, 1976; Stride et al., 1977; Le Pichon and Angelier, 1979; Le Pichon et al., 1982; Ryan et al., 1982; Jongmsa, 1987) and of its peculiar char-

acteristics such as the unusual width (250 km) and the low tapering angle at the deformation front (tapering angle 1.5–2°). The occurrence, at shallow depth, of Messinian evaporites and their variable thickness are considered



BB: BANNOCK BASIN; MB: MEDRIFF BASINS (URANIA, L'ATALANTE, DISCOVERY); TB: TYRO BASIN

Fig. 2. Structural scheme of the eastern Mediterranean and location of brine lakes discussed in this paper (courtesy of Angelo Camerlenghi). MB = MEDRIFF brine lakes; TB = Tyro Basin; BB = Bannock Basin.

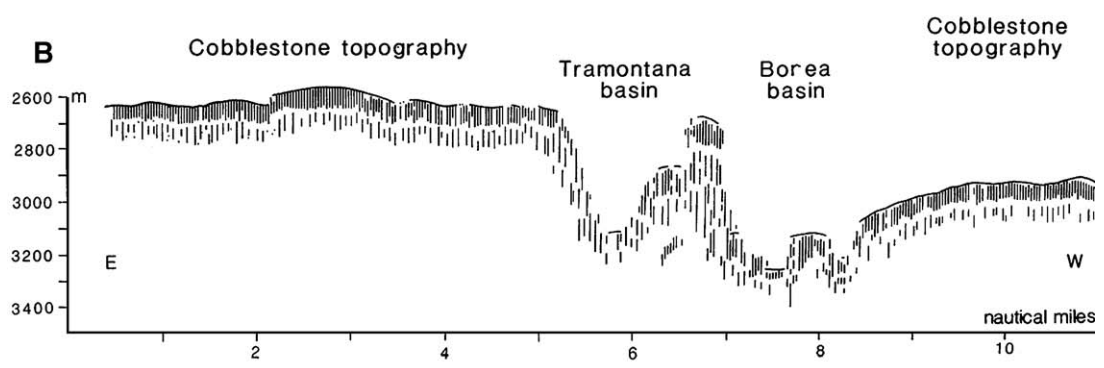
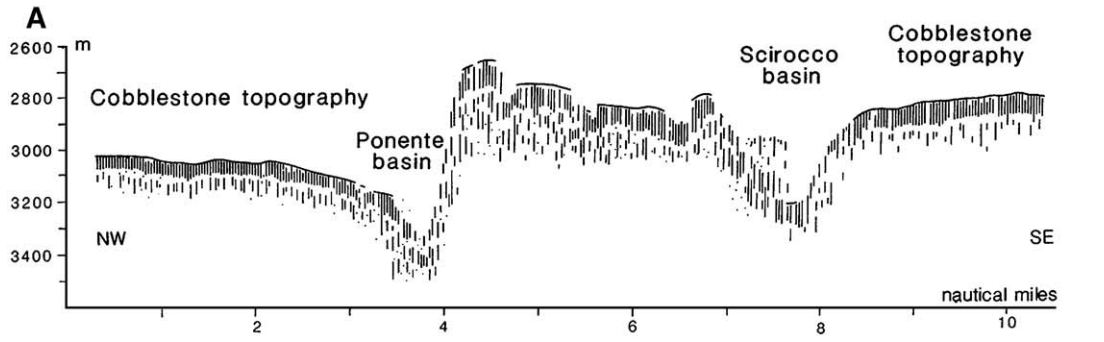
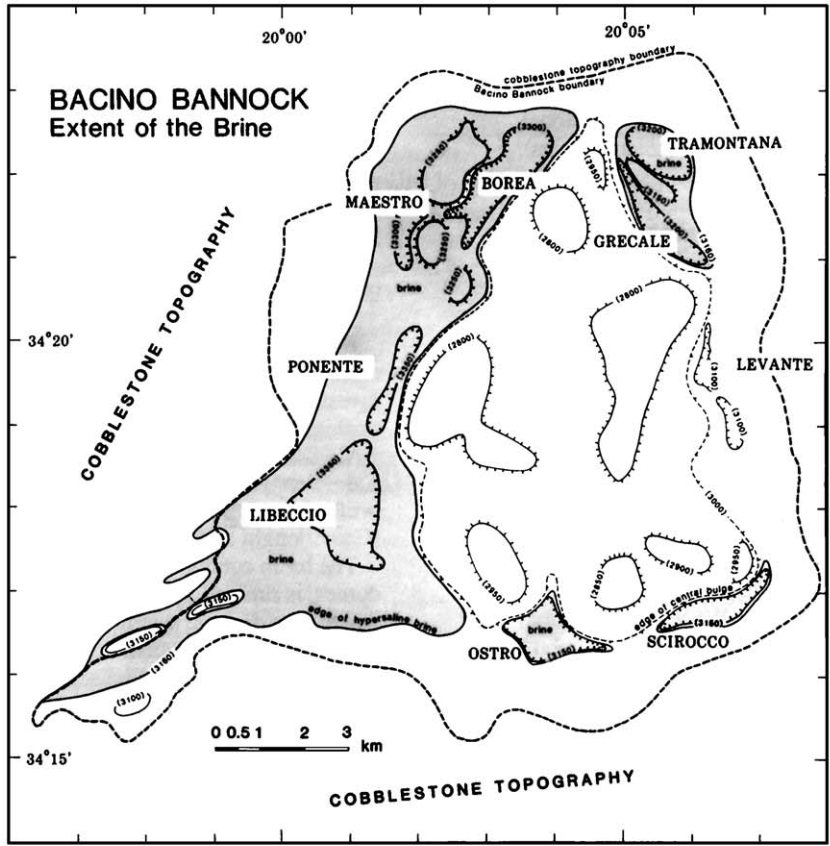


Fig. 3. Simplified contour map of the Bannock Basin (top) and narrow-beam profiles (bottom) (after Camerlenghi and McCoy, 1990; Cita, 1991, modified).

responsible for all these anomalies (see Kastens, 1981; Kastens and Spiess, 1984; Camerlenghi, 1988; Kastens et al., 1992; Chaumillon et al., 1996; Camerlenghi, 1998; Westbrook and Reston, 2002; Reston et al., 2002; Costa et al., 2004).

The western part of the Mediterranean Ridge differs from the eastern part because it is perpendicular to the direction of the convergence between the African and European plates (the rate of convergence is 35 to 38 cm/y according to Le Pichon et al., 1982), whereas the eastern

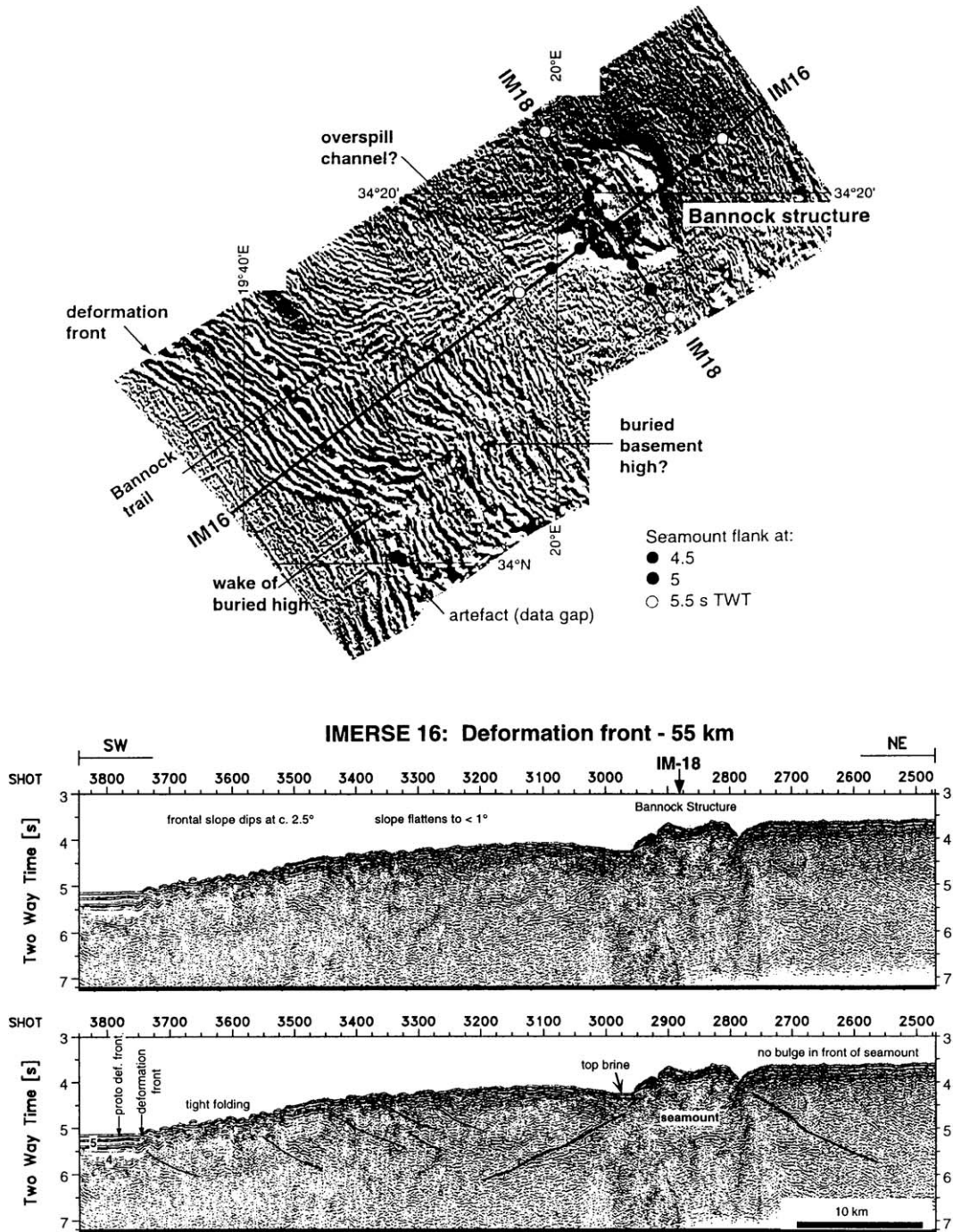


Fig. 4. The Bannock structure as mapped with the most advanced techniques (top) and interpretation of the deep penetration seismic reflection profiles (bottom) (after von Huene et al., 1997).

