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Evaporitic source rocks: mesohaline responses to cycles of "famine or feast" in layered brines

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ABSTRACT

Organic matter in modern saline systems tends to accumulate in bottom sediments beneath a density-stratified mass of saline water where layered hydrologies are subject to oscillations in salinity and brine level. Organic matter is not produced at a constant rate in such systems; rather, it is generated in pulses by a halotolerant community in response to relatively short times of less stressful conditions (brackish to mesohaline) that occur in the upper part of the layered hydrology. Accumulations of organic matter can occur in any layered brine lake or epeiric seaway when an upper less-saline water mass forms on top of nutrient-rich brines, or in wet mudflats wherever waters freshen in and above the uppermost few millimetres of a microbial mat. A flourishing community of halotolerant algae, bacteria and archaeal photosynthesizers drives the resulting biomass bloom. Brine freshening is a time of "feast" characterized by very high levels of organic productivity. In a stratified brine column (oligotrophic and meromictic) the typical producers are planktonic algal or cyanobacterial communities inhabiting the upper mesohaline portion of the stratified water mass. In mesohaline holomictic waters, where light penetrates to the water bottom, the organic-producing layer is typically the upper algal and bacterial portion of a benthic laminated microbialite characterized by elevated numbers of cyanobacteria.

Short pulses of extremely high productivity in the upper freshened part of a stratified brine column create a high volume of organic detritus settling through the column and/or the enhanced construction of benthic microbial mats in regions where freshened waters reach the hypersaline base of the column. With the end of the freshening event, ongoing intensely arid conditions mean that salinity, temperature and osmotic stress increase rapidly in the previously freshened water mass. This leads to a time of mass die-off of the once flourishing mesohaline community ("famine"). First, these increasingly salty waters no longer support haloxene forms. Then, halotolerant life dies back, and finally by the halite precipitation stage, only a few halophilic archaea and bacteria remain in the brine column (typically acting as heterotrophs and fermenters). Repeated pulses of organic matter, created during a feasting event followed by a famine event, create laminated organic-enriched sediment on an anoxic bottom.

There are three, possibly four, major mesohaline density-stratified settings where organic-rich laminites (petroleum source rocks) accumulated in ancient "famine or feast" saline settings: (1) basin-centre lows in marine-fed evaporitic drawdown basins, associated with basinwide evaporites; (2) mesohaline intra-shelf lows on epeiric platforms, associated with platform evaporites; (3) saline-bottomed lows in under-filled perennial saline lacustrine basins; (4) closed seafloor depressions in halokinetic deep-water marine slope and rise terrains. An inherently restrictive hydrology means that the same mesohaline settings show a propensity to evolve into regions characterized by the accumulation of widespread evaporite salts. If this happens soon after deposition of a layer of organic-rich sediment there is an increased likelihood of evaporite plugging in the source-rock layer, this in-turn decreases expulsion efficiency and downgrades the laminite bed's ability to act as a prolific source rock.

Keywords: Oil and gas, source rocks, halobiota, hypersaline, salinity

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INTRODUCTION

Back in 1988, Evans & Kirkland made the observation that some 50% of the world's oil may have been sourced in evaporitic carbonates. Heresy or not, the notion that much of the oil sealed by evaporite salts may also have also been sourced in sediments deposited in earlier less saline, but still related, evaporitic (mesohaline) conditions, is worthy of consideration. The association between saline waters, the accumulation of organic-rich sediments and the evolution of the resulting evaporitic carbonates into source rocks has been noted by many, including: Woolnough (1937), Sloss (1953), Moody (1959), Dembicki *et al.* (1976), Oehler *et al.* (1979), Malek-Aslani (1980), Kirkland and Evans (1981), Hite *et al.* (1984), Jones (1984), Eugster (1985), Sonnenfeld (1985), ten Haven *et al.* (1985), Warren 1986, 2006, Busson (1988), Evans & Kirkland (1988), Edgell (1991), Hite & Anders (1991), Beydoun (1993), Benali *et al.* (1995), Billo (1996), Carroll (1998) and Schreiber *et al.* (2001). The current paper draws on material and references discussed in greater detail in Warren (2006).

As long ago as the middle of the last century, Weeks 1958, 1961 emphasized the importance of evaporites as caprocks to major hydrocarbon accumulations. Weeks 1958, 1961 pointed out that many of the cycles of deposition that involve organic-rich carbonate marls or muds also end with evaporites. Many authors have noted the association of Type I–II hydrogen-prone kerogens in evaporitic source rocks and related their occurrence to the ability of[1] halotolerant photosynthetic algae and cyanobacteria to flourish in saline settings (Fig. 1A). Such kerogens tend to be oil-prone rather than gas prone (Fig. 1B). This paper examines chemical pathways and the conditions that favour various species that live in hypersaline environments. It compares modern saline settings with ancient systems and attempts to define those ancient saline settings that facilitated deposition of organic matter and subsequent evaporitic source rocks.

First, usage of the terms hypersaline and mesohaline in saline brines and the associated mineral precipitates is defined (Table 1). For seawater-derived and thalassic (seawater-like) brines the use of the term "hypersaline" encompasses all waters more saline than seawater (mesohaline, penesaline and supersaline). There is an associated predictable suite of evaporite minerals, starting with carbonate (usually aragonite) in modern mesohaline waters, and evolving through gypsum and halite in penesaline waters, into bitterns from supersaline waters. However, ionic proportions in seawater have changed over time (Warren 2006). Accordingly, some ancient evaporite primary carbonates were dolomitic, especially in the Precambrian (although reflux dolomite has always been a widespread early diagenetic evaporite precipitate), and Archaean water probably precipitated a trona-halite-dominated set of salts rather then the halite-gypsum salts of the Phanerozoic.

Bittern salts from modern seawater concentrates show a carnallite-$MgSO_4$ association and a propensity to accumulate aragonite in the early stages of concentration, as they did also in the Permian

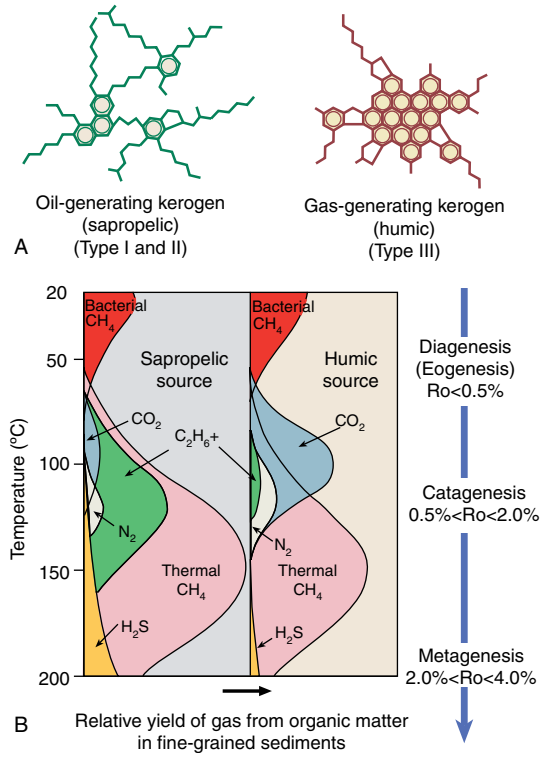


Fig. 1. Organic matter and source rocks. (A) Molecular structure of typical oil-generating (sapropelic) and gas-generating (humic) organic matter showing the greater preponderance of long-chain hydrocarbons in the sapropelic material (after Hunt, 1996). (B) Relative volumes of gases and liquids derived from a sapropelic and a humic source rock (after Hunt, 1996). Evaporitic source rocks tend to be sapropelic and contain less iron as a reductant so they are also likely to generate more H_2S.

[1] (see Glossary at the end of this article for explanation of the specialist terminology used herein).

Table 1. Salinity-based classification of concentrated seawater and thalassic (seawater-like brines). Water density and dominant mineral precipitates are indicated (adapted from Warren, 2006)

Brine Stage		Mineral precipitate	Salinity (‰)	Degree of evaporation	Water loss (%)	Density ($g\,cm^{-3}$)
Brackish		None	<35	<1	0	1.000–1.040
Normal marine seawater		Alkaline earth carbonates (aragonite, Mg-calcite)	35	1	0	1.040
Hypersaline	Mesohaline or vitahaline	Alkaline earth carbonates (aragonite, Mg-calcite, dolomite)	35–140	1–4	0–75	1.040–1.100
	Penesaline	$CaSO_4$ (gypsum/anhydrite)	140–250	4–7	75-85	1.100–1.126
		$CaSO_4 \pm$ halite	250–350	7–11	85–90	1.126–1.214
	Supersaline	Halite (NaCl)	>350	>11	>90	>1.214
		Bittern salts (K-Mg)	Extreme	>60	~99	>1.290

(icehouse climate mode). Bitterns at other times in the Phanerozoic (greenhouse climate mode) tend to lack the $MgSO_4$ minerals and have a propensity to form Mg-calcites in the mesohaline phase.

Use of the term hypersaline in modern continental (non-marine) waters is much less well defined and is variably applied to waters with total dissolved salt contents (TDS) that are more saline than 3 to 5‰. Nonmarine or continental waters can have ionic proportions considerably different to seawater (athalassic), and so a broader range of minerals can precipitate at all stages of brine concentration.

METABOLISM IN PRODUCERS AND CONSUMERS

Cyanobacteria and algae are the dominant primary producers in most mesohaline waters, along with lower and varying inputs from the higher plants and photosynthesizing bacteria. Algae and cyanobacteria typically make up the bulk of the planktonic biomass in the upper layer of a stratified mesohaline brine column and construct the upper parts of microbial mats in oxygenated settings where light penetrates to the water bottom. Cyanobacteria are prokaryotal (cell lacks a nucleus) bacteria and, like eukaryotic (cell with nucleus) algae and higher plants, are photoautotrophic and require oxygen to photosynthesize. The typical aerobic photosynthetic reaction for all three groups is:

$$CO_2 + 2H_2O = CH_2O + H_2O + O_2 \quad (1)$$

That is, carbon dioxide and water react in the presence of chlorophyll and sunlight to form carbohydrate plus water plus oxygen.

All aerobic photosynthesizing organisms contain the pigments chlorophyll-α and phycobilin and use water as their electron source in reactions that generate oxygen. Chlorophyll-α is a green pigment that absorbs red and blue-violet light, hence the typical green colour of photosynthesizers (Fig. 2A, B). It is made up of molecules that contain a porphyrin 'head' and a phytol 'tail' (Fig. 2A). The polar (water-soluble) head is made up of a tetrapyrrole ring and a magnesium ion complexed to the nitrogen atoms of the ring, its phytol tail typically extends into the lipid layer of the thylakoid membrane. Phycobilisomes (phycocyanin, phycoerythrin) are proteins that absorb light of more energetic wavelengths than chlorophyll and are widespread pigments in the cyanobacteria and red algae (Fig. 2B). Their presence allows some members of the halotolerant community to photosynthesize into deeper brine and sediment depths, where light with longer wavelengths is less transmitted and therefore less available directly to chlorophyllic photosynthesizers (blue-green spectrum). Phycobilisome molecules are linear tetrapyrroles and are structurally related to chlorophyll-α, but lack the phytol side chain and the magnesium ion. In chlorophyll-rich oxygen-evolving reaction centres in a cell (chloroplasts) the phycobilisomes help transmit photic energy and in cyanobacteria they are located in chloroplasts in an extensive, intracellular system of flattened, membranous sacs, called thylakoids, the outer surfaces of which are studded with regular arrays of phycobilisome granules. Cyanobacteria are the only prokaryotes that contain chlorophyll-α in their chloroplast and so show strong affinity with the algae and the green plants. In the pre-genomic era of microbial studies this meant they were typically classified as

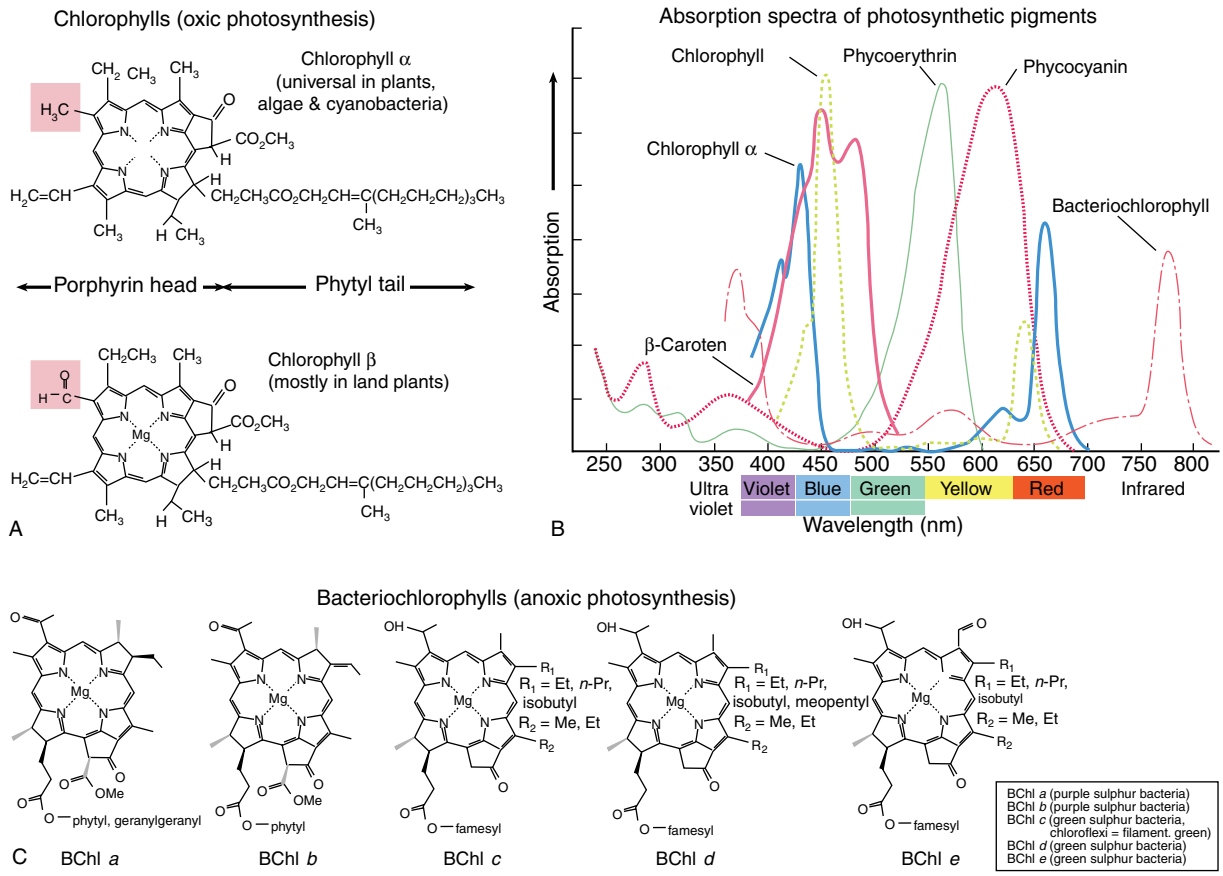


Fig. 2. Structures and features of the main photosynthetic pigments. (A) Chlorophyll-α and -β showing porphyrin head and phytyl tail. Pink box shows difference in structure that defines the two forms. (B) Absorption spectra of the chlorophylls, β-carotene and phycobilisomes (phycoerythrin in dominant in blue-coloured cyanobacteria and phycocyanin in red-coloured cyanobacteria. (C) Bacteriochlorophyll structures.

"blue-green algae." However, in terms of their genomic signature and the fact that the cell lacks a nucleus, they are better classified as prokaryotic bacteria.

In contrast to the cyanobacteria, all other photosynthetic bacteria in saline waters are anaerobes and utilize a single type of photosynthetic reaction centre with a different pigment (bacteriochlorophyll). When compared to chlorophyll and phycobilin, bacteriochlorophyll can absorb light with longer, less energy-rich wavelengths that extends into the infrared spectrum. Such light-requiring bacteria (e.g. purple bacteria) live in anoxic conditions and their ability to utilize the infrared spectrum means they can thrive deeper in a sediment or water column than aerobic photosynthesizers (Figs 2B and 13). The green sulphur bacteria (Chlorobiaceae) and purple sulphur bacteria (Chromatiaceae) use elemental sulphur, sulphide, thiosulphate, or hydrogen gas as the electron donor, whereas the purple and green nonsulphur bacteria use electrons from hydrogen or organic substrates (Table 2). As in aerobic photosynthesis, the resulting electrons (derived from the "light reaction" of photosynthesis) are stored in glucose and then used for CO_2 fixation (aka the "dark reaction" of photosynthesis).

The following simplified equation typifies anoxic photosynthesis of purple sulphur bacteria:

$$CO_2 + 2H_2S = CH_2O + H_2O + 2S \qquad (2)$$

That is, carbon dioxide and hydrogen sulphide react with bacteriochlorophyll and sunlight to form a carbohydrate (such as glucose) as well as water and sulphur. The light-absorbing pigments of the purple and green bacteria consist of bacterial chlorophylls and carotenoids. Phycobilins, characteristic of the cyanobacteria, are not found in these bacteria. All photoautotrophs (including

Table 2. Summary of Prokaryotes focusing on archaea and halophilic bacteria

Phylum or family			Informal group	Metabolic lifestyles (selected halophilic species)
Prokaryotes	Halo-adapted bacteria	Cyanobacteria	Cyanobacteria	Aerobic photoautotroph with chlorophyll-α plus phycobilicins, split water and generate oxygen (*Arthrospira platensis, Dactylococcopsis sauna, Aphanothece halophytica, Microcoleus chthonoplastes*)
		Proteobacteria	Purple sulphur bacteria	Anaerobic obligate photoautotroph – use H_2S or sulphur as electron donor (*Halorhodospira halophila* may be a significant primary producer in some settings, e.g. at a halocline; *Chromatium glycolicum, Ectothiorhodospira marismortui*)
			Purple non-sulphur bacteria	Anaerobic photoautotroph (tolerate low oxygen levels) – use hydrogen, but not from water, as the electron donor (e.g. *Rhodospirillum sp.)*
		Chlorobiaceae	Green sulphur bacteria	Anaerobic obligate photoautotroph – use H_2S or sulphur as electron donor (*Chlorobium limicola*)
		Flexibacteria	Green non-sulphur bacteria	Anaerobic (thermophilic) photoautotroph – use hydrogen, but not from water, as the electron donor (*Chloroflexus aurautiacus)*
		Spirochetes	Spirochetes	Free-living obligate anaerobe (*Spirochete halophila* oxidizes Fe and Mn). Chemolithotrophic, some species can be symbiotic or parasitic
		Bacteriacea	Flavobacteria	Anaerobic organotrophs and chemoautotrophs, some species can be parasitic (*Flavobacterium gondwanese* and *F. salegens* are psychrotolerant halophiles isolated from Antarctic Lakes) (*Salinibacter ruber* is phylogenetically affiliated with this group)
	Archaea	Euryarchaeota	Halophile	Aerobic photoautotroph, chemoautotroph (family Halobacteriales, includes: *Halobacterium* sp.; *Haloarcula* sp.; *Halobaculum* sp.; *Halococcus* sp.; *Haloferax* sp.; *Natroncoccus* sp.)
			Methanogen	Anaerobic chemoautotroph (*Methanocalculus* sp., *Methanohalophilus* sp., *Methanococcus* sp.)
		Crenarchaeota (sulpho-archaea)	Thermophile	Anaerobic chemoautotroph (Crenarchaeota-domain clone sequences documented in hypersaline sediments including Shark Bay stromatolites, anthropogenic salterns and sediments of Lake Qinghai, China)
			Acidophile	Aerobic- anaerobic chemoautotroph (as above), organotroph
		Nanoarchaeota	Symbiont on Ignoccus	Hosted on hot vent Archaea in Iceland. Its cell is only 400 nm long
		Korarchaeota	New group of extreme thermophile	Only described from RNA samples (if it is a real phylum then it is the closest to life's universal ancestor of the earliest Archaean ~3.7 Ga)

See Fig. 3 for additional information.

higher plants, cyanobacteria and bacteria) contain carotenoid pigments, which are red-orange and yellow in colour as they absorb the blue-violet and blue-green wavelengths missed by chlorophyll (Fig. 2B). The green sulphur bacteria are probably the most energetically efficient of all phototrophic organisms and can live in environments with long-term light intensities that are less than 0.01% of typical daylight. Many purple and green sulphur bacteria store elemental sulphur as a reserve material that, like glucose, can be further oxidized, in this case to SO_4, and so act as a photosynthetic electron donor.

Modern chemoautotroph communities in saline microbial communities generally form a metabolizing layer beneath the photosynthesizers (in both mats and stratified brine columns) and on top of the methanogens; some species in the chemoautotrophic layer are lithotrophs. Lithotrophic sulphur oxidizers active in saline environments include a number of species of both bacteria (e.g. *Thiobacillus*) and archaea (e.g. *Sulfolobus sp.*). *Thiobacillus* is widespread in marine and hypersaline microbialites and oxidizes thiosulphate and elemental sulphur to sulphate. Other lithotrophic bacteria use substances such as nitrate and reduce it to nitrite and include at least two species (*Nitrobacter akalicus* and *Nitrosomas halophila*) that flourish in the freshened water stages in the Kenyan soda lakes (Sorokin & Kuenen, 2005). *Sulfolobus sp.* tend to be hydrothermal vent dwellers that prefer settings characterised by hot, saline and acidic waters (see later).

Sulfolobus is a species within the archaeal domain (formerly known as the archaebacterial domain), which constitutes the "third domain of life" (see Glossary). While members of the archaea resemble bacteria in morphology and genomic organization, they resemble eukarya in their method of genomic replication. The archaeal domain is further subdivided into two kingdoms: the Crenarchaeota, of which all members presently isolated are extreme thermophiles, and the Euryarchaeota, a diverse group, that includes the halophilic order Halobacteriaceae, certain thermophiles and all members of the methanogen group (Table 2). All archaea are characterized by: (1) the presence of characteristic tRNAs and ribosomal RNAs; (2) the absence of peptidoglycan cell walls; (3) the presence of ether-linked lipids built from branched-chain subunits; and (4) their occurrence in unusual habitats (that seem extreme from an anthropocentric worldview).

Archaea are mostly extremophiles, that is they thrive in extreme conditions including: extremely saline (halophile), extremely hot (thermophile), extremely dry (xerophile), extremely acid (acidophile), extremely alkaline (alkaliphile), and extremely cold (psychrophile) environments. Some extremophiles are capable of surviving the multiplicity of extreme conditions that characterize arid environments and are known as polyextremophiles (Kates *et al.*, 1993).

Archaea and bacteria that require extreme salinities to metabolize are called halophiles, those that can tolerate salinities in excess of 25% are termed hyperhalophiles, and almost all documented modern hyperhalophiles are archaea. One of the more impressive halophilic archaea is *Halobacterium lacusprofundi*; it is both a halophile and a psychrophile, it thrives in bottom waters of the supersaline (~350‰) and cold (<0°–11.7 °C) Deep Lake, Antarctica (Franzmann *et al.*, 1988). The lake is too saline to freeze over, is thermally stratified and lies in an endoheic depression in the Vestfold Hills with a water surface that is some 50 m below sea level.

Throughout this paper, it will be discussed in detail why microbes (archaea and bacteria) in saline waters are halophilic, but it is notable that many halophiles are also thermophiles. Worldwide, aerobic halophilic archaea of the order Halobacteriales tend to have high growth optima at warm temperatures, typically between 35° and 50 °C and sometimes even higher (Oren, 2006). This may be an adaptation to the elevated temperatures that characterize stratified heliothermic waters in salt lakes worldwide. Likewise, within the anaerobic halophilic bacteria of the order Haloanaerobiales there are several moderately thermophilic representatives. *Halothermothrix orenii*, the first truly thermophilic halophile discovered, was isolated from Chott El Guettar, a warm saline lake in Tunisia. It grows optimally at 60 °C and up to 68 °C at salt concentrations as high as 200‰ (Cayol *et al.*, 1994). The halophilic *Acetohalobium arabaticum* strain Z7492 has a temperature optimum of 55 °C, can grow at salinities between 100‰ and 250‰ with an optimum around 150–180‰ and, like the halophilic archaea, has adapted to high salinities via the uptake of intracellular KCl (Zahran, 1997).

Even more extreme in its environmental preferences is the archaea *Sulfolobus tokodaii;* it is a hot spring dweller and intracellularly transforms H_2S to elemental sulphur. It flourishes at

temperatures in excess of 90 °C and can live in saline environments where pH hovers around 1. Many such sulphur-dependant archaea are anaerobic chemoautotrophs that live in the vicinity of hydrothermal/volcanogenic vents in saline lacustrine rifts, or in marine hydrothermal brine springs, or in the basal waters of density-stratified brine lakes and seaways. They also inhabit deep seafloor brine pools on top of dissolving salt allochthons and they can survive and possibly metabolize hundreds of metres below the surface in bathyphreatic halite beds and sulphate caprocks (Grant *et al.*, 1998). Like these archaea, some chemoautotrophic bacteria can survive in extreme conditions, even living in saline subterranean settings, as evidenced by the recovery of viable halophilic chemolithotrophic bacteria (*Haloanaerobium sp.*) from highly saline oil fields brines in Oklahoma where pore-water salinities are ~150–200‰ (Bhupathiraju *et al.*, 1999).

Many halotolerant and halophilic bacteria and archaea are heterotrophs feeding on the remains of other organisms that had flourished in the same water mass at lower salinities. Heterotrophic metabolism shows variation in the terminal electron acceptor. In aerobic respiration it is oxygen and the breakdown product is CO_2, in anaerobic respiration it may be sulphate or nitrate and the breakdown product is H_2S or nitrite.