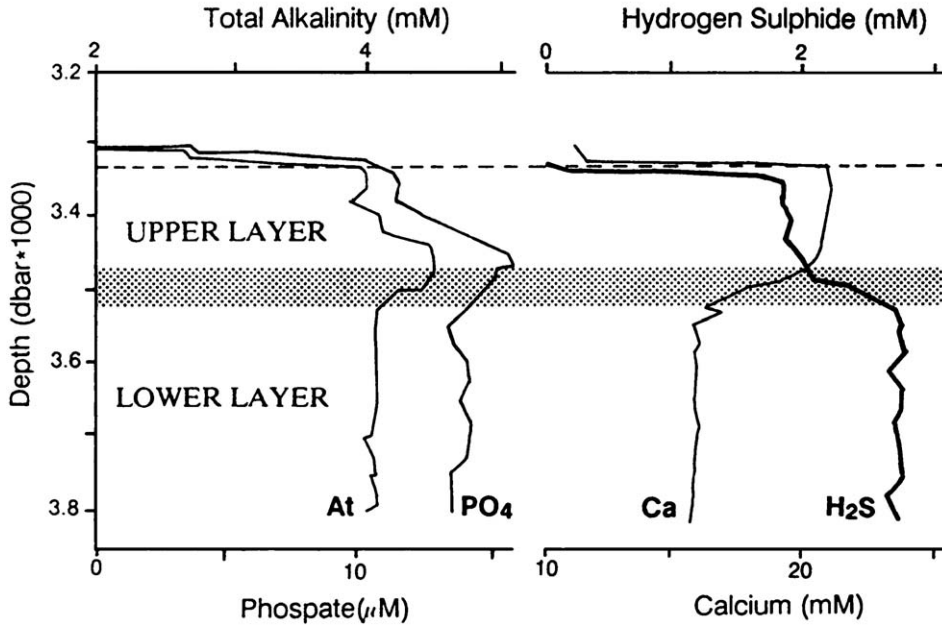


Fig. 5. Curves showing the variations in various chemical parameters measured in the brines of the Bannock Basin, Libeccio subbasin (after Catalano et al., 1989). Notice the distinction of two discrete layers.

part of the ridge is oblique to convergence (Costa et al., 2004). The Ridge is characterized by the so-called “cobblestone topography” (Hersey, 1965; Kastens, 1981; Cita et al., 1982; Camerlenghi and Cita, 1987), a rugged surface which is related to the presence of Messinian evaporites at shallow depth, but may derive — especially in the eastern part of the ridge — by shale

diapirism (see Cita et al., 1981, 1989; Camerlenghi et al., 1992, 1995; Cita et al., 1996a,b).

The Plio–Quaternary deposits overlying the Messinian evaporites are thin, ranging from 100 to 200 m, due to the low sedimentation rate of hemipelagic marls (Blechsmidt et al., 1982; Cita et al., 1982; Parisi et al., 1987) and the absence of turbidites in elevated areas.

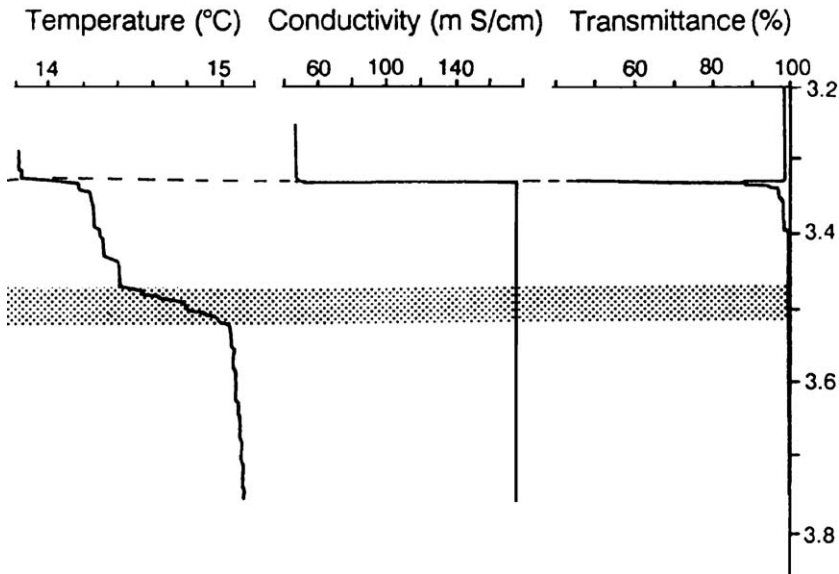


Fig. 6. CTD profiles measured across the brine-normal sea-water interface in the Libeccio subbasin (after Rabitti and Boldrin, 1989). The thermal structure is distinctly double-layered.

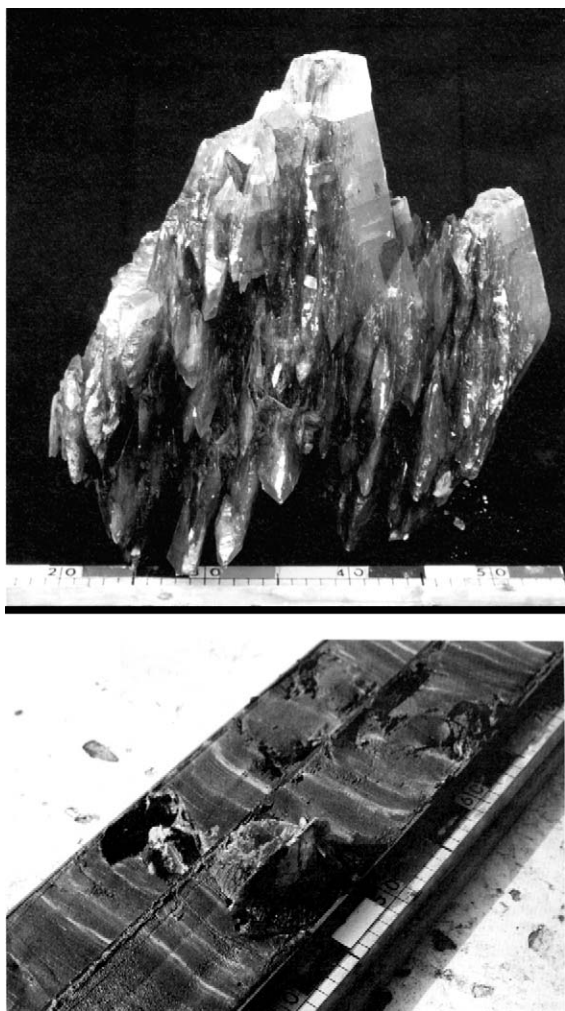


Fig. 7. Photographs of a gigantic gypsum crystal dredged from the fault scarp bordering the Ostro basin (top) and of a typical sediment core raised from beneath the anoxic brines (bottom). Notice the dark color, the finely laminated nature of the sediment, that contains bacterial mats, and the occurrence of gypsum crystals.

Fig. 2 shows the main structural characteristics of the Mediterranean Ridge and the location of the five brine-filled basins, whose description follows, from west to east.

3. The anoxic brine lakes originated by submarine dissolution of Messinian evaporites (described from W to E)

3.1. Bannock Basin

Bannock Basin was discovered in 1984 (Scientific Staff of Cruise Bannock 1984–12, 1985; Cita et al., 1985): it is a big structure located close to the Mediterranean Ridge deformation front facing the

Sirte Abyssal Plain (Fig. 3, top). It is elevated above the general relief of the ridge, characterized by the “cobblestone topography” (see Fig. 3, bottom), horse-shaped, with a central bulge surrounded by a number of subbasins of variable shape and depth; it has a vertical relief in excess of 700 m, as resulting from PDR and narrow-beam echo sounding (Cita et al., 1985; Camerlenghi, 1990; Camerlenghi and McCoy, 1990). Recent investigations with the most advanced geophysical techniques (deep penetration seismic profiling with two-ships, ocean bottom seismographs) during the IMERSE Cruise (von Huene et al., 1997; Reston et al., 2002) demonstrated that the Bannock structure is developed on top of a seamount approaching subduction (see Fig. 4, top and bottom).