Halotolerant bacteria isolated from mesohaline settings tend to be anoxygenic photosynthesizers such as *Chromatium salexigens, Thiocapsa halophila,* and *Rhodospirillum salinarum,* with optimal growth in these species between 60 and 110‰ (Fig. 3; Caumette, 1993). In contrast to the cyanobacteria, which are oxygenic phototrophs, these anoxic phototrophs use H_2S, organic compounds or sulphur compounds as electron donors to produce various oxidized sulphur metabolites, the final product being sulphate. These anoxygenic halotolerant to halophilic photobacteria create dense biogenic laminae in a variety of anoxic, generally poorly lit environments. Phototrophic sulphur-oxidizing bacteria in many salt lakes grow in narrow niches defined by interfaces that are lit and also contain sulphide. In microbial mats they grow below the cyanobacterial and the phototrophic bacterial layers, while in stratified brine columns they inhabit waters of the halocline. Intense blooms of purple or green sulphur bacteria

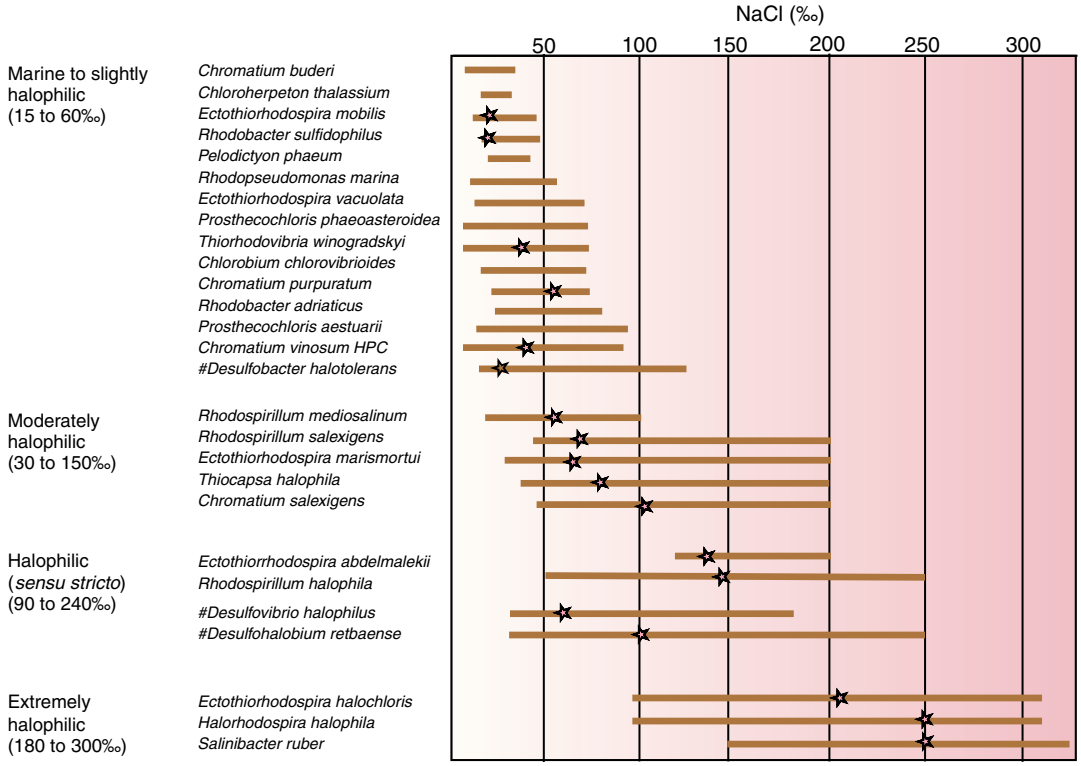


Fig. 3. Salinity tolerances of phototrophic halophilic bacteria, sulphate-reducers (#) and *Salinibacter ruber*. Star on bar indicates the salinity for optimal growth (after Ollivier *et al.*, 1994; Caumette, 1993; Imhoff, 1988; Ventosa, 2006).

can form brightly coloured water masses or sediment layers. Most of the H_2S they metabolize is biogenic rising from below and generated by microbial sulphate reduction, except around brine springs and hydrothermal vents where there can be high levels of abiogenic H_2S (Knauth, 1998). The biodiversity of bacterial photosynthesizers fall off as higher salinities are reached (Pedrós-Alió, 2005).

Purple and green bacteria growth is only possible in settings where the chemical gradient of sulphide is stabilized against vertical mixing. In layered microbial mats this occurs at the interface between the oxygenated layer created by the photosynthesizing cyanobacteria and the underlying anoxic layer created by the sulphate reducers. In stratified brine columns, chemical gradients are stabilized by density and temperature differences between the cooler less saline surface waters and the warmer more saline bottom layers and so they tend to inhabit the halocline. Examples of sulphur-oxidizing bacteria in hypersaline settings include *Atium volutans* from Solar Lake, *Beggiatoa alba* from Guerrero Negro, and *B. leptiformis* from Solar Lake (DasSarma & Arora, 2001). A unicellular halophilic, chemoautotrophic sulphur-oxidizing bacterium, *Thiobacillus halophilus*, has also been described in a hypersaline Western Australia lake where it grows in waters with salinities of up to 240‰ (Wood & Kelly, 1991).

All modern halophilic sulphur-oxidizing bacteria are filamentous, CO_2-fixers, typically motile and utilize sulphide as an electron donor for their photosynthesis. Purple sulphur bacteria seem to flourish across a broad range of continental brine salinities. For example *Ectothiorhodospira* halophilic species dominate in the microbial sediments of alkaline soda lakes in Egypt and Central Africa, while the moderate halophile *Ectothiorhodospira marismortui* is a strict anaerobe found in the waters of hypersaline waters (170‰) of sulphur springs in the Dead Sea, where spring waters had a pH around 5.2 and a temperature of 40 °C (Fig. 3). Isolates of this species grew poorly at a pH or 5.5 but thrived in the neutral pH range between 7 and 8 (Oren *et al.*, 1989). Another extremely halophilic sulphate-oxidizer *Ectothiorhodospira halochloris* was isolated from Wadi Natrun in 1977, in the laboratory it showed optimal growth in salinities in the range 140–270‰, a pH-range between 8.1 and 9.1 and temperatures between 47°C and 50°C (Fig. 3).

Dissimilatory sulphate reduction can occur up to quite high salt concentrations and black, sulphide-containing sediments form on the bottom of modern coastal salinas and salt works well into the penesaline salinity range (Oren, 2001). Amongst the bacteria, most salt-tolerant halophilic sulphate-reducer thus far found is *Desulfohalobium retbaense*; it is a lactate oxidizer and was isolated from Lake Retba in Senegal. In the laboratory it remained viable at NaCl concentrations of up to 240‰, with a growth optima of 100‰ (Ollivier *et al.*, 1994). Two other sulphate-reducing halophilic isolates are *Desulfovibrio halophilus* and *Desulfovibrio oxyclinae,* which can tolerate periods of NaCl concentration of up to 225‰ (Fig. 3; Caumette, 1993; Krekeler *et al.*, 1997). Another isolate, similar to *Desulfovibrio halophilus* has been identified in brine pool samples collected in the allochthon-associated deep-water brine lakes on the floor of the Red Sea where it grows in salinities up to 240‰, but only slowly.

In sulphate reduction, the oxidation of acetate and CO_2 yields more energy per cell compared to the precursor oxidation of lactate. Recently the first halophilic acetate-oxidizing sulphate-reducing bacterium was isolated: *Desulfobacter halotolerans (*or *Desulfohalobium utahense)*. It was collected from the hypersaline bottom sediments of the North Arm of Great Salt Lake, Utah, and was found to have a rather restricted salinity tolerance, it grows optimally at 10–20‰ NaCl, does not grow above 130‰ and is unable to survive above 240‰ NaCl (Fig. 3; Brandt & Ingvorsen, 1997; Jakobsen *et al.*, 2006). Even so, it possesses the highest NaCl-tolerance reported for any member of the genus *Desulfobacter*. In terms of metabolic pathways in the various salt-tolerant or halophilic sulphate reducers, it seems species that oxidize lactate, such as *Desulfovibrio halophilus,* can tolerate higher salinities of up to 250‰ than those species capable of oxidizing acetate, such as *Desulfobacter halotolerans,* which do best in salinities of less than 100–120‰ (Figs 3 and 4). In contrast to the sulphate-reducers, it seems no viable sulphur-oxidizing communities can survive at similar extreme salinities compared to the lactate oxidizers (Fig. 4).

Living below or among the sulphate-reducer communities in both microbial mats and stratified brine columns are the fermenters and the methanogens. One group of halophilic bacteria especially well adapted to the fermentative lifestyle is the Haloanaerobiales (Oren, 1992). Fermenters live in anaerobic saline conditions when there is no electron acceptor, and different sugars and in some cases amino acids are fermented to products

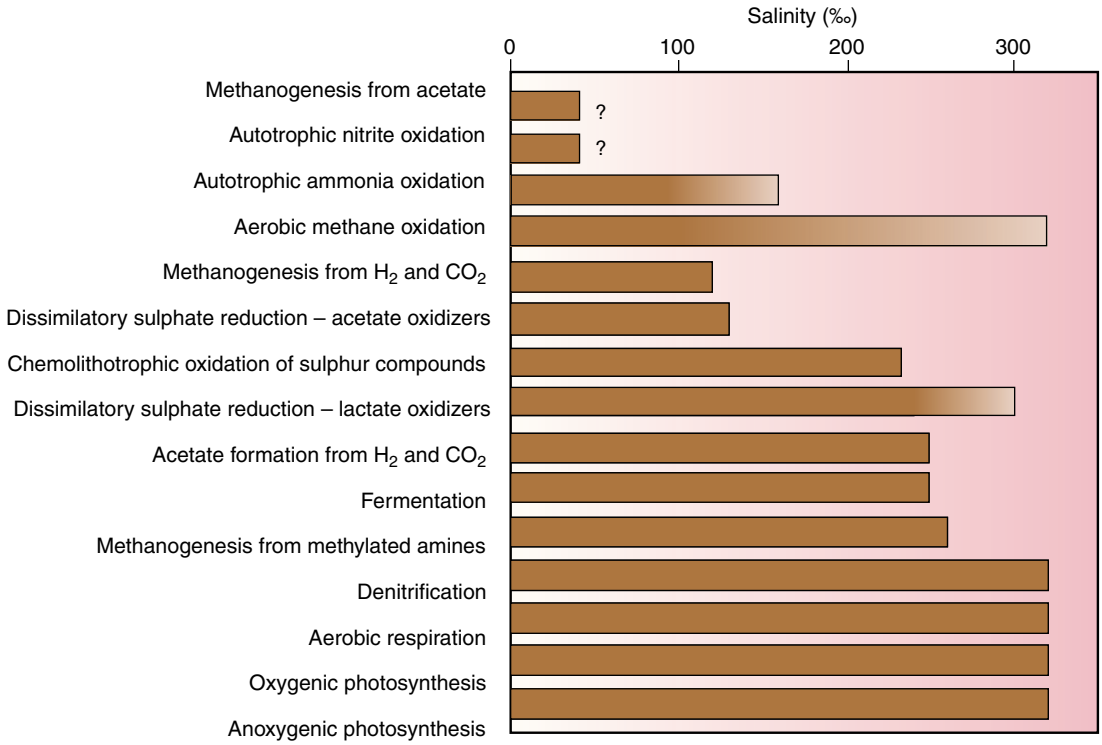


Fig. 4. Approximate upper salinity limits of selected microbial metabolic pathways (after Oren, 2001 and references therein). Values presented are based on laboratory studies of pure cultures (solid brown bars) and on activity measurements of natural communities in hypersaline environments (graded-colour extensions to bars).

such as acetate, ethanol, butyrate, hydrogen, and carbon dioxide. Fermentation breaks down an organic compound, such as a sugar or an amino acid, into smaller organic molecules that then accept the electrons released during the breakdown of the energy source. When glucose is broken down to lactic acid, each molecule of glucose yields only two molecules of ATP, and considerable quantities of glucose must be degraded to provide sufficient energy for microbial growth. Fermentation means only a relatively small output of energy per glucose molecule consumed as any organic molecule is only partially oxidized. Fermentation tends to be the sole metabolic mechanism in the well-adapted halotolerant and halophilic species of the Haloanaerobiales that inhabit the lowers parts of a microbial mat or brine column. It can be an emergency metabolic system in other microbes that find themselves in this same environment. The presence of biomarkers of fermentative microbes in saline and hypersaline Phanerozoic sediments or oils indicates depositional conditions that were anoxic and highly stressed with respect to higher life forms. Such brine- and pore-water conditions tend to facilitate the preservation of hydrogen-prone organic end-products (proto-kerogens).

Methanogens are archaea that create methane gas as they remove excess hydrogen and fermentation products produced by other forms of anaerobic respiration. The methane then rises through the sediment or brine column to be utilized by the sulphate-reducers. Today some two-thirds to three quarters of the biogenic methane passed into the atmosphere worldwide is the work of a few dozen species of methanogenic archaea most of which live in relatively low salinity environments. The remainder of the world's methane comes from higher plants (Keppler *et al.*, 2006; Houweling *et al.*, 2006). All methanogenic archaea are obligate anaerobes thriving in three habitats: (a) bodies of anoxic fresh to hypersaline surface and subsurface water (e.g. the bottom brines of Solar Lake; (b) the vicinity of thermal brine springs; and (c) the digestive tracts of ruminants).

The main methanogenic processes in freshwater environments and in the guts of ruminants are the reduction of CO_2 with hydrogen and the aceticlastic split mechanism where organic matter is split by oxido-reduction into methane and carbon dioxide,

but neither of these reactions has been shown to occur at high salt concentrations (Oren, 2006 and references therein). It seems that oxidation of organic matter is incomplete in settings with high levels of NaCl when compared with that in other ecosystems (temperate lacustrine and marine ecosystems) where acetate, $H_2 + CO_2$ are efficiently metabolized to produce CH_4, or are oxidized by sulphate-reducing bacteria whenever sulphate is available. At salinities higher than 150‰, the mineralization of organic compounds is limited by poor rates, or the complete absence, of microbial sulphate reduction of acetate and the inherently slow rates of methanogenesis utilizing H_2 (Fig. 4). The highest salt concentration at which such methanogenesis (from $H_2 + CO_2$) occurs in nature is in the 88‰ bottom waters of Mono Lake, California (Fig. 4: Oremland & King, 1989). The resulting accumulation of hydrogen and volatile fatty acids (VFA) in saline sediment beneath brine columns more saline than this, implies that catabolism via interspecies hydrogen transfer hardly occurs at all in more hypersaline environments (Ollivier *et al.*, 1994). Hence sediment from the floor of the Great Salt Lake contains up to 200 μM dissolved H_2. Similar results were obtained from Dead Sea sediments stimulated to reduce sulphate with H_2 and formate, although the same sediments did not respond with acetate, propionate, or lactate treatments. Energetic constraints may explain the apparent lack of truly halophilic methanogens capable of growing on $H_2 + CO_2$ or on acetate, as these methanogens use the energetically more expensive option of synthesizing organic osmotic solutes (see later, "low salt in" discussion).

Methanogenesis occurs at much higher salt concentrations but only via a less productive metabolic pathway that utilizes methylated amines, methanol, and dimethylsulphide substrates (Fig. 4; Oren, 2001, 2006). The most salt-tolerant methanogens known are *Methanohalobium evestigatum* and *M. portucalensis*, which grow in up to 250–260‰ NaCl. Additional moderately halophilic methanogens have been isolated, growing optimally at 40–120‰ salt (e.g. *Methanohalophilus mahii*, *M. halophilus*, *M. portocalensis*, *M. zhilinae*). Modern halophilic methanogens can form rich microbial communities in the density-stratified waters of deep-seafloor brine lakes, including suprasalt allochthon areas on the deep Mediterranean seafloor where some anoxic bottom brines have evolved to the bittern stage ($MgCl_2$ saturation; van der Wielen *et al.*, 2005). It may well be that Earth-bound primordial life first evolved as methanogens in hypersaline waters (Dundas, 1998; Knauth, 1998).

Fermenters live in anaerobic saline conditions using a metabolic pathway where there is no electron acceptor, where different sugars, and in some cases amino acids, are fermented to products such as acetate, ethanol, butyrate, hydrogen and carbon dioxide (Hite & Anders, 1991). When evaporite salts precipitate, these liquid organics are often encased as brine inclusions in halite and other salt crystals and so are not picked up in standard TOC determinations. Their relative contribution to any source rock potential is poorly understood in subsurface evaporitic systems where cross-flowing basinal brines are dissolving buried halite beds. They may be locally significant contributors volumetrically to the hydrocarbons moving in carrier beds in contact with dissolving evaporites.

The last groupings to be considered in this discussion of the various metabolic pathways active in hypersaline settings are the haloviruses and bacteriophages that must infect the haloarchaea and bacteria. Compared to the literature-base for the halophilic archaea and bacteria little is known and most published studies to date deal with the haloviruses infecting the haloarchaea (Ventosa 2006; Dyall-Smith *et al.*, 2005). Nonetheless, given that in the natural world virus populations are greater than those of their prokaryotic hosts and that each host species is susceptible to infection by several different viruses, it may be deduced that a great diversity of such viruses must exist in hypersaline environments.

Electron microscopy of hypersaline waters shows that they maintain high levels of virus-like particles (about 10 times higher than the cell population), with recognizable morphotypes including head–tail and lemon-shaped particles (Ventosa, 2006 and references therein). Guixa-Boixereu *et al.* (1996) determined the abundance of viruses in two different salterns in Spain and observed that the number of viruses increased in parallel to that of prokaryotes, from $10^7\,mL^{-1}$ in the lowest salinity ponds to $10^9\,mL^{-1}$ in the most concentrated ponds (crystallizers), thus maintaining a proportion of 10 virions per prokaryotic cell throughout the salinity gradient. A lemon-shaped virus was found infecting square archaea; its abundance increased along the salinity gradient together with the abundance of the square archaea. Following a *Dunaliella sp.* bloom in freshened surface waters of the Dead Sea, Oren *et al.* (1997) observed the

presence of large numbers of virus-like particles in water (up to 10^7 virus-like particles mL^{-1}), with a variety of morphologies, from spindle-shaped to polyhedral and tailed phages. Details of the halobiotal bloom in the Dead Sea will be discussed later. It may be concluded that viruses and bacteriophages are abundant in the archaea and bacteria that inhabit hypersaline waters, but the various metabolic pathways operating within this infesting community have yet to be fully established and await further study.

In summary, halophilic bacteria as a group are capable of using several metabolic styles and so are more biochemically divergent than the halophilic archaea. Some purple bacteria and gram-positive bacteria are chemoautotrophic halophiles, while halophilic cyanobacteria are oxygenic photoautotrophs. Under suitably stressed conditions many halophilic bacteria become heterotrophic, utilizing either anaerobic or aerobic respiration pathways. By evolving oxygen respiration some 2.5 billion years ago, the cyanobacteria came to flourish and ultimately displace the archaea. Ancient cyanobacteria lived in symbiosis with early eukaryotes; by the Mesoproterozoic this had allowed eukaryotic photosynthesis to develop and ultimately led to the evolution of the higher plants and animals. Once oxygen was plentiful in the atmosphere (~2.2 Ga), it was difficult for anaerobes (including photosynthesizing archaea and bacteria) to flourish in most surface waters. Some retreated to anaerobic environments, some acquired aerobic bacteria as endosymbionts, and some continued to thrive in aerobic/dysaerobic conditions that typify the hypersaline bottom waters of most density-stratified brine bodies.

BIOADAPTATIONS TO INCREASING SALINITY

In 1957, in his classic book on evaporites, Lotze made the statement: "Nicht das Leben, sondern der Tod beherrscht die Salzbildungsstätten" (Not life, but death rules the locales of salt deposition). Saline environments were considered biotal deserts, largely devoid of biological activity and hence were considered to be sedimentary systems with little source rock potential. The following discussion shows that this is not the case. Rather, saline environments and water bodies are sites of periodic but intense organic activity where numerous highly specialized algal, bacterial and archaeal species grow and die (cycles of "famine or feast"). They can leave behind substantial volumes of oil-prone organic residues in the bottom sediments, especially in laminated mesohaline carbonates, which on burial can evolve into prolific source rocks. Even in modern saline environments, where evaporite depositional settings are not as diverse or widespread as those of much of the past, conditions are such that mesohaline carbonates can preserve high levels of total organic carbon (TOC; Fig. 5).

Salinity ranges of the modern halobiota

Progressive brine concentration leads to sequential blooms of a macro and microbial biota adapted to different ranges of salinity in both marine and continental settings (Fig. 6A and B). As a modern surface brine is concentrated from 60‰ to around 200‰, dense eukaryotic algal and cyanobacterial populations appear, grazed by ostracods, brine shrimp and brine fly larvae. Halotolerant protozoa can be found feeding in this salinity range, as can yeasts and other fungi (Gunde-Cimerman *et al.*, 2005). Halotolerant microbial mats cover the bottom of many hypersaline ponds and shallow lakes in this salinity range. In anoxic waters in this salinity range there are a variety of sulphur-oxidizing, sulphate-reducing, homoacetogenic, methanogenic and heterotrophic bacteria and archaea, especially near the base of stratified brine columns or in the lower parts of mesohaline microbial mats.

From about 240‰ to more than 320‰, red-orange haloarchaea (halophilic and hyperhalophilic archaea) and halobacteria (e.g. *Salinibacter ruber*) come to dominate, mostly living on the products of decomposing organic matter left over from an earlier lower salinity time (Pedrós-Alió, 2005). At the elevated salinities where these halophiles and hyperhalophiles flourish, only a few eukaryotes such as brine shrimp (*Artemia* and *Parartemia sp.*) can survive to graze on the remaining species of cyanobacteria and algae, especially *Dunaliella sp.* – a unicellular green alga (Fig. 6A). Above 300‰ no aerobic photosynthesis occurs, or at least is not known to occur based on the absence of chlorophyll-α in the brines. As ever more elevated salinities are attained, most other microbial activity first slows and then ceases.

A variety of obligate and facultative halophytic plants can survive in the moderate-to-high salinity soils that surround saline pans and lakes, e.g. *Atriplex halimus, Mesembryanthemum crystallinum* and *Salicornia sp.* Only a few species of

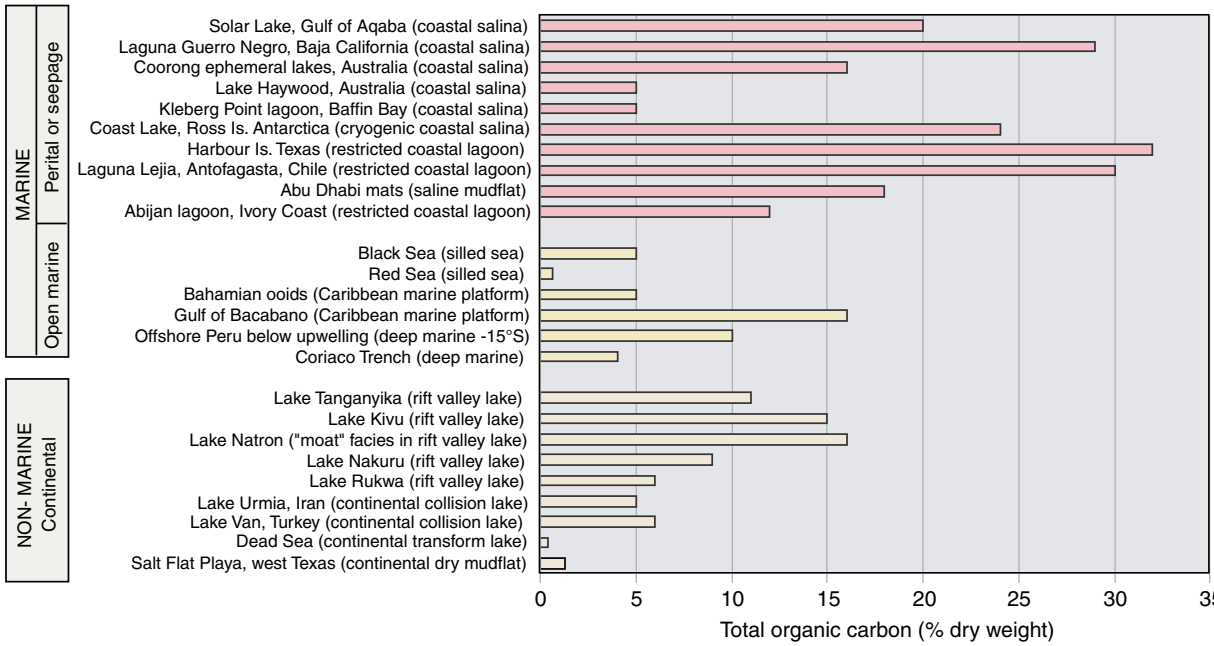


Fig. 5. Total organic carbon (TOC, dry wt%) in modern saline settings. Compiled from sources listed in Warren (1986, 2006).

animal can tolerate hypersaline conditions (Fig. 6A and B; DasSarma & Arora, 2001). The highest salinity at which viable vertebrates have been observed is around 60‰. For example, the white-lipped or alkaline tilapid fish (*Oreochromis alcalica*) flourishes in the mesohaline waters of the African rift lakes. This setting includes thermal spring waters at 36–40 °C along the moat-like edges of Lake Natron and Lake Magadi, where waters can have a pH as high as 10.5–11 and salinities in excess of 65–70‰.

Large numbers of invertebrates can survive in low to moderately mesohaline environments. Examples include salt-tolerant rotifers (aka wheel animalcules) such as *Brachionus angularis* and *Keratella quadrata*, and tubellarian worms (flatworms) such as *Macrostomum sp*. Insects from hypersaline environments include halotolerant brine flies, such as *Ephydra hians* and *E. gracillis*, which feed and lay their eggs in microbial mats and organic scum about the strandlines of modern saline lakes. Likewise, brine fly larva are adapted to saline conditions, *Ephydrella marshalli* larvae collected from commercial salt work lagoons on Port Phillip Bay, Victoria, have survived several days immersed in hypersaline sodium chloride media at an osmotic concentration of 5848 mOsm L^{-1} (175‰ NaCl; Marshall *et al.*, 1995).

Halotolerant crustaceans include ostracods such as *Cypridis torosa, Paracyprideinae sp., Diacypris compacta* and *Reticypris herbsti*, copepods such as *Nitocra lacustris* and *Robertsonia salsa*, and brine shrimps such as *Artemia salina, Parartemia zietzianis* and other related species. Brine shrimp survive a wide range of salinities from 25 to 240‰ with their optimal range around 60–100‰; they are well adapted to the fluctuating oxygen and salinity levels that characterize many mesohaline ecosystems. Geddes 1975a–1975c argued that increased osmotic stress, not oxygen level, is the dominant limit on the upper salinity tolerance of Australian brine shrimp (*Parartemia zietzianis*), and this is probably also true for *Artemia* sp. (Geddes, 1981).

Halotolerant ostracods and brine shrimp feed on plankton living in the upper water mass of density-stratified brine columns and ingest benthic mats where this less-saline water mass intersects the lake margin or when bottom-water salinities are suitably lowered (de Deckker, 1981; De Deckker & Geddes, 1980). They produce pelleted carbonate detritus, which is a common component of many modern and ancient evaporitic laminites (Warren, 2006).