All the subbasins but one contain, in their deeper parts, dense anoxic brines. Actually, the first discovery was based on a piston core raised in the Maestro subbasin (Fig. 3) that contained a 5 m thick succession of dark, finely laminated muds overlying normal hemipelagic marls of post-sapropel S-6 (circa 185,000 y BP old) age.

A strong reflecting interface (mid-water reflector) separates normal sea-water (above) from high density, anoxic brines (below). The density contrast, of some 20%, is sharp and is accompanied by an abrupt change in all the various parameters measured with CTD and water samples (Bregant et al., 1988; Catalano et al., 1989; Rabbitt and Boldrin, 1989; De Lange et al., 1990a,b) (see Figs. 5 and 6).

An abrupt but ephemeral negative peak in water transmittance corresponds to the presence of thick bacterial mats (Fig. 6). Similar bacterial mats with the appearance of gelatinous pellicles are commonly recorded inside the laminated sediments deposited underneath the anoxic brines (Erba et al., 1987a; Cita et al., 1988; Rodondi and Andreis, 1990; Erba, 1991; Camerlenghi and Erba, 1992) (see Fig. 7b). Microbiological investigations were carried out on the laminae and also on living bacteria from the anoxic brines (Brusa et al., 1997), see later (Urania basin).

Libeccio subbasin is the deepest: here the brines are some 500 m thick and are distinctly layered (see Figs. 5 and 6). The distinction of an upper layer, some 150 m thick, and a lower layer is based on chemical composition (Fig. 5) and in thermal structure (Fig. 6). Hydrogen sulphide increases significantly in the lower layer, as does temperature, that raises from less than 14 °C above the brines to more than 15 °C in the lower layer, with a strong increase recorded at the boundary separating the upper and lower brine layer. Gigantic gypsum crystals were dredged from the steep fault scarp bordering Borea subbasin to the east (Fig. 7, top) (Corselli and Aghib, 1987; Cita, 1991). Isotopic

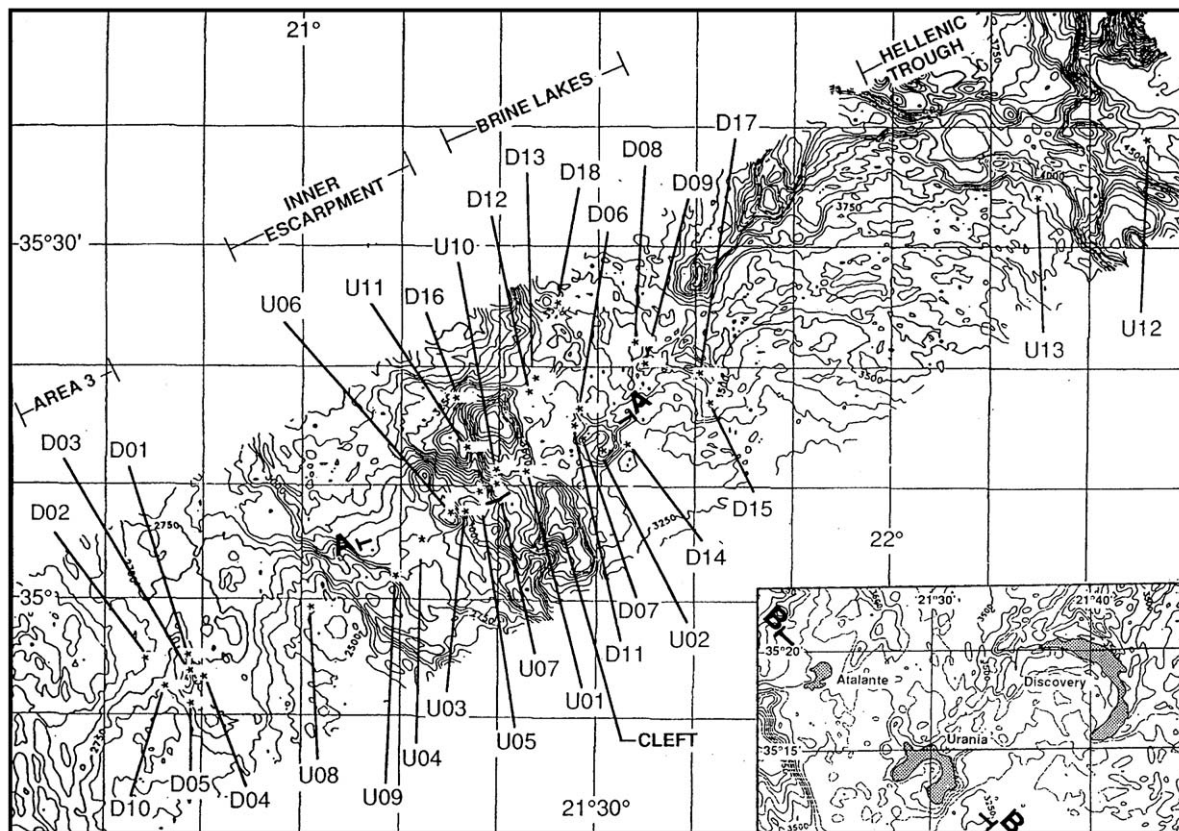


Fig. 8. Contour map of the MEDRIFF corridor and location of the Urania and Discovery cores investigated (after Fusi et al., 1996). B-B in the insert shows the location of the sparker line of Fig. 9.

measurements on the $^{234}\text{U}/^{230}\text{Th}$ ratio on gypsum crystals give an age younger than 22 ka (Ullmann, 1989).

Of the numerous deep-sea cores raised from the Bannock structure, those from water depth of less than 3200 m consist of hemipelagic marls (dominant lithology), sapropels and tephra typical of the eastern Mediterranean deep-sea record, whereas those from greater water depth consist of dark laminated muds deposited in the brine lakes (Fig. 7, bottom) (Cita et al., 1988; Cita, 1991; Sanvoisin, 1993).

Sediment traps have been placed in the Libeccio Basin within the brines and above them in order to investigate the biogenic and non-biogenic flux (EC Projects MARFLUX and PALEOFLUX, see Ziveri et al., 1995, 1996). A strong seasonality in the biogenic fluxes was noticed, and occasional African-derived non-biogenic components. The experiment is still running.

Experiments were run at Cardiff University to investigate the behaviour of pelagic turbidites when reaching the interface (Rimoldi, 1993, 1995). The experiments support previous interpretation and show that turbidity currents originating from nearby walls split

when reaching the interface, with the surficial part of the turbid flow running fast above the high density layer, whereas the lower part breaks the thick bacterial mat and settles down at the bottom, incorporating fragments of mucilaginous pellicles (Rimoldi et al., 1996).

Two long cores were raised from Bannock Basin during the MARION DUFRESNE Cruise in 1995 (see Rimoldi, 1995). The core from the deepest Libeccio subbasin is 26.05 m long, contains five discrete turbidites including a 13.7 m-thick homogenite (see later under Tyro Basin), and indicates persistent anoxic hypersaline conditions to the very bottom. A similar situation is recorded in the KC08 core raised from the shallower Scirocco subbasin, where four discrete turbidites were recorded, including a 12.5 m-thick homogenite.

3.2. Medriff Brine lakes

Medriff Brine lakes (Urania, Atalante and Discovery) were discovered in 1994–1995 in three discrete cruises by the research ships where from their names derive, within

the European Community funded project MEDRIFF (Mediterranean Ridge Fluid Flow, Project leader G.F. Westbrook), see Fig. 8 and Table 1.

The Medriff corridor runs SW–NE across the western Mediterranean Ridge along the same transect originally investigated by OGS (Line MS-33 of Finetti and Morelli, 1973), and along which DSDP Sites 125, 126 and 127 of the first drilling campaign in the Mediterranean Ridge were located (Ryan et al., 1973). Site 125, near the crest of the ridge, in a water depth of 2782 m, terminated in Messinian evaporites at 121 m subbottom, after penetrating a continuous Plio–Pleistocene pelagic succession.

DSDP Site 126, north of the crest, was located in a large depression (cleft) where no Messinian evaporites were recovered. A thick Quaternary succession with turbidites unconformably overlies mid-Miocene marls and shales (Ryan et al., 1973; see also Hsü et al., 1978, from Site 377 in the same location). The cleft is 1 km deeper than the ridge (water depth at Site 126 was 3730 m) and the terminal depth was 127 m subbottom. A subaerial erosion of Messinian evaporites or non-deposition was

hypothesized, but strongly criticized in the early seventies as too speculative.