Diatoms (halotolerant bacillariophytal yellow-green algae with siliceous tests) are common planktonic forms in mesohaline and penesaline waters. They flourish at times of bloom in freshened salt-lake waters or in zones of perennial seepage and dissolution ponds (posas) about the edges of some salars. Their siliceous tests become a major detrital

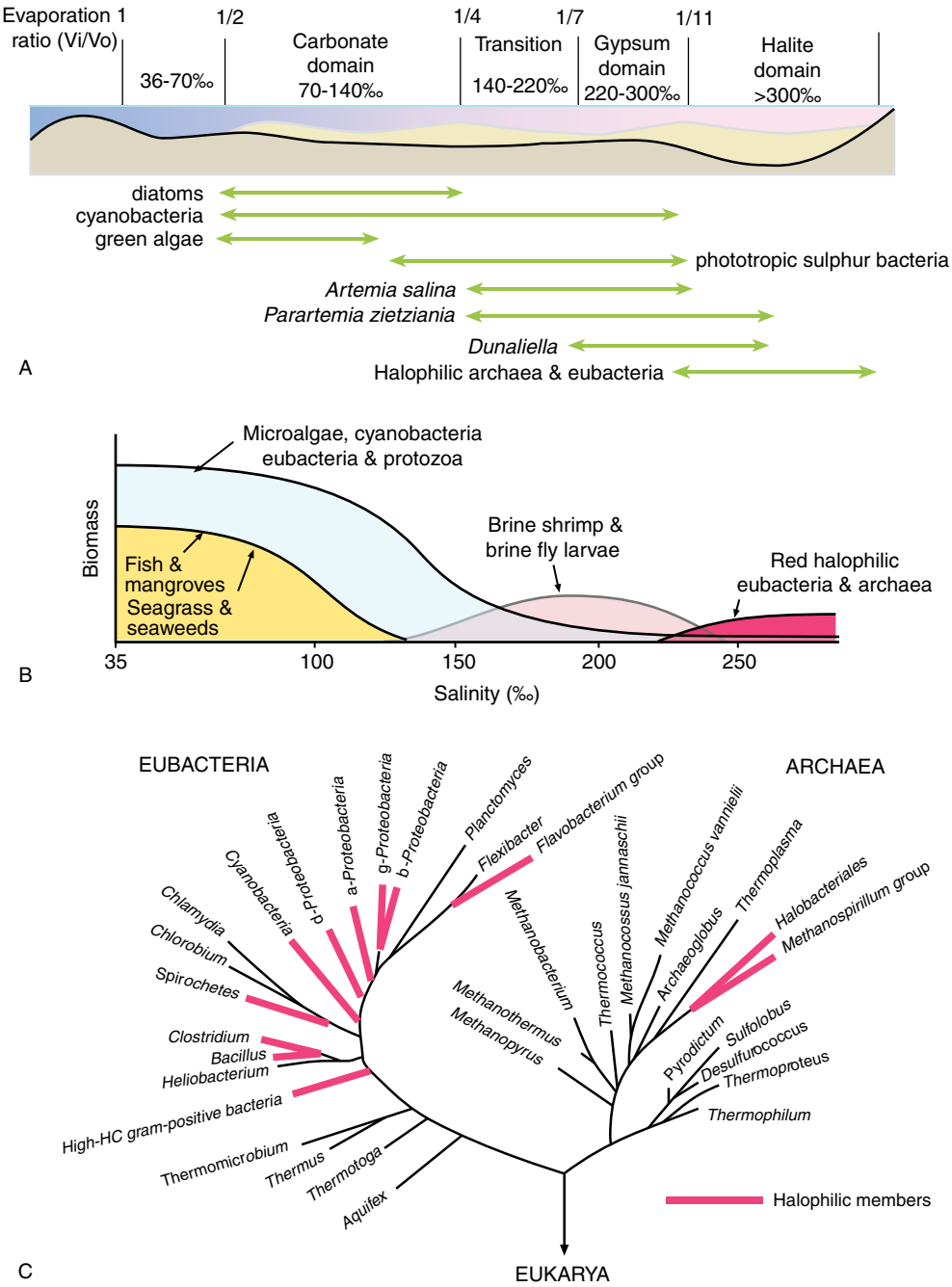


Fig. 6. Salinity tolerances of key biota. (A) Typical salinity ranges of the halotolerant biota where Vi is the volume of inflow to the basin and Vo is the volume of outflow (includes evaporation and reflux; after Barbé *et al.*, 1990). (B) Typical salinity ranges and biomass proportions of the biota in modern marine saltwork ponds. (C) Phylogenetic tree of the bacteria and the archaea, based on 16S rRNA sequencing comparisons. Thick red lines indicate branches containing representatives able to grow at or near optimal rates at NaCl concentrations exceeding 15% (after Ventosa *et al.*, 1998).

component in some lacustrine stromatolites (Winsborough *et al.*, 1994). Some halotolerant varieties of diatoms live in mesohaline lake brines with salinities around 120‰, while the upper limit for diatom growth is around 180‰ (Clavero *et al.*, 2000). The most halotolerant diatom taxa in the saltern ponds of Guerrero Negro, Baja California Sur, Mexico, are *Amphora subacutiuscula*, *Nitzschia fusiformis* (both *Amphora* taxa), and *Entomoneis sp.*; all grow well in salinities ranging

from 5 to 150‰, Three strains of the diatom *Pleurosigma strigosum* are unable to grow in salinities of less than 50‰ and so are true halophilic alga.

In most moderately hypersaline (mesohaline to penesaline; 60–200‰) settings halotolerant cyanobacteria and green algae, rather than diatoms, are the dominant primary organic producers and green algal densities can be more than $10^5\,mL^{-1}$. These planktonic blooms can support many birds; one of the most spectacular examples is the pink flamingo population of African rift lakes. Mesohaline algae are mostly obligately aerobic, photosynthetic, unicellular microorganisms with some species producing large quantities of orange-coloured β-carotene pigment. Planktonic blooms in saline lakes can colour saline waters pink or red, especially at the higher end of this salinity range. Green algae of the genus *Dunaliella* (e.g. *Dunaliella salina, D. parva,* and *D. viridis*) are ubiquitous in modern Northern Hemisphere brine lakes, such as Great Salt Lake and the Dead Sea, and are the main source of food for brine shrimp and larvae of brine flies (DasSarma & Arora, 2001). Most species of green algae are moderate halophiles, with only a few extremely halophilic species (e.g. *Dunaliella salina* and *Asteromonas gracilis*) that survive in marginward refugia, even when the upper and low water layers in the Dead Sea are NaCl-saturated (see later).

Protozoa occur in most mesohaline waters, they are chemoheterotrophic protists that lack a cell wall and typically ingest algae and bacteria (Hauer & Rogerson, 2005). Identified species include the moderate halophile *Fabrea salina* from a west Australian salt lake and the extreme halophile *Porodon utahensis* from the Great Salt Lake. The number of known protozoan species identified in hypersaline waters (at salinities ranging from 90‰ to 220‰) has grown from <50 in the 1970s to more than 200 today, and include a range of amoebae, ciliates and flagellated protozoa. Fungi, mostly yeasts, are another heterotrophic component of a modern saline salt lake biomass (DasSarma & Arora, 2001; Gunde-Cimerman *et al.*, 2005). They are chemoheterotrophic eukaryotes, some of which are well adapted to tolerate markedly hypersaline environments. They grow best in aerobic conditions on carbohydrate substrates at moderate temperatures and in acidic to neutral pH brines. *Debaromyces hansenii* is a halotolerant yeast that, when isolated from seawater, can grow aerobically in salinities up to 250‰ and is capable of assimilating hydrocarbons. Another saprophytic hyphomycete (fungi), *Cladosporium glycolicum*, was found at a salinity exceeding 260‰ growing on submerged wood panels in the Great Salt Lake. Halophilic fungi (e.g. *Polypaecilum pisce* and *Basipetospora halophila*) have also been isolated as a cause of spoilage in salted fish and bacon, but their distribution in hypersaline waters is not well known.

Above 200–240‰ most photosynthetic algae and halotolerant cyanobacteria cease to function and the halophilic archaea and bacteria come to dominate, mostly as decomposers (Fig. 6A and B; Pedrós-Alió, 2005). The transition into a more archaeal-rich biota means that while eukaryotic metabolic pathways and biochemistry dominates mesohaline waters, prokaryotic and archaeal metabolisms come to dominate at higher salinities (see later biomarker discussion).

"Halobacteria" flourishing in supersaline waters belong to the archaeal family Halobacteriaceae. All known extremely halophilic archaea stain gram negative, do not form resting stages or spores, and reproduce by binary fission (Oren, 2006). They are highly specialized micro-organisms, most of which will not grow at total salt concentrations below 2.5–3 M (145–175‰ NaCl) and are destroyed by lower salinities (see cellular adaptations). At present with the archaeal family Halobacteriacea there are 14 known genera and 35 validly described species. Six of these genera are monotypic: *Halobacterium; Halobaculum; Natrosomonas; Natrosobacterium; Halogeometricum; Haloterrigena*. The other genera (Table 3; Oren, 2006) are: *Natrialba* (2 species); *Natrononcoccus* (2 species); *Natrinema* (2 species); *Natrorubrum* (2 species); *Halococcus* (3 species); *Haloferax* (4 species); *Halorubrum* (7 species), *Haloarcula* (7 species). *Halococcus sp*. are strict aerobes, their name reflects their coccoid cell shapes and they form pairs, tetrads, sarcinae or irregular clusters. Cells produce several orange or red carotenoid and retinal pigments needed to better cope with high levels of ultraviolet light that characterize supersaline brine settings. *Haloferax* prefers high-Mg waters and is a major constituent in the halophilic biota of the Dead Sea. The various Halococcoid species, along with *Haloferax* and *Haloarcula*, flourish worldwide in hypersaline lakes, coastal salinas and brine lakes on the deep sea floor.

Most interesting, but most problematic, are the square-shaped archaea growing in many halite-precipitating brines. In 1980, A. E. Walsby described the abundant presence of "square bacteria" in

Table 3. Constituent groups of the archaeal family Halobacteriaceae (after Oren, 2006)

Family	Genus	Species
Halobacteriaceae	*Halobacterium*[T]	*Halobacterium salinarum*[T]
	Halobaculum	*Halobaculum gomorrense*[T]
	Halorubrum	*Halorubrum saccharovorum*[T]
		H. sodomense
		H. lacusprofundi
		H. coriense
		H. distributum
		H. vacuolatum
		H. trapanicum
	Haloarcula	*Haloarcula vallismortis*[T]
		H. marismortui
		H. hispanica
		H. japonica
		H. argentinensis
		H. mukohataei
		H. quadrata
	Natronomonas	*Natronomonas pharaonis*[T]
	Halococcus	*Halococcus morrhuae*[T]
		H. saccharolyticus
		H. salifodinae
	Natrialba	*Natrialba asiatica*[T]
		N. magadii
	Natronobacterium	*Natronobacterium gregoryi*[T]
	Halogeometricum	*Halogeometricum borinquense*[T]
	Natronococcus	*Natronococcus occultus*[T]
		N. amylolyticus
	Haloferax	*Haloferax volcanii*[T]
		H.x gibbonsii
		H. denitrificans
		H. mediterranei
	Natrinema	*Natrinema pellirubrum*[T]
		N. pallidum
	Haloterrigena	*Haloterrigena turkmenica*[T]
	Natronorubrum	*Natronorubrum bangense*[T]
		N. tibetense

[T] = type genus of the family or type species of the genus.

a small, halite-saturated brine pool, in the Sinai Peninsula (Walsby, 1980). These micro-organisms were collected from the surface of the pool, had a large number of gas vesicles, and presented unique cell morphologies never observed previously in the microbial world. The cells are squares and very thin, with sizes from 1.5 to 11 μm and a thickness of about 0.2 μm. Division planes were observed, with an arrangement indicating that division occurred in two planes alternating at right angles, so that each square grows to a rectangle which then divides into two equal squares, producing sheets divided like postage stamps (Walsby, 1980). In addition, different gas vesicles were observed, from spindle-shaped to cylindrical with conical ends and, in many cases, they were concentrated at the cell periphery. Ultrastructure studies confirmed that the square cells observed by Walsby were micro-organisms with a typical prokaryote structure.

Direct observations of brines of salterns and other hypersaline environments showed that these square cells were very abundant in such habitats, especially in the most concentrated ponds with salinities higher than 3–4 M NaCl (at halite saturation, 175–233‰ NaCl), and they have been reported to occur in many geographical locations in both the Northern and Southern Hemispheres (Oren, 1999a). For more than 20 years these were considered uncultivable, until the work of Burns *et al.* (2004) and Bolhuis *et al.* (2004), who independently cultivated what Bolhius and coworkers informally named *"Haloquadratum walsbyi"*. The isolation of the square archaea by two independent research groups introduced a new methodology that now permits the isolation of new fresh isolates

of square archaea from various areas. Future work will establish whether they are represented by a single or several novel haloarchaeal species capable of living amongst halite crystals. Work to date suggests that it is a new genus of the Halobacteriaceae, rather than a species within the existing genera of the order. The question arises as to whether the square cellular shapes of this archaeal group, and the cubic outline of pores and inclusions in and amongst the halite meshwork it inhabits, are more than fortuitous. Two haloarchaeal groups live only in high-pH high salinity waters of soda lakes such as Wadi Natrun and Lake Magadi; these are *Natronobacterium* and *Natronococcus*. They grow only in hypersaline waters with high pH (8.5–11.0) and very low levels of Mg (<0.024 g L^{-1}), and so are known as alkaliphiles. They have not been found in marine-fed salterns or less alkaline continental systems. However, the precise definition of genome systematics in halophiles living in soda lakes is still in a state of flux (Grant *et al.*, 1999).