So, the discovery of three brine lakes in a limited area (MEDRIFF Consortium, 1995; Westbrook et al., 1995; see Figs. 2 and 8) was surprising, as surprising was the discovery that the mid-water reflector was laying at different water depth in the Urania (3455 m) and Atalante (3344 m) Basins, just a few kilometres apart (Fig. 9). The sparker line illustrated in this figure allows to identify the M-reflector, which lies at different levels and is offset by faults. M-reflector is higher than the level of the brine lake SE of the horse-shaped Urania Basin, but it is deeper than the surface of the brine lake in the Atalante Basin. The two brine lakes behave as two different hydrologic systems and have different composition. Atalante is strongly enriched in potassium (5100 mmol/L), suggesting a derivation from the potassium chlorides which are characteristic of the uppermost levels of the evaporitic suite. The chloride content of the brine in the Urania Basin is 120 g/L, compared with 22 g/L for the Mediterranean sea-water (MEDRIFF Consortium, 1995). Fig. 10 (after

Table 1
Geological setting, length and water depth of the cores raised from the MEDRIFF corridor (Urania and Discovery cruises) after Fusi et al. (1996)

Cores	Latitude	Longitude	Depth (m)	Length (cm)	Setting	Lithology
U 01 GC	35°11'48.00"	21°24'45.00"	3227	375	Top of mound 1	Pelagic
U 02 PC	35°12'58.12"	21°30'41.35"	3454	519	Urania Basin	Anoxic mud
U 03 GC	35°07'30.82"	21°16'15.97"	2764	418	Top of mound 3	Pelagic
U 04 PC	35°04'30.92"	21°12'15.19"	2768	649	Slope between mound 1 and mound 3	Pelagic
U 05 GC	35°09'26.49"	21°18'42.94"	2921	78	Mound 2 slope	Milonitic breccia
U 06 PC	35°07'15.21"	21°15'05.43"	2582	472	Top of mound 3	Pelagic
U 07 GC	35°10'02.10"	21°19'51.60"	3132	0	Lower slope of mound 2	Mud breccia?
U 08 GC	34°59'26.40"	21°01'08.09"	2150	588	Mediterranean Ridge crest	Pelagic
U 09 GC	35°01'54.45"	21°09'34.84"	2703	472	Mound 4 slope	Pelagic
U 10 GC	35°10'24.06"	21°19'38.18"	3157	0	Slope of mound 2, down slope of 07	Milonitic breccia
U 11 PC	35°12'56.87"	21°16'38.25"	3462	510	Northern sub-cleft basin	Milonitic breccia
U 12 GC	35°39'50.04"	21°25'48.50"	4435	131	Hellenic trough	Pelagic
U 13 PC	35°33'26.02"	21°13'34.87"	3658	388	Hellenic trough	Pelagic
D 01 PC	34°55.55'	20°48.17'	2710	479	Near Area 3 thrust-outcrop trough	Pelagic
D 02 PC	34°54.10'	20°45.59'	2706	42	Top of circular mound	Mud breccia
D 03 PC	34°53.16'	20°48.54'	2825	840	Centre of Area 3 thrust-outcrop through	Pelagic
D 04 PC	34°52.80'	20°51.27'	2680	826	Area 3 thrust-outcrop trough	Pelagic
D 05 PC	34°52.64'	20°48.80'	2817	538	Area 3 thrust-outcrop trough	Pelagic
D 06 PC	35°16.40'	21°28.14'	3420	471	Basin near Urania Basin	Anoxic mud
D 07 PC	35°13.87'	21°28.31'	3385	744	Deepest part of Urania Basin	Anoxic mud
D 08 PC	35°21.09'	21°33.78'	3390	606	Linear Basin near Urania Basin	Pelagic
D 09 PC	35°20.39'	21°35.05'	3465	552	Linear Basin near Urania Basin	Pelagic
D 10 PC	34°52.78'	20°46.78'	2671	566	Area 3 thrust-outcrop trough	Pelagic
D 11 PC	35°14.59'	21°28.00'	3305	558	West of the Urania Basin	Pelagic
D 12 PC	35°18.12'	21°23.12'	3355	520	Atalante Basin	Anoxic mud
D 13 PC	35°19.15'	21°23.64'	3355	877	Atalante Basin	Anoxic mud
D 14 PC	35°12.60'	21°32.16'	3226	485	Slope of the SE side of Urania Basin	Pelagic
D 15 PC	35°16.36'	21°41.07'	3500	485	Basin floor of Discovery Basin	Anoxic mud
D 16 PC	35°17.53'	21°15.89'	3220	448	Top of circular mound	Mud breccia
D 17 PC	35°19.51'	21°40.83'	3500	354	Discovery Basin	Anoxic mud
D 18 PC	35°25.58'	21°25.00'	3605	473	Deep Basin	Pelagic

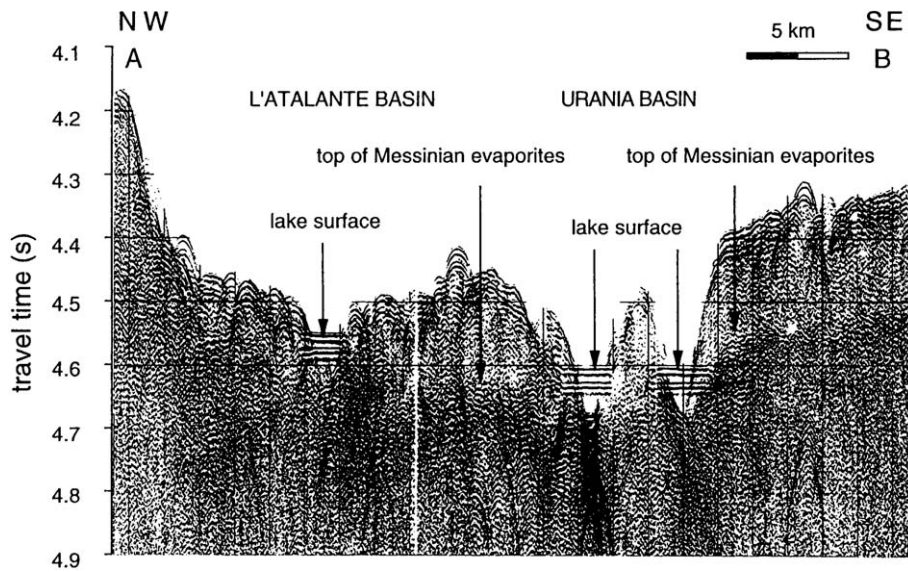


Fig. 9. Sparker line across the area shown in Fig. 8, that documents very clearly that the mid-water reflector (= interface separating high density anoxic brines from normal sea-water) lies at a different water depth in the Atalante and Urania basins. Also shown is the position of M-reflector (= top of Messinian evaporites) (after MEDRIFF Consortium, 1995).

MEDRIFF Consortium, 1995) shows plots of chloride in the three brine lakes of the Medriff corridor. The upper plot shows the increase in concentration through the surface of the Urania Basin brines. Notice that chlorosity (= number expressing chlorinity as g/L, obtained multiplying chlorinity of a sample by its density at 20 °C), is distinctly lower, less than half (2850 mmol/L), than that of Bannock and Tyro Basins (Table 2). The lower plot of Fig. 10 shows the variation in concentration measured in pore water from sediment cores raised from the brines. No data from the water column are available from Discovery Basin.

Urania Basin is distinctly horse-shaped, with a pit at the western corner which is 80 m deep: this deep hole is developed in the evaporites. The two cores raised from nearby locations display quite unusual characters as presence of methane and lumps of pale yellow sulphur (Fusi et al., 1996). Fig. 11 shows the thermal stratification in Urania and Atalante Basins (MEDRIFF Consortium, 1995). A distinct layering is noticed, with two layers distinguishable in Urania and three in Atalante. A very strong temperature increase is recorded in the Urania pit of western horn up to 55 °C.

Living bacteria were found and investigated in Urania Basin (Brusa et al., 1997); they include a *Vibrio* (*Nitrosovibrio* spp.), a coccus (*Stephylococcus* spp.) and some rods of the family Pseudomonadaceae. Laminar formations were observed by Brusa et al. (1997) in growth medium of mixed cultures that could be interpreted as the first stages of the mucillaginous pellicles seen in the cores.

Fig. 12 shows several pore water profiles measured from two piston cores raised from the Discovery Basin (PC 15 from its southern termination, PC 17 from the central part (see Fusi et al., 1996; Wallmann et al., 1997, 2002). With a chlorinity of 9100 mmol/L and a density of 1.32, Discovery Basin brines have the highest salinity ever found in the marine environment. They were formed by the dissolution of bischofite ($\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$). This discovery provided clear evidence for large scale bischofite formation during the Messinian salinity crisis, thus demonstrating that the eastern Mediterranean became evaporated to near dryness.