Haloarchaeal species growing at salt concentrations above 150–200‰ characterize not only the Halobacteriaceae but also moderately halophilic methanogenic archaea, such as species of *Methanohalophilus* and *Methanococcus* (Table 2; Pflüger *et al.*, 2005). The existence of methanogenic archaea in hypersaline environments is related to the presence of noncompetitive organic substrates such as methylamines, which originated mainly from the breakdown of osmoregulator amines, rather than the presence of carbon dioxide, acetate and hydrogen (Fig. 4). The extremely halophilic methanogen, *Methanohalobium evestigatum*, with a NaCl optimum of 260‰, is also a thermophile with a temperature optimum of 50 °C. Halophilic methanogens are common contributors to the biota of methane hydrates associated with saline seeps and deep-sea brine pools above salt allochthons in the Gulf of Mexico (Lanoil *et al.*, 2001). Interestingly, unlike the Halobactericaea, these various methanogenic species seem to adapt to the increased salinity by a build up of osmolytes in the cell, and so are not obligate halophiles.

As well as halophilic archaea, there are halophilic bacteria flourishing in waters with salinities in excess of 240‰. One of the most interesting is *Salinibacter ruber*; which can constitute between 5 and 25% of the prokaryotic community in a number of halite-saturated settings worldwide (Antón *et al.*, 2005; Bardavid *et al.*, 2007). Until the late 1990s, when *Salinibacter ruber* was first isolated and cultured from samples in anthropogenic salterns, the microbial population of halite-saturated waters was thought to be made up of a few species of archaea, including the distinctive archaeal phenotype with its square cell, which because of its unique four-sided morphology is widely known as the SHOW phylotype (Square Haloarchaea Of Walsby; Bolhuis, 2005; Dyall-Smith *et al.*, 2005).

It now seems that *Salinibacter ruber* is ubiquitous (some 5–25% of the biomass) in halite-saturated waters worldwide, and is typically commingled with the SHOW phylotype (Antón *et al.*, 2005). Most workers now agree that *S. ruber* and the square haloarchaea are the dominant microbial species at these elevated halite-saturated salinities (Ventosa, 2006). Once isolated in pure culture, it was evident that the similarity of *S. ruber* to many haloarchaea could have hampered the isolation of the bacterium. Both types of prokaryotes are extremely similar at the phenotypic level: both are extreme halophiles, aerobes, and heterotrophs and pigmented by carotenoids. *S. ruber*, like many haloarchaea, accumulates high concentrations of $K+$ to counterbalance the osmotic pressure of the medium, has a high proportion of acidic amino acids in its proteins, as well as enzymes functional at high salt concentrations and even has a high proportion of $G+C$ in its genome (65–70% for *S. ruber*, in the range of 59–70% for haloarchaea; Antón *et al.*, 2005.). All these similarities, together with the fact that *S. ruber* and *"Haloquadratum walsbyi"* dominate the biota in halite-saturated waters whenever prokaryotic density is high, pose interesting questions as to the evolutionary process. For example, what environmental conditions in the Precambrian led to such a high degree of metabolic similarity between two groups that now occur in very genetically separate domains of life? It also shows that *S. ruber* is a bacterium that is as halophilic and as salt dependant as any member of the Halobacteriaceae.

Other than *Salinibacter ruber*, two groups of halophilic bacteria are well represented in salinity ranges in excess of 150‰; the fermentative bacteria belonging to the family Haloanaerobiaceae and the phototrophic sulphur-oxidizing bacteria of the family Ectothiorodhospiraceae (Figs 3 and 6C). Both groups are mostly made up of moderate halophiles. Phototrophic halophilic bacteria are further divisible into purple and green bacteria according to their respective bacteriochlorophylls

and carotenoids (Fig. 2C). For example, the shallow parts of soda lakes in the Wadi Natrun may be intensively red coloured due to the development of *Halorhodospira halophila* (purple sulphur bacteria), while green non-sulphur bacteria dominate the photosynthesizing layer of the hypersaline microbial mats in brines of similar salinity in Guerrero Negro, Baja Mexico (see "red waters and brines" in Glossary). Small brine puddles in many hypersaline locations may show separate development of green- and red-coloured species of *Halorhodospira*, while top layers of the sediments of Wadi Natrun lakes (Egypt) show separate layers of the green-coloured and the red-coloured *Halorhodospira* species (Imhoff *et al.*, 1979). *Halorhodospira abdelmalekii*, *Halorhodospira halochloris*, and in particular *Halorhodospira halophila* are among the most halophilic phototrophic bacteria known (Imhoff, 1988). Isolates of *Halorhodospira halophila* from soda lakes in the Wadi Natrun have salt optima of 250‰ total salts and can survive in halite-saturated solutions (Fig. 3).

Oren (2001) has shown that in general in saline ecosystems the bioenergetic constraints of various metabolic pathways at the cellular level define the upper salinity limit at which the different dissimilatory processes can occur (Fig. 4). Dissimilatory sulphate reduction of a lactate substrate provides relatively little energy, and so the need to spend a substantial part of the cell's available energy for the production of organic osmotic solutes probably sets the relative low upper limit to the salt concentration at which sulphate-reducing bacteria can grow (Oren, 2001).

Our understanding of which microbial species dominate the halobiota at elevated salinities is not yet fully developed. As Ventosa (2006) emphasized, numerous ecological studies have demonstrate that haloarchaea may reach high cell densities ($>10^7$ cells mL^{-1}) in such hypersaline waters. Traditional microbial studies based on cultivation of viable cells from samples collected in such waters suggested that the predominant species found in most neutrophilic hypersaline environments were related to the genera *Halobacterium*, *Halorubrum*, *Haloferax* and *Haloarcula.* However, more recent molecular ecological studies based on cultivation-independent methods indicate that, in most natural hypersaline environments, members of these now well-documented halophilic genera constitute no more than a small proportion of the microbial biomass. They are seen more often because they are more readily cultivated. Several more recent studies carried out in actual hypersaline environments and not the culture dish have allowed some general conclusions to be drawn (Ventosa, 2006): (a) square haloarchaea are very abundant, but they have not been isolated (cultivated) until recently; (b) many environmental clones within the haloarchaeal group are also obtained from natural hypersaline settings that are not phylogenetically closely related to previously described cultivated species of archaea and bacteria. In other words, the search to define the number of halophilic species and their relative contribution to the biomass made up haloadaptive microbes has only just begun.

Cellular biochemical adaptations to hypersalinity

Halotolerant and halophilic species have developed special biochemical mechanisms to cope with life's fatal propensity to desiccate in mesohaline and hypersaline waters, namely; motility, slime, osmolytes and halo-adapted cellular membranes and proteins. Many of the halotolerant cyanobacteria (still called "blue-green algae" by many geologists) form a significant component of photosynthesizing microbial mats in modern sabkhas and shallow brine lakes subject to both periodic desiccation and hypersalinity. Such microbial mats show a worldwide recurrence of a few cosmopolitan cyanobacterial species: *Microcoleus chthonoplastes; Lyngbya sp.; Entophysalis sp.;* and *Synecococcus sp.* All of these mat-forming taxa are embedded in matrices of extracellular polymeric mucous (slime), which hold large amounts of water to protect the photosynthesizing cell from osmotic stress and act as a buffer against extreme temperatures and ultraviolet rays (Gerdes *et al.*, 2000a, 2000b).

Aside from a greater likelihood of subaerial desiccation, one of the effects of increasing salinity is to increase osmotic pressure on all cellular life floating in a brine column. It may well be that the dominant biomass control in subaqueous hypersaline and supersaline environments is not lowered oxygen levels but increased osmotic pressure. At a concentration of 300‰, a sodium chloride brine exerts an osmotic pressure on a cell of more than 100 atmospheres (Bass-Becking, 1928; Reed *et al.*, 1984). Cells of haloxene species that typically inhabit marine or brackish waters quickly desiccate in such brines, leading to rapid death (e.g. Geddes, 1975b).

Accidental exposure of pelagic and bottom-living metazoans to osmotic stress and anoxia associated with hypersaline bottom waters has contributed to many ancient *lagerstatte* associations (fossil "death communities"), along with the inherent excellent preservation of fine details of the entrained largely undecomposed fossil forms. For example, there are the numerous "death-dance" trackways in the Cretaceous Solnhofen micritic plattenkalk of Bavaria. The tracks lead to the fossil remains of intimately preserved marine crustaceans that once wandered into the high osmotic pressures associated with hypersaline and anoxic bottom-waters of the lagoon that now preserves their remains (Viohl, 1996). Likewise, the feathers and skeleton of the bird-like dinosaur *Archeopteryx* were well preserved by the same anoxic hypersaline bottom waters.

Communities of haloxene chemosynthetic mussels, which inhabit nutrient-rich deep dark bottoms about the edges of modern anoxic brine lakes atop dissolving salt allochthons, can suffer mass extermination and immaculate preservation when sediment slumps occur and these mollusc biostromes are carried into lethal anoxic H_2S-rich hypersaline waters of the brine lake on the deep seafloor (MacDonald, 1992). Rich fossil-fish layers characterize subaqueous lacustrine laminated sediments of the Laney Shale Member of Eocene Green River Formation. Almost all the fish in the *lagerstatte* are freshwater species, and this death assemblage indicates the presence of inimical bottom waters tied to a salinity-stratified water column. This stratified column formed during the freshened highwater stage of the lake when dissolution of the underlying sodic evaporites of the Wilkins Peak Member released brines that created a condition of perennial anoxia in the deeper parts of lake water column (Boyer, 1982). A similar brine column stratification probably favoured the preservation of organic matter in the muddy lacustrine/lagoonal sediments that overlie the Mesozoic Purbeck evaporites that crop out along the Dorset coast (Schnyder et al., 2009).

Microbes that flourish in hypersaline waters have adapted at the cellular level to survive the increased osmotic stress that accompanies increased salinity. At the intracellular molecular level, *Dunaliella parva,* a halotolerant unicellular green alga that flourishes in mesohaline waters worldwide (optimum ~120‰, survival 20–340‰), distributes glycerol throughout its cytoplasm. This increases the total solute concentration in the cell and so the algae can better cope with the high osmotic pressure of its high salinity surrounds. Glycerol is an osmotically active substance (osmolyte) that takes up space in the cellular fluids. It lowers the relative water content of the cell and so raises the internal osmotic pressure. Cytoplasmic concentrations of glycerol in *Dunaliella parva* can reach $7\,\mathrm{mol\,L^{-1}}$ and can constitute over 50% of the dry weight of cells growing in salinities ~280‰. Glycerol is also used as an osmolyte by other halotolerant and halophilic algae, as well as yeasts, fungi and brine shrimp. Halotolerant and halophilic prokaryotes can use a variety of other sugars, sugar alcohols, amino acids and compounds derived from them (such as glycine, betaine and ecotoine) as osmolytes, leading to characteristic biomarker assemblages in ancient saline sediments.

In contrast to an osmolyte solution, halophilic archaea have two main defence mechanisms to cope with the extreme osmotic gradients induced by hypersaline to supersaline waters. One is a modification of the plasma (cell) membrane; the other is an adaptation the protein structure itself. Unlike most cell membranes, the plasma membrane of halophilic archaea is dominated by rhodopsins and the cell membrane does not actively exclude salts, so the overall internal salt concentration in haloarchaeal cytoplasm is high. This adaptive mechanism is sometimes called the "salt-in" strategy. However, the cell membrane is selective, it tends to exclude sodium, while actively pumping potassium into the cell against a thousand-fold concentration gradient. The total ionic strength remains the same on both sides of the plasma membrane, but the ratios of specific ions differ inside and outside the cell wall. Potassium is the dominant cation within the cell, many cell functions require potassium, but would be disrupted by high levels of sodium. Cells of halophilic archaea can contain up to $4\,\mathrm{mol\,L^{-1}}$ of potassium chloride, which is eight times its concentration in seawater. Anaerobic bacteria of the order *Haloanaerobiales* use a similar "high potassium in the cell" strategy, as does *Salinibacter ruber* (Oren, 1999b).

Halobacterium halobium is a well-studied example of a well-adapted halophilic archaea; its cell carries a combination of orange-red carotenoid pigments, mostly β-carotene (C-40), and bacterioruberins (C-50). It is an aerobe-facultative anaerobe. When oxygen levels fall, but light penetrates the brine, photophosphorylation takes place in the absence of chlorophylls and redox carriers, so waters and sediments where it flourishes can take

on a blue or purple tint. Bacteriorhodopsin's characteristic purple colour has led to many haloarchaea in their photo-active stage being described historically (pre-genomic) as purple bacteria, not archaea. The main cellular metabolism of *Halobacterium halobium* is heterotrophic in brines with higher oxygen levels, and it flourishes in such conditions in Great Salt Lake, Solar Lake and Lake Magadi.

Cells in the heterotrophic mode are mostly coloured by carotenoids, and waters where it is thriving appear red. This normal respiratory metabolic chain depends on b and c cytochromes as well as cytochrome oxidase to create ATP. This is not a particularly unusual metabolic pathway for most life forms, except that in this case the cell itself is halophilic. As a result, in brines with relatively high levels of oxygen, these highly salt-adapted halophilic cells respire and produce ATP using their red membrane (carotenoids). Under anaerobic conditions they can survive but produce lesser volumes of ATP, either by fermentation of arginine or by anaerobic respiration with fumarate as an electron receptor. It means that they can still live, although at lower metabolic rates, in well-lit dysaerobic to anoxic hypersaline conditions as they utilize their purple membrane patches to pump protons and so maintain their cellular metabolism (Oesterhelt & Marwan, 1993; Kates *et al.*, 1993).