3.3. Tyro Basin

First discovered in 1983 (Jongsma et al., 1983), Tyro Basin is located in the Western Strabo Trench, in a pull-apart setting. Horizon M and the Messinian evaporites are offset by a fault in a steep fault scarp (see Fig. 13, top, after Jongsma, 1987). It is the smallest (diameter ca. 4 km) brine lake explored so far in the Mediterranean: simple, funnel-shaped, with a rounded rim (Fig. 13, bottom), it lies east of a rimmed basin, called Kretheus, and west of another one, called Poseidon. Both are not anoxic and brine-filled, because of the presence of near bottom currents that prevent the concentration and accumulation of high-density brines (as discussed in Erba et al., 1987b). The tectonic activity in the western Strabo trench has been, and still is, very strong. The reworked microfossils recorded in the turbiditic intervals indicate that pre-Neogene formations are exposed

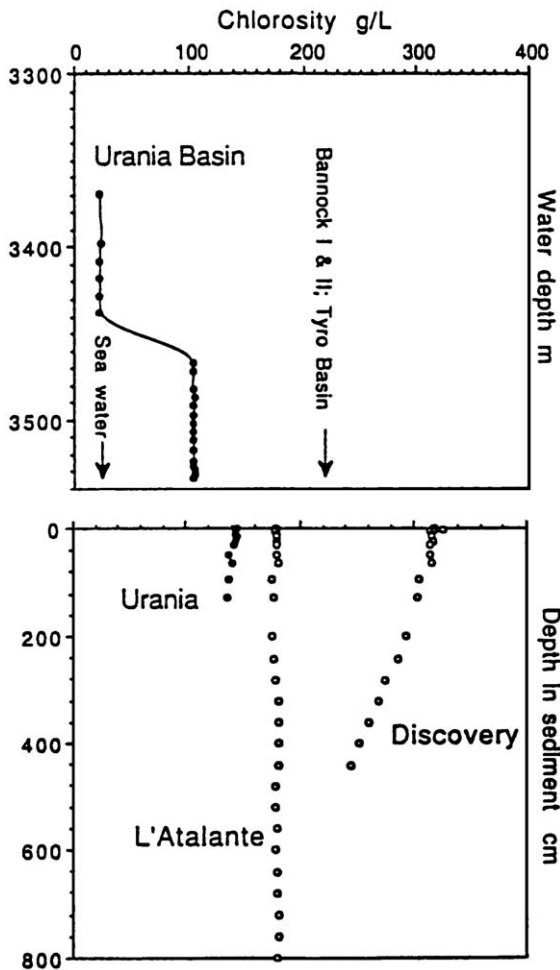


Fig. 10. Plots of chlorides measured in the three brine lakes of the MEDRIFF Corridor.

on the steep fault scarp shown in Fig. 13 (bottom, a and b). A 2 m thick homogenite (pelagic turbidite interpreted as tsunamiite, see Cita and Aloisi, 2000) recorded in Core P46 (Troelstra, 1987) from the centre of Tyro basin gave C^{14} ages of 7660 ± 390 and 6680 ± 290 yr whereas a 3300 ± 200 C^{14} age was obtained from below the homogenite. This age is compatible with that obtained by Heiken and McCoy (1984) for the tsunami associated with the collapse of the Santorini caldera.

Thickness of the brines is limited (less than 60 m) and no internal layering is noticed. The age of brine-forming conditions is unknown, since none of the cores collected so far reached a pre-anoxic conditions stage. Composition of the brines (Catalano et al., 1989; Henneke and De Lange, 1989; De Lange et al., 1990a,b) is similar to that of the Bannock brines (Table 3).

Tyro Basin was originally interpreted as an extant example of sapropel deposition (De Lange and ten

Haven, 1983), but the interpretation was later abandoned because anoxia related to dissolution of evaporites is persistent and diachronous, in contrast with the isochronous, episodic, repetitive, climatically induced, basin-wide anoxia recorded throughout the Eastern Mediterranean (Cita et al., 1991).

4. Discussion

The focus of this discussion is centered on two topics as follows: 1. Brine lakes/brine pools, and 2. Relationships between dissolution of Messinian evaporites and mud diapirism.

4.1. Brine lakes versus brine pools

The five anoxic basins investigated share a number of characteristics that are considered essential for their recognition and for providing boundary conditions for the interpretation of their origin.

- (1) Their size is of the order of a few kilometres in diameter (10 km for Bannock Basin, see Fig. 3a, b; 5 km for Urania Basin, see Fig. 9; 4 km for Tyro Basin, see Fig. 13). The vertical relief of the surrounding steep slopes (fault scarps) is of the order of a few hundred metres (up to 500 m in the Ponente subbasin of Bannock B.; 300 ms TWT in Urania and Tyro Basins, see Figs. 2 and 13).
- (2) The maximum thickness of the high density brines has been measured in the Bannock Basin, Libeccio subbasin (500 m). In other brine lakes thickness of the brines is around 100 m.
- (3) In the brine lakes where lowerings with CTD have been performed, thermal layering has been recorded in Bannock, Atalante and Urania. The only basin where a strong increase is noticed (45°C according to MEDRIFF Consortium, 1995; 55°C according to Fusi et al., 1996) is Urania, in a 80 m deep pit located at the western horn of the horseshoe-shaped basin. A core taken close to this pit (Discovery 07 GC) contains sulphur, methane and sedimentary structures suggestive of upward displacement of mineralized sediments along a fault scarp (Aloisi et al., in press). Pockmarks were observed in the vicinity of the pit, also suggestive of fluid venting.
- (4) During three cruises of the MEDRIFF project, 154 geothermal heat flow measurements and 7 CTD profiles in the water column collected along a 300 km transect crossing the entire accretionary complex showed no thermal anomalies suggestive of fluid outflow (Della Vedova et al., 2003).

Table 2

Physical and chemical parameters and sedimentary characteristics of some eastern Mediterranean brine lakes (after Fusi et al., 1996)

		Bannock (Libeccio)	Urania	L'Atalante	Discovery	
Brine characteristics	Density (g/cm ³)	1.21 ^a	1.12 ^b	1.23 ^b	1.32 ^b	
	Chloride (mmol/L)	5378 mmol l ⁻¹ ^a	2850 ^b	5100 ^b	9.100 ^b	
	H ₂ S (mM)	Upper brine	1.8	6.9		
		Lower brine	2.7 ^a	4.5		
	CH ₄ (mmol/L)	Trace	Max 3.8 ^b	Max 0.15 ^b	Max 0.05 ^b	
	pH	6.55 ^a	6.46			
	Alkalinity and/or total inorganic carbon (mmol/L)	4.2 (mM) ^a	37.3 ^b	7.25 ^b	4.70 ^b	
Sediment characteristics	Temperature °C	14–15 ^a	18–28, max 55	13–14		
	Gypsum	Present	Present	No	Present	
	Sulphur	No	Present	No	No	
	Sediment color	Gray mud 10 GY 4/1		Gray mud N 5/0	2.5Y	5Y 2.5/1
		Green mud 10 GY 3/2		Green mud 5 Y 4/2	3/0 Very	Black
	Bacterial pellicles	Present	Present	Dark gray	Present	
	C org (%)	Gray mud	0.5	Gray mud	0.5	1–3
		Green mud	1–2	Green mud	>2	1–6
	CaCO ₃ (%)	20–40	20–40	?	15–35	
	Sedimentary structures	Laminated		Thin turbidites + laminated intervals; isochronous lithologies recognizable in U 02	Faintly laminated (D12)	No structures, homogeneous mud
		very thick turbidite (homogenite) in basinal setting; isochronous lithologies obscured				
	Sedimentation rates	3–4 times higher than in non-anoxic situations		10 times higher than in non-anoxic situations (14 cm/1000 y)	Not measurable	Very low in D 15
Oldest age of persistent anoxia	180,000 y BP		35,000 y BP	Younger than 53,000 y BP	25,000 y BP	

^a De Lange et al., 1990a,b.^b Suess, per. comm.

- (5) A mid-water reflector present in all these brine-filled depressions has been calibrated with the interface separating high density anoxic brines from normal sea-water. This mid-water reflector ranges in depth from –3200 m (Bannock Basin) to –3455 m (Urania Basin). Some minor discrepancies in the numerical values given in the published reports are accounted to the frequent use of millibars instead of metres. In most cases the sound velocity within the brines is unknown.
- (6) A very strong bacterial activity has been recorded at the interface, originating mucilaginous pellicles that are responsible for the strong decrease in transparency in coincidence with the mid-water reflector. Living anaerobic bacteria have been recorded within the brines and are considered responsible for a sulphate reduction. Only Discovery Basin is devoid of microbial pellicles.
- (7) Density of the brines is around 20% higher than normal sea-water (1.21 in Bannock Basin), see Table 2.

All these characteristics speak in favour of an origin of the brines deriving from submarine dissolution of Messinian evaporites whose presence in outcrop or subcrop (= exhumation) is documented by seismic reflection profiles, as shown in Figs. 9 and 13.

The difference in chemical composition of the various brine lakes has been accounted to the dissolution of different layers of the Messinian evaporitic succession. As said before, deep drilling in the Mediterranean was able to calibrate the upper evaporites and probably the “couche fluante”, but not the lower evaporites. Halite and potash salts (kainite, bischofite) are the last (youngest) salts deposited in a normal evaporitic suite.