Some halophilic archaeal strains, including *Halobacterium*, contain another rhodopsin pigment in their purple membrane called halorhodopsin. This acts as a Cl-pump, once again suitable for generating energy in highly saline conditions. It is usually present in the cell membrane in much smaller amounts than bacteriorhodopsin, but contains the same retinal pigment. It too absorbs light, which it converts to an ion gradient. However, instead of pumping protons out, like bacteriorhodopsin, it pumps chloride ions inwards, which helps maintain osmotic balance in highly saline conditions. Since chloride ions have a negative charge, moving chloride inwards is equivalent in terms of energy to moving a proton outwards. Thus halorhodopsin generates a chloride ion gradient, which also supplies energy to the cell.

Membrane adaptation shifts the osmotic balance problem from the cellular to the molecular level. Ions within the cell's cytoplasm still compete with proteins and other biomolecules for that universal solvent, water. In order to cope with high osmotic stress at the molecular level, halophilic archaeal proteins have evolved so as to maintain a high negative charge on the protein surface. This attracts water molecules and envelops the protein in a protective shroud of bound water.

Consider the halophilic archaea *Haloarcula marismortui*, which flourishes during times of freshened surface waters in the Dead Sea. Proteins of its metabolic enzyme (malate dehydrogenase) and its electron transfer protein (ferredoxin) are wrapped in coats of acidic amino acid sidechains so that both proteins carry a negative charge in neutral media. A predominance of charged amino acids on the surfaces of cellular enzymes and ribosomes better stabilizes the hydration shell of the various cytoplasm molecules, even when the extracellular brines are well into the halite saturation field. This high-density surface charge binds water molecules to the protein surface much more effectively than any mesophile protein. Hence, *Haloarcula* proteins do not dehydrate or unfold (denature) even when exposed to extremely high salinities. However, the high levels of shielding cations are lost by diffusion in low salinity environments and an excess of negatively charged ions then destabilizes the molecular structure by ionic repulsion and so intracellular proteins tend to lyse or disintegrate. This means any species using a "salt-in" cytoplasm strategy has an innate restriction to highly saline environments (obligate halophiles) and does not cope well with rapidly oscillating schizohaline waters. Ironically, intracellular acids that unfold normal proteins in non-halophiles counteract this tendency in the halophiles.

In summary, bioadaptations at the cellular level to highly saline conditions can be divided into two groups of responses (Oren, 2001):

(a) *The "high-salt-in" option*
Accumulation of salts in the cytoplasm are maintained at concentrations equal to or higher than those of the outside medium. Generally KCl is used as the main intracellular salt. Aerobic halophilic archaea (family Halobacteriaceae) utilize this strategy, as do fermenting bacteria, eubacterial acetogenic anaerobes (*Haloanaerobium, Halobacteroides, Sporohalobacter, Acetohalobium*), the extremely halophilic *Salinibacter ruber* and some sulphate-reducers. Energetically, this strategy is relatively inexpensive, but requires far-reaching adaptations of the intracellular enzymatic machinery to the presence of high salt

concentrations. Cells utilizing this strategy show limited adaptability to changing salt concentrations (obligate halophiles) and do best in environments where long-term salinities remain elevated. That is, they do best in the perennial hypersaline portions of salt lakes such as the upper water mass of the Dead Sea and do not do as well in parts of the depositional setting characterised by rapid and frequent bouts of schizohalinity.

(b) *The "low-salt-in" option*
Exclusion of salts from the cytoplasm and the accumulation of organic osmotic "compatible" solutes (osmolytes) may be employed to provide osmotic balance. This strategy is used by halophilic and halotolerant eukaryotal microorganisms, by most salt-requiring and salt tolerant bacteria, and also by halophilic methanogenic archaea. This strategy is energetically expensive; the energetic cost depends on the type of organic solute synthesized. No major modification of the intracellular machinery is needed compared to non-halophiles, and in most cases cells can rapidly adapt to changes in salinity. As such, they do better than the "salt-in" biota in conditions of rapid and frequent schizohalinity.

As Oren (2001) clearly illustrated, organisms living in increasingly high salinity environments have to devote increasing large proportions of their bioenergetic budgets to osmoregulation, either to synthesize organic solutes or to activate and maintain ionic pumps. This creates a natural salinity-related control over various metabolic pathways and their energy efficiencies and hence to biomarker distributions in the resulting sediments. The following metabolic adaptations and groups function best at high salinities (Fig. 4):

(1) Processes that use light as energy source and are generally not energy-limited;
(2) Heterotrophs (bacteria as well as archaea) that perform aerobic respiration, denitrification, and other dissimilatory processes that yield large amounts of ATP;
(3) All types of metabolism performed by organisms that use the "high-salt-in" strategy, even if the efficiency and amount of ATP obtained in their dissimilatory metabolism is low.

Thus, the growth of phototrophic microorganisms in hypersaline surface waters is generally limited by the availability of inorganic nutrients and not by lack of light energy (Oren, 2001). Accordingly, both oxygenic (*Dunaliella*, cyanobacteria) and anoxygenic phototrophs (*Halorhodospira, Thiohalocapsa, Halochromatium*) produce organic solutes for osmotic stabilization. They may be found up to very high salt concentrations and in several cases survive well into the halite-saturation field. However, in the case of chemolithotrophs and anaerobic heterotrophs, the amount of energy generated in the course of their dissimilatory metabolism is often insufficient to supply the demands of cell growth, osmotic adaptation, and life maintenance. Long-term growth and survival in hypersaline environments is not possible in such species. The "high-salt-in" strategy is preferable for strongly energy-limited organisms (haloarchaea) as it is energetically much less costly than the production of organic osmotic solutes. Oren (2001) documented an excellent correlation between the amount of energy generated in the course of the different dissimilatory processes and the salinity-related occurrences of various metabolic styles (Fig. 4). Clearly the resulting biomarkers from the various metabolic pathways will likewise preserve salinity-related indicator markers in the rock record.

Biomarkers and microbial responses to salinity changes

The salinity-controlled transition between a halotolerant and halophilic biota can been seen in their organic residues and subsequent biomarkers preserved in evaporitic source rocks. Biomarkers can be thought of as molecular or chemical fossils whose basic carbon skeleton is derived from once-living organisms and are found in modern sediments, as well as in petroleum and rock extracts. They can provide information about species diversity, depositional environment, thermal maturity, migration pathways and hydrocarbon alteration (Peters *et al.*, 2005a, b).

Commonly accepted environmental generalizations based on biomarkers include the notion that variation in the ratio between the isoprenoids pristane and phytane indicates oxidizing versus reducing conditions (pristane and phytane are both breakdown products of chlorophyll). In an oxidizing environment the cleavage of the phytol side chain of chlorophyll is followed by decarboxylation to produce phytane. In a reducing environment the sidechain cleavage of chlorophyll is followed by its reduction to ultimately produce

pristane. Low pristane/phytane ratios in marine and terrestrial settings are thought to indicate reducing conditions, while higher values (>1) indicate oxidizing conditions (Table 4). Philp & Lewis (1987) have shown that the chemistry of chlorophyll breakdown is much more complicated in many natural systems, and that variations in the ratio may also indicate varying inputs from archaeal membranes, which contain much higher levels of phytane chains than bacteria and can dominate the halobiota at higher salinities. Phytane can also come from bacteriochlorophyll-a and tocopherols, which can also be locally commonplace (Peters *et al.*, 2005a, b; Koopmans *et al.*, 1999).

Likewise, differences in the distribution of n-alkanes are thought to indicate depositional differences in the source contributors. Waxes in

Table 4. Depositional significance of selected biomarkers (see text for detail)

Setting	Biomarker/indicator	Detail
Hypersaline	Gammacerane	High relative to C_{31} hopanes in oils derived from sources deposited under hypersaline depositional conditions. High values indicate stratified water column during source deposition (Sinninghe Damste *et al.*, 1995).
	Pristane/phytane	Very low values (<0.5) in oils derived from source rocks deposited under hypersaline conditions, indicates contribution of phytane from halophilic bacteria/archaea (ten Haven *et al.*, 1987, 1988).
	Acyclic isoprenoids	Acyclic isoprenoid hydrocarbons are the predominant components in the organic matter extracted from sedimentary cores and oils of various hypersaline settings (Wang, 1998).
	Low diasteranes	Oils from the hypersaline sources typically have very low amounts of diasteranes, which commonly suggests a source rock that has low content of catalytic clays, consistent with carbonate or evaporite source rocks (Mello & Maxwell, 1991; Peters & Moldowan, 1993). The amount of diasteranes in oils also decreases in highly reducing noncarbonate environments with increasing salinity (Philp & Lewis, 1987).
	Other biomarkers	Even-over-odd dominance in the n-alkanes, presence of β-carotene and γ-carotene, dominance of the C_{27} steranes.
	Organic sulphur compounds	There is a high abundance of organic sulphur compounds (thiolanes, thianes, thiophenes and benzo-thiophenes) in many anoxic hypersaline settings (Wang, 1998). The distributions of the C-20 isoprenoid thiophenes in combination with those of the methylated 2-methyl-2-(4,8,12-trimethyltridecyl) chromans can be used to discriminate non-hypersaline from hypersaline paleoenvironments (Sinninghe Damste *et al.*, 1989)
	Carbon isotopes	Heavy ^{13}C values (−20 to −30‰) are consistent with typical saline lake environments and reflect depletion of CO_2 by photosynthetic organisms (Peters *et al.*, 1996).
Anoxic	C_{35} homohopanes	High relative to total hopanes in oils derived from source rocks deposited under anoxic conditions (Peters & Moldowan, 1993). Abundance of C_{35} homohopanes in oils (relative to C_{31}–C_{34} homopanes) is correlated with source rock hydrogen index (Dahl *et al.*, 1994).
	Pristane/phytane	>1.0 can indicate anoxic conditions, but the ratio is affected by many other factors.
	Isorenieratane & derivatives	Presence in oil indicates anoxic photic zone during source rock deposition, these compounds are biomarkers for green sulphur bacteria (Summons & Powell, 1987).
	V/(V + Ni) Porphyrins	High = reducing conditions (Lewan, 1984).
	28,30-bisnorhopane	High in certain reducing environments (Schoell *et al.*, 1992; Moldowan *et al.*, 1994).
Lacustrine	Botryococcane	Presence = lacustrine source. Absence = meaningless (e.g. Moldowan *et al.*, 1985).
	β-Carotane	Presence = lacustrine source. Absence = meaningless (Jiang & Fowler, 1986).
	Sterane/Hopanes	Low in oils derived from lacustrine source rocks. (Moldowan *et al.*, 1985)
	C_{26}/C_{25} tricyclic terpanes	>1 in many lacustrine-shale-sourced oils (Zumberge, 1987)
	Tetracyclic polyprenoids	High in oils from freshwater lacustrine sources (Holba *et al.*, 2000).

higher plants have significant concentrations of the long chain $C_{22–36}$ alkanes with a pronounced odd/even distribution (Fig. 1A). Such organics tend to be relatively rare in evaporitic source rocks, unless surface waters were periodically freshened by run-off from the land. Much of the terrestrial organic material entering an evaporitic depression has been oxidized and biodegraded before it makes it to the final site of deposition on the brine pool floor. In contrast, a high algal input is thought to be characterized by n-alkanes in the $C_{16–18}$ region.

Waples *et al.* (1974), along with ten Haven et al. (1986), noted that Tertiary sediments deposited in saline evaporitic lagoons possess high concentrations of regular C_{25} isoprenoids (Table 4). The activities of *Chlorobiaceae*, an anaerobic green sulphur bacteria, thought to flourish in mesohaline to hypersaline seaways, leads to the preservation of a series of 1-alkyl-2,3,6-trimethyl benzenes, thought to be derived from the breakdown of aromatic carotenoids in sulphate- and sulphide-rich brines (Summons & Powell, 1987). ten Haven *et al.* (1988) went on to propose a number of biomarker indicators of hypersalinity, including short-sidechain steranes and 5α(H), 14β(H), 17β(H) pregnanes and homopregnanes, as well as high gammacerane indices (gammacerane/C_{30} hopane). Gammacerane is a pentacyclic C_{30} triterpane thought to be a diagenetic alteration product of tetrahymenol, a natural product produced by bactiverous ciliates, such as *Tetrahymena* (Table 4).

At its simplest, much of the utility of biomarkers in saline environments comes from salinity-related differences in contribution to organic matter of the general categories of primary producers (autotrophs), namely prokaryotes (cyanobacteria and bacteria) and eukaryotes (higher plants, algae) and the archaea. Most triterpanes are associated with prokaryotic sources, whereas eukaryotic organisms produce steranes. Thus, the triterpane/sterane ratio can be a rough measure of the prokaryote/eukaryote contribution to the organic material. As salinity increases, the less salinity-tolerant eukaryotic organisms (mostly sterane-producing green algae) give way to more halotolerant bacteria and cyanobacteria (tricyclic and hopane producers) with a corresponding increase in the triterpane/sterane ratio. Thus high alkalinity/salinity settings are characterized by tricyclics (C_{20}–C_{24}; m/z 191), β-carotene ($C_{40}H_{56}$ compound; m/z 125), gammacerane (C_{30} triterpane; m/z 191), all with prokaryote sources. Hence, high levels of gammacerane and β-carotene are typically associated with non-marine highly saline environments (Peters & Moldowan, 1993).