In order to give some constraints to a geologically realistic scenario, it is pointed out that

- large amounts of halite with minor potash salts are well known and exploited in salt mines in Sicily;
- in the Balearic Basin (DSDP Site 134, water depth (WD) 2864 m) halite has been recorded at 364 m subbottom;

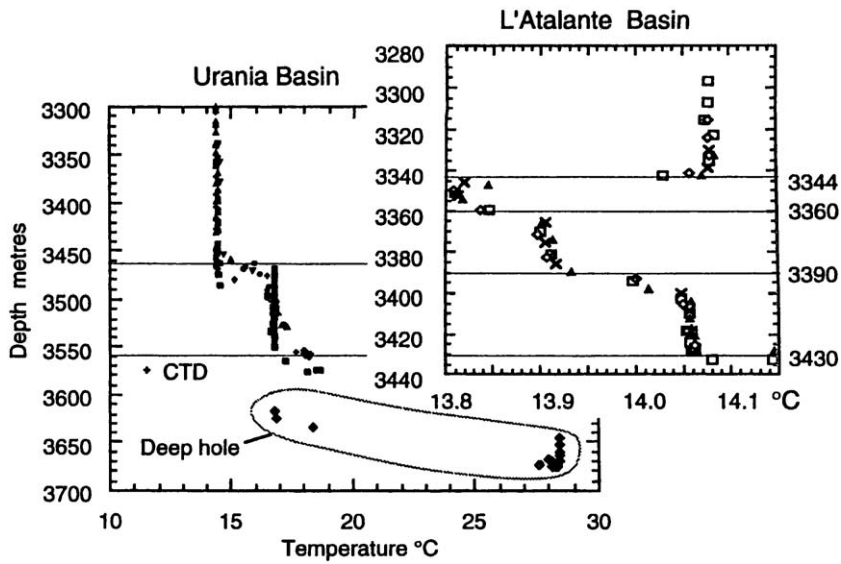


Fig. 11. Thermal stratification observed in CTD measurements run in the Urania Basin and with thermistors on heat-flow probes in Urania and Atalante Basins (after MEDRIFF Consortium, 1995).

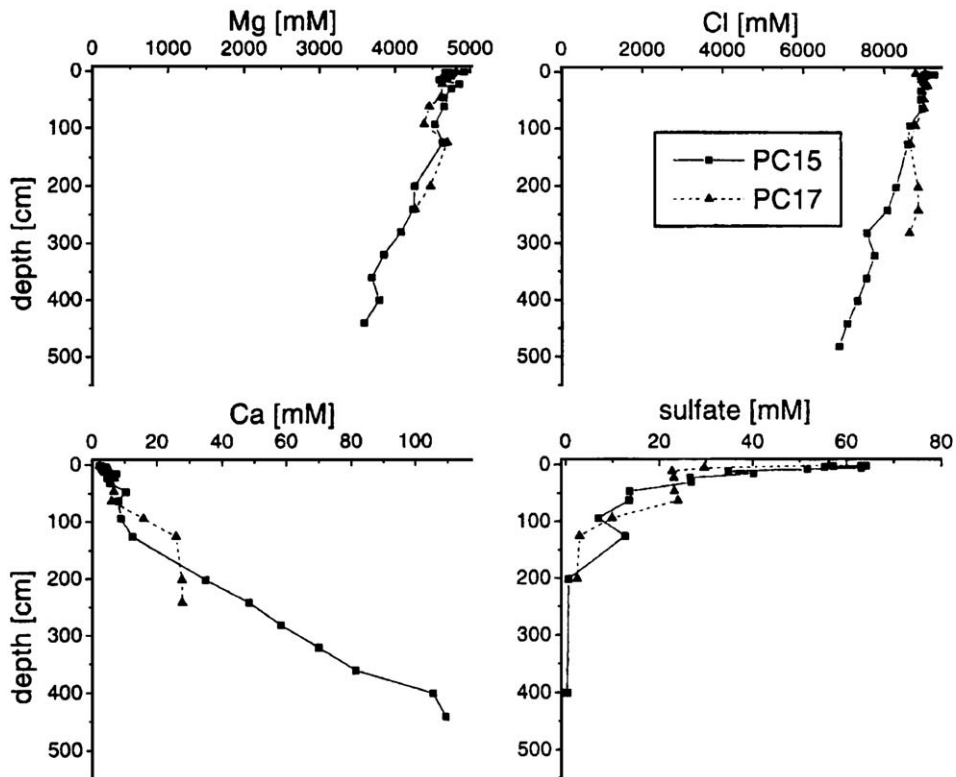


Fig. 12. Pore waters profiles measured in two piston cores raised from the deep hole (pit) identified in the SW corner of the horseshoe-shaped Urania Basin (PC15) and from the central part of the basin (PC17) (after Wallmann et al., 2002).

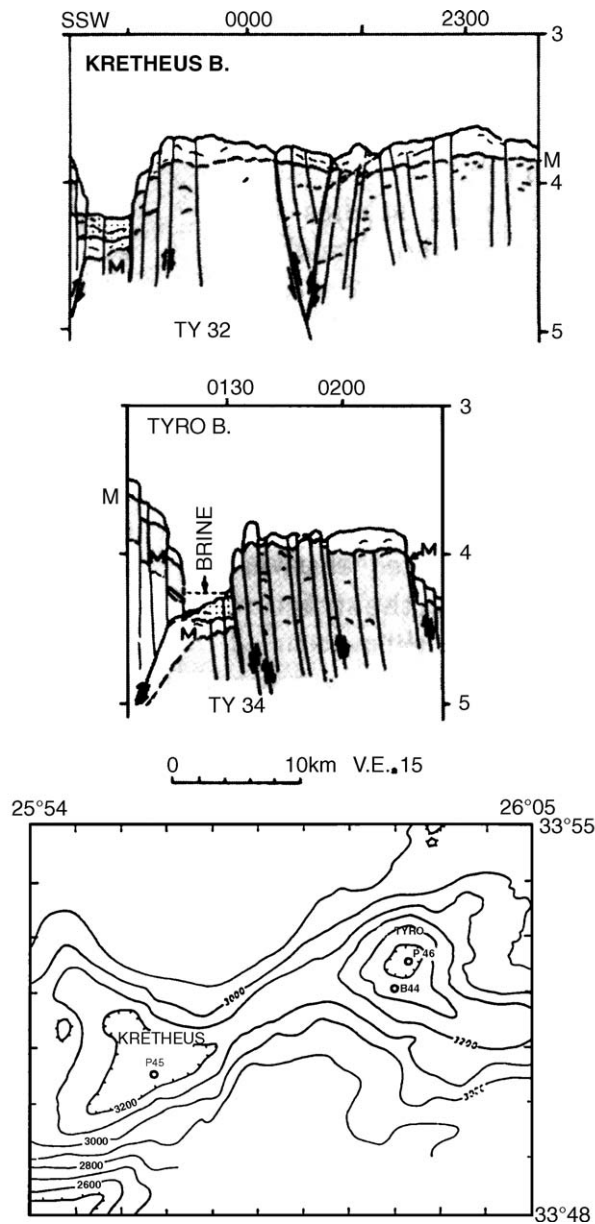


Fig. 13. Top: Interpreted seismic reflection profiles crossing the Strabo Trench in the Kretheus (a) and Tyro (b) Basins (after Jongsma, 1987). M-reflector is the top of the Messinian evaporites, that are clearly offset by faults. Bottom: Contour map of the Tyro and Kretheus basins in the Strabo Trench (after Troelstra, 1987).

- in the Ionian Basin (DSDP Site 374, WD 4088 m) halite was recovered at 374 m subbottom;
- in the Levantine Basin (DSDP Site 376, WD 2117 m) halite is present at 216 m subbottom.

A substantial thickness of hemipelagic and turbiditic sediments of Plio–Quaternary age separates the salt layer from the sea-floor. In the eastern Mediterranean drillsites, post-evaporitic sediments indicative of the

“lago-mare” paleoenvironment are sandwiched between the basal Pliocene (lower Zanclean, *Sphaeroidinellopsis* Acme-zone) and the evaporites. Evidence of upward fluid migration deriving from dissolution of evaporites is only recorded at DSDP Site 374 where fine-grained dolomitic mudstones containing the rare mineral lüneburgite directly underlie the basal “Trubi” marls, where pervasive dolomitization is observed. The location of Site 374 is in the deepest abyssal plain of

Table 3
Average chemical composition of Tyro brines (from De Lange et al., 1990b)

Na	Cl	Mg	K	Ca	Sr	SO ₄	Li
5300	5350	71.1	19.02	35.4	0.329	52.7	0.075
H ₃ BO ₃	F (mmol)	Ba (mmol)	T (°C)	Mn (mmol)	Fe (mmol)	Si (mmol)	HPO ₄ (mmol)
1	45.30	579	14.17	4.08	<1	266	19.01
NH ₄ ⁺ (mmol)	pH (NBS)						
1.03	6.75						

Concentrations are in mmol l⁻¹ (not specified) or in μmol l⁻¹ (specified).

the entire Mediterranean, exceeding 4000 m. The deepest part of the Mediterranean, however, lies in the Hellenic Trench. No evidence of anomalous density and/or salinity is recorded there; no evidence of near bottom anoxia and no mid-water reflector even in recently acquired high resolution subbottom profiles (CHIRP) crossing the Matapan Trench published by Rebesco et al. (2000).

In order to further argue in favour of the exhumation/dissolution interpretation it seems necessary to point out the increasing importance of highly specialized geochemical investigations carried out in the last ten years on interstitial waters, that suggest as alternative interpretation the interaction of residual Messinian age fluids (“relics of ancient Miocene brines” as worded by Vengosh et al., 1994).

Leading scientists well known worldwide, including the best specialists, with extended experience on the Barbados, Cascadia, Aleutian and Nankai accretionary complexes, in mid-ocean ridges fluid vents, in Dead Sea brines are involved (Wallmann et al., 1997; Vengosh et al., 1998; Charlou et al., 2003; inter alias).

The EC funded MEDRIFF MAST Project was highly successful scientifically, however a second planned phase was not funded. A French–Dutch project MEDINAUT/MEDINET was carried out in 1998, with the use of the deep diving submersible NAUTILE. “Linking Mediterranean brine pools and mud volcanism” is the title of the first published report (see MEDINAUT/MEDINET, 2000).

The concept of brine lakes = anoxic basins, with reference to large (several kilometres in diameter) depressions within the Mediterranean Ridge “cobblestone” terrains, containing in their deepest parts substantial amounts of high density brines has been extended to brine pools and brine sheets a few metres thick, that are obviously related to fluid venting by active mud volcanoes (as on Napoli Dome, see later) or close to major faults as Nadir Lake (Charlou et al., 2003). Nadir

Lake is 250 m in diameter and 15 m in depth, or one order of magnitude smaller and shallower than the five brine lakes under discussion. The brine pools within the rim of the active Napoli mud volcano are even shallower and smaller: they probably are ephemeral in duration and do not last long, being related to fluid venting from an active mud volcano (Cita et al., 1995). Woodside and Volgin (1996) identified as a brine pool an echo-free patch well visible in a deep-tow side-scan sonar profile, not sampled and not calibrated by coring.

Having said that, it is clear that the preceding and following argumentations refer only to the five anoxic basins = deep-seated brine lakes considered, that are not accompanied by emissions of methane, with the only exception of Urania Basin (p.p.).

The Mediterranean Ridge differs substantially from the Barbados, Cascadia, Aleutian and Nankai accretionary wedges because none of them contains an important evaporitic sedimentary unit.

The fluid emissions of the Mediterranean Ridge are cold seeps, unlike the hot springs of the Mid-Ocean Ridges.

The Dead Sea brines are deposited in a land locked basin that differs in size from the eastern Mediterranean by two orders of magnitude.

If the deep-seated brines derive from residual Messinian age fluids entrapped and/or extruded from the evaporites, they should be present in the large and deepest depressions of the eastern Mediterranean (Matapan Trench, Messina Abyssal Plain, cleft basin), but they are not. The structural setting of the five brine lakes ranges from a continental seamount approaching the subduction zone (Bannock Basin) to a pull apart basin in the western Strabo Trench (Tyro Basin), to a complex supra-backstop setting where Messinian evaporites are thin, as clearly documented by seismic reflection profiles (see Fig. 9).

If the deep-seated brines were residual Messinian age brines, they should share approximately the same geochemical composition reflecting the last, post-evaporitic

phase subaqueous deposition, but instead they display strong differences from basin to basin, even in the case of the MEDRIFF basins, which are only a few kilometres apart from one another (see Fig. 9).

4.2. Relationships between anoxic basins and mud volcanoes

Mud diapirism was first discovered in the Mediterranean Ridge in 1978 by the American R/V EASTWARD. The conical, positive feature was called Prometheus Dome, consisted of a clast-supported mud breccia of deep origin, containing a purely Aptian age fossil fauna (Cita et al., 1981). A similar physiographic feature was visible in a Seabeam track run by Lyberis (in Le Pichon et al., 1982) south of Crete, named Prometheus 2 and explored by the Italian R/V BANNOCK in 1988, that discovered and investigated a number of nearby mud domes (see Cita et al., 1989; Camerlenghi et al., 1992; Staffini et al., 1993; Camerlenghi et al., 1995), see Fig. 14.

Mud diapirism in the Mediterranean Ridge, as compared with the Black Sea, was the major topic of an expedition of the UNESCO funded TREDMAR Project run in 1993 with the Russian R/V GELENDZIK (see Cita et al., 1996a,b; Akhmanov, 1996; Limonov et al., 1996; Premoli Silva et al., 1996) that investigated with a multidisciplinary approach the Olimpi area and nearby crestral area of the Mediterranean Ridge (Fig. 15, top). All this scientific information was used as Site Survey for

preparing the drilling proposal for ODP Leg 160, dealing with Milano and Napoli Domes. Drilling has been very successful and originated a number of interesting publications (Emeis et al., 1996; Robertson et al., 1998; Robertson and Kopf, 1998a,b; Dehayle and Kopf, 2001; Charlou et al., 2003 inter alias).

Drilling Milano and Napoli domes proved that the oldest extrusions or sediments injections date back to approximately 1 million years (early Pleistocene). A probable occurrence of gas hydrates was suggested and further exploration with the French submersible Nautilie showed that a methane plume over 100 m high is present on top of Milano Dome and is interpreted as change in physics of gas hydrates. Active venting from Napoli Dome was documented by TREDMAR and MEDI-NAUT as well as the presence of a chemosynthetic bottom fauna (Corseili and Basso, 1996).

Fig. 15 (bottom) (after Akhmanov et al., 2003) shows the location of Mediterranean Ridge mud volcanoes sampled by coring. According to Charlou et al. (2003, p. 942) mud volcanoes on the crest of the Mediterranean Ridge are more than 200. The Mediterranean Ridge is considered the region with the highest abundance of mud volcanoes and diapirs in the world (Kopf, 2002; Hieke, 2004). Mud volcanism is usually associated with methane emissions, and evidence of gas in sediments or of gas escapes from the Mediterranean Ridge are reported by Camerlenghi et al. (1992, 1995), Cita et al. (1995, 1996b), Fusi et al. (1996), Emeis et al. (1996),

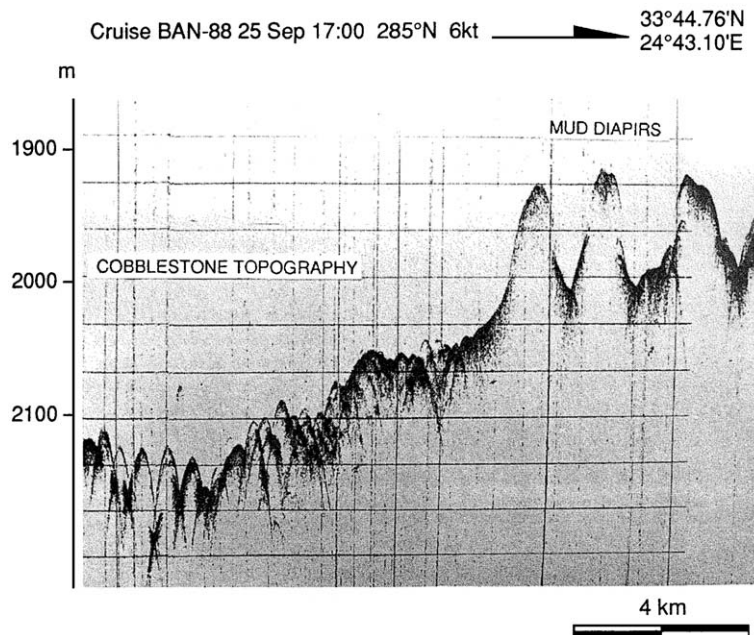


Fig. 14. PDR (3.5 kHz) profile of the Olimpi mud diapirs (after Cita et al., 1989).

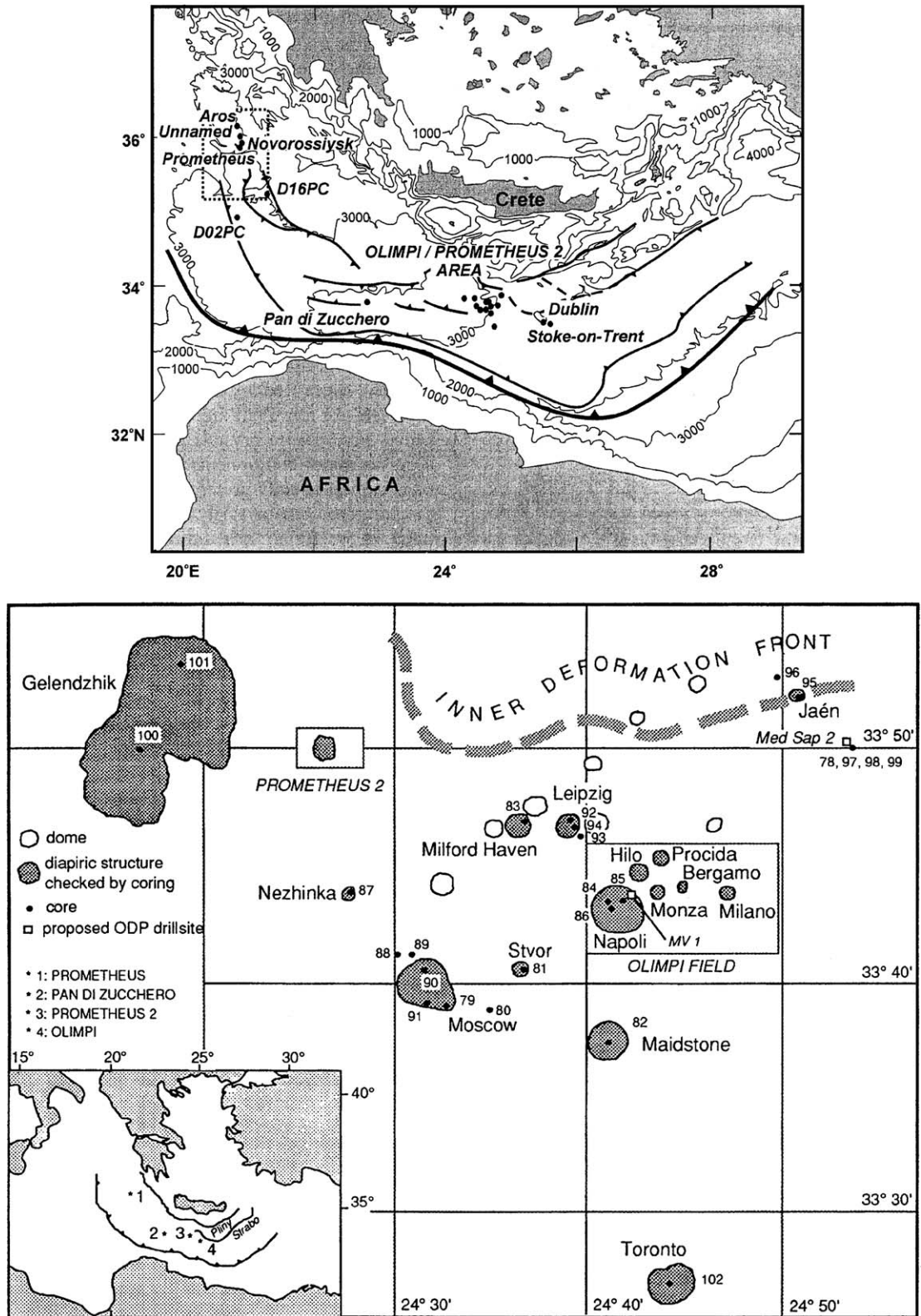


Fig. 15. Location of the mud volcanoes and diapirs surveyed during Cruise TTR3, Leg 2 (after Cita et al., 1996b) (top) and location map of eastern Mediterranean mud volcanoes sampled by coring (after Akhmanov et al., 2003) (bottom).

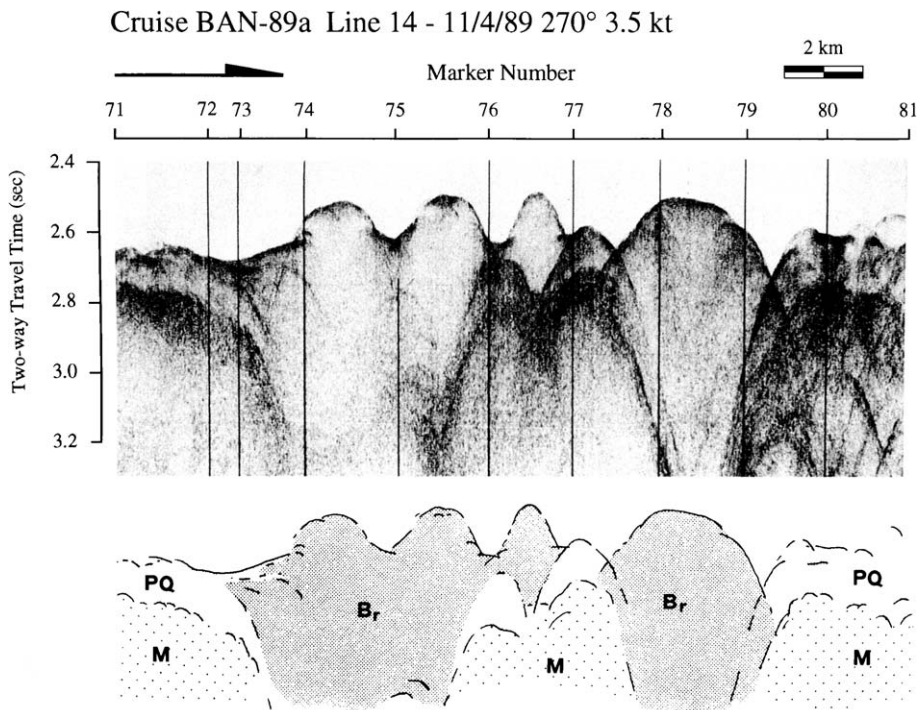


Fig. 16. Sparker line across the Olimpi field of mud diapirs (for location, see Fig. 15) showing the M seismic unit (Messinian evaporites), the PQ seismic unit (Plio–Quaternary nanofossil oozes) and the Br unit (diapiric breccia) (after Camerlenghi et al., 1995). Flower structure characterizes all the mud diapirs explored and calibrated by coring.

Hieke et al. (1996), and Hieke (2004). In the Olimpi area (see Figs. 14–16), Kopf (1999) calculated the following annual gas flux: 1.68×10^6 to 2.85×10^7 m³.

In conclusion, mud volcanism — whose origin and characterization are not the subject of this paper — are a much more widespread phenomenon in the Mediterranean Ridge accretionary complex than anoxic brine lakes.

The existence of Messinian evaporites of variable thickness within the body of the accreted terrains has an obvious influence on both phenomena. This influence is increased by the fact that the post-Messinian sedimentary succession (Zanclean to Holocene in age, or 5.33 to 0 Ma) is thin, of the order of 120–200 m (or 1.50 ms) on the ridge, as a result of slow rate of accumulation, low productivity and absence of turbidites and other re-sediments in an uplifted and still raising setting. Fig. 16 from the Olimpi area as well as other seismic lines illustrated by Camerlenghi et al. (1995) clearly documents this situation. A combination of locally strong tectonic deformation offsetting the late Neogene–Quaternary succession, including Messinian evaporites of different chemical composition and of basin collapse may create the conditions leading to the formation of deep-seated brine lakes. The only case in which a combination of fluid expulsion and submarine dissolution is observed is in the

pit of Urania Basin, in particular the western horn of the horseshoe-shaped basin (see previous section).

The several cores raised from this basin (see Rimoldi, 1995; Fusi et al., 1996; Aloisi et al., *in press*) deserve additional investigations that should help to understand the relationship among presence of sulphur, anomalously high temperature, occurrence of sedimentary structures suggestive of upward displacement of soupy sediments, accompanied by the absence of flower structures in the sparker line (see Fig. 9). Additional investigations would be instrumental to clarify these controversial issues, and are planned in the near future.

5. Conclusions

Submarine dissolution of Messinian evaporites occurs where syn- and post-Messinian tectonic deformation is strong and where post-Messinian (Plio–Quaternary) sediments are thin.

The accumulation of dissolved salts (brines) is possible only if some kind of closed depressions exist, otherwise near-bottom currents dilute and remove the salt brines, and prevent their further concentration.

The interface separating normal sea-water from the brines is very sharp and is rich in bacterial mats. Living

bacteria have been recovered from the brine lakes and cultivated in laboratory. No similar phenomena were observed in the Balearic and Herodotus Abyssal Plains, where very thick Messinian evaporites occur, and salt diapirism is well documented (Montadert et al., 1978).

Exhumation and submarine dissolution of Messinian evaporites may occur in different structural settings (i.e. pull-apart basin as in Tyro Basin; subducting seamount as in Bannock Basin; top of continental backstop as in the Medriff basins).

All the anoxic basins or brine lakes considered in the present article belong to the western Mediterranean Ridge, an accretionary prism that started to develop in Miocene time (Westbrook and Reston, 2002), so that the present-day water depth of the sites is shallower than it should have been some 5.5 million years ago, during the acme of the Messinian salinity crisis. The interface separating anoxic brines from normal sea-water (brine lake surface) is always deeper than 3000 m, ranging from 3200 m in Bannock Basin to 3450 m in Urania Basin, strongly supporting a substantial lowering of sea-level in late Messinian time.

The chemistry of the brines is strongly variable and suggests dissolution of different layers or levels of the Messinian evaporitic suite. Discovery brines are the saltiest ever recorded in natural environment. Their saturation in Mg chloride (bischofite), the end product of sea-water evaporation, indicates that the deepest parts of the eastern Mediterranean were close to dryness in late Messinian times.

The deep basin desiccation scenario for the origin of the Messinian evaporites receives a fundamental support by these new findings, that should not be ignored by the scientific community of geologists and stratigraphers that work on land on problems related to the Messinian salinity crisis.

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It is almost impossible to mention all the partners and students of the various cruises performed in the eastern Mediterranean, that contributed in various ways to the exciting scientific exploration of the Mediterranean Ridge. I want to remember here the endless discussions with the late Rob Kidd on intrusion versus extrusion models for the mud volcanoes; the interesting meetings in Bruxelles, Trieste and Paris with the MEDRIFF partners; the burden of describing carefully all the cores; the guilt feeling for being unable for various reasons to dedicate more efforts to reporting so many new findings. I thank J.M. Rouchy and an anonymous reviewer that with their comments and constructive criticism contributed to

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