For archaea, the cell membrane itself, due to its inherent high thermal stability, is a very good candidate for a biomarker. Archaeal cytoplasmic membranes do not contain the same lipids that prokaryotes and eukaryotes do. Instead, their membranes are formed from isoprene chains (ether lipids) made up from C_5 isoprenoid units (as for the side chains of ubiquinone) rather than C_2 units (ester lipids) in the normal fatty acids of the non-archaea (Fig. 7A). Moreover, the isoprenoid chains are typically attached to glycerol by ether linkages instead of esters. Thus the cell wall of archaea is constructed of lipids, mainly of glycerol, connected to phytanyl chains 20 carbons in length by ether bonds to form phytanylic diether. Typically these are organized in bilayers. In the case of archaea living in extreme conditions, two glycerol molecules can be connected to a double chain of phytanol to create a tetraether structure of forty carbons (Fig. 7B). Isoprene derivatives indicative of ancient archaea have been found in Mesozoic, Palaeozoic, and Precambrian sediments (Hahn & Haug, 1986). Interestingly, their chemical traces have even been found in sediments from the Isua district of West Greenland, the oldest known sediments on Earth, some 3.8 billion years old.

Lipids entrained as organic residues in modern evaporitic carbonate and gypsum from modern saline pans (mesohaline and lower penesaline waters), are mostly derived from cyanobacteria and heterotrophic bacteria. Their n-alkane distributions show a high predominance of n-docosane. Thus, in the evaporitic carbonate domain (mesohaline waters), the presence of the C_{20} highly-branched isoprenoid olephines, tetrahymanol and large amounts of phytol constitute precursors to most lipids found in buried evaporitic sediments. In contrast, the main lipid contributors in organics accumulating in halites and bittern beds can be the extremely halophilic archaea and their organic signatures are enriched in the isoprenoids, especially phytane (Barbé *et al.*, 1990; Wang, 1998). However, both archaea and halophilic bacteria can flourish in upper penesaline and supersaline waters at salinities higher than 200–250‰, so the biomarker signatures are not mutually exclusive (Caumette, 1993; Ollivier *et al.*, 1994). Any high-salinity biota also includes the metabolic products of fermentators, homoacetogens, sulphate-reducers and methanogens.

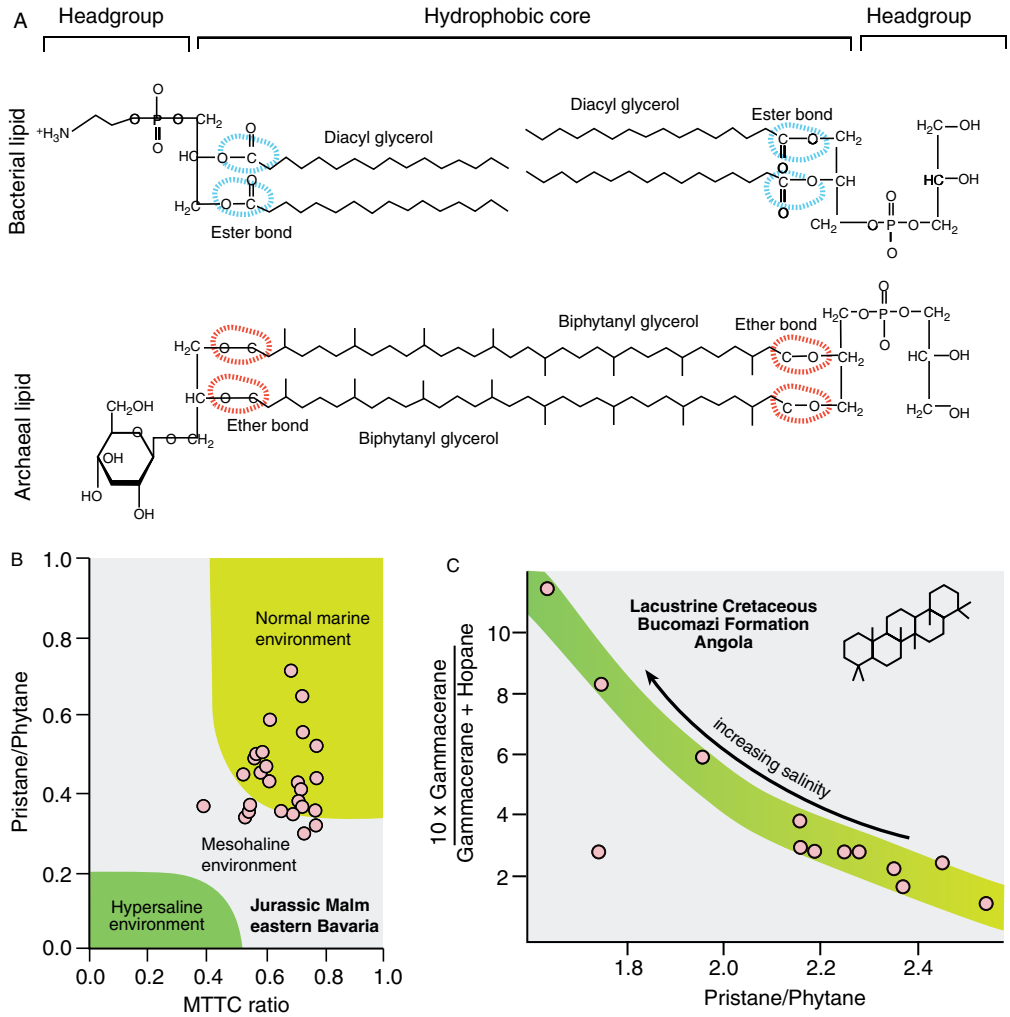


Fig. 7. Biomarkers: lipid structures and some rock characteristics. (A) Lipids from archaea and bacteria. Upper portion shows how phosphatidylanolamine forms a bi-layer lipid in bacterial cells. The acyl chain is usually, but not always straight. Some bacterial lipids have a methyl branch of a cyclohexal group at the end of the acyl chain, other lipids have one or more unsaturated bonds and the connection of glycerol to the acyl chain is via an ester linkage. The lower part shows how lipids are monolayers in archaea and the phytanyl chain contains isoprenoid-like branches. An ether linkage connects the phytanyl chain. Archaeal membranes also contain bilayer-forming diether lipids. (B) Relationship between pristane/phytane and the methyltrimethyltridecylchhroman (MTTC) ratio in Jurassic Malm carbonates of eastern Bavaria (after Schwark *et al.*, 1998). The MTTC ratio is defined as 5,7,8-trimethylchroman/total MTTCs. (C) Variations in pristane/phytane ratio and the gammacerane index for oils from lacustrine source rocks in Angola (inset shows gammacerane structure). Independent biomarker evidence suggests a marine source for the point that lies off the shaded trend (after Peters *et al.*, 2005a).

A predominance of degraded green algal and cyanobacterial biomarkers in mesohaline settings is indicated by biomarkers preserved in organically immature, evaporitic mesohaline laminates at the base of the Permian Zechstein evaporite succession in NW Europe (Bechtel & Puttmann, 1997; Pancost *et al.*, 2002). There the degree of methylation of 2-methyl-2-trimethyl-tridecylchromans (MTTCs) and the abundance of maleimides and bacteriochlorophylls in the organic-rich Kupferschiefer shales at the base of the Zechstein evaporite succession implies a subaqueous euhaline to mesohaline ($\geq$30–40‰) transition into a hypersaline marine-fed drawdown basin. These biomarkers are thought to have been derived from green/purple sulphur bacteria (decomposers) within organic-rich laminites and suggest that the bottom waters were saturated with H_2S at the time of deposition. Maximum water depths were probably less than 100 metres (it was a stratified mesohaline drawdown basin at the onset of Zechstein salinity; Warren, 2006). Decomposers probably

lived near the brine boundary between the photic zone and the anoxic (euxinic) bottom water at typical water depths of 10–30 metres below the water surface, as in modern marine-fed density-stratified systems, much like in Lake Mahoney today (Overmann *et al.*, 1996). Primary production in the upper water column was dominated by photosynthetic cyanobacteria or green algae, while sulphate reduction in the sediment was tied to the availability of abundant sulphate and organic detritus from the overlying water column.

Methanogenesis was also active in or at the base of the water column during Kupferschiefer deposition. This is reflected in the light carbon-isotopic composition of organic matter that had originated via recycling of CO_2 generated by methane-oxidizing bacteria in the water column (Bechtel & Puttmann, 1997). Saccate pollen is the only morphologically preserved body fossil in organic matter within the laminated Kupferschiefer sediment, all other traces of cellular morphologies are gone. Euxinic (anoxic) conditions were confirmed by Pancost *et al.* (2002) over a much larger area of Kupferschiefer deposition than studied by Bechtel and Puttmann (1997). They concluded that almost all of the Kupferschiefer seaway was subject to periods of photic zone stagnation and stratification during the early mesohaline history of the Zechstein Sea.

By themselves, high pristane/phytane ratios, high amounts of gammacerane, and high MTTC ratios are not totally reliable indicators of hypersalinity. More reliable determinations can be made when two or more of these biomarkers are crossplotted and the resulting output shows a consistent trend. Figure 7B plots pristane/phytane ratio against the MTTC ratio in the Jurassic Malm Zeta laminites of eastern Bavaria in SW Germany (Schwark *et al.*, 1998). The plot shows a covariant decrease in the two measures, which is interpreted as indicating a trend from normal marine to mesohaline deposition.

A similar covariant trend can be seen in saline lacustrine source rocks when the pristane/phytane ratio is crossplotted against the gammacerane index in Mesozoic source rocks from offshore West Africa (Peters *et al.*, 2005a). Figure 7C plots variations in pristane/phytane (a redox and archaeal indicator) and gammacerane index for oils from a set of lacustrine source rocks. Increasing salinity in the depositional setting explains the covariant trend in the plot, whereby higher salinity was accompanied by density stratification and associated reduced oxygen-levels in bottom waters. Independent biomarker evidence suggests a marine source for the point that plots off the shaded salinity trend in this figure.

Although the levels of entrained organics are very low, similar covariant trends in pristane/phytane and gammacerane occur in C_{21-25} isoprenoids, along with relatively heavy $\delta^{13}C$ signatures, in biomarkers extracted from the Miocene halites of the halokinetic Sedom Formation in Israel. They indicate a predominance of halophilic archaea when the salt was deposited in a CO_2 limited system (Grice *et al.*, 1998; Schouten *et al.*, 2001).

Light and sulphide in modern hypersaline environments typically occur in opposing gradients, so the growth of halotolerant and halophilic phototrophic sulphur bacteria is confined to narrow zones of overlap in stratified brine or water columns. In Precambrian sediments bacterial life forms were much more widespread in any water mass as the column was mostly anoxic. For example, in Neoproterozoic and early Cambrian hypersaline settings such as the Ara Salt Basin of Oman there were no higher life forms present in the depositional setting, and so this possibly normal-marine setting, and the subsequent encasement in salt, led to preservation of a unique set of bacterial biomarkers in blocks of salt-encased marine platform source rocks (Terken *et al.*, 2001; Schoenherr *et al.*, 2007).

The presence of mesohaline and marine carbonate muds, rather than aluminosilicate clays, in the matrix of many buried organic-rich evaporitic source rocks can change maturity and migration parameters compared with shale source rocks with non-carbonate matrices. For example, mesohaline carbonate source rocks are susceptible to early generation of bitumens and volatiles compared with terrigenous shales (ten Haven *et al.*, 1986; di Primio & Horsfield, 1996). The proportion of bitumens (extractables) in the organics of carbonate source rock is high compared with that of shales, as most mesohaline carbonates are largely isolated from high levels of terrigenous influx and the associated load of "spent" or oxidized terrestrial organic matter (Warren, 1986). For the same reason, much of the early asphaltic (hydrogen-prone) product in a mesohaline carbonate laminite begins to migrate early in the burial history, driven in-part by recrystallization of the carbonate matrix, whereas similar materials are held to greater burial depths in the lattice of aluminosilicate clays (Warren, 1986; Cordell, 1992).

Espitalie *et al.*, (1980) showed that carbonate source rocks are likely to provide larger volumes of hydrocarbons for pooling compared with analogous terrigenous shales for the same levels of TOC. Geochemical analyses show that heavy oils from carbonate source rocks can form at marginally mature stages and at lower temperatures than required for oil generation from terrigenous shales (Jones, 1984).

Lastly, some widely-used biomarker-derived maturity indicators formulated in marine sediments, are not as reliable in relatively young saline-lacustrine basins or in hypersaline oils with high sulphur contents, such as those sourced from hypersaline Oligocene laminites in the northern Qaidam Basin, China or the Miocene mesohaline carbonates of the Mediterranean (Hanson *et al.*, 2001; di Primio & Horsfield, 1996). The discrepancy between mature indications coming from vitrinite in these very young evaporitic source rocks and the immature indications derived from various sterane isomerization ratios or other standard source rock evaluation techniques, are in part explained by a lack of time for various sterane equilibria to develop and by the complicating effects of high sulphur levels on reaction kinetics in systems with high levels of early asphaltenes. Some of these hypersaline heavy oils in China come from hydrogen-rich type-I lacustrine sources that may be as little as 3 million years old in the Qaidam Basin.

LAYERED BRINES AND ORGANIC SIGNATURE

So far the biological factors and metabolic pathways that control the type and volume of organic matter accumulating in saline settings have been discussed, without much consideration of the physical conditions or hydrologies that control the condition or position of the brine and pore fluids in which the organics accumulated. The presence or absence of organics in an evaporite basin is predicated on suitable hydrologies to manufacture the requisite factors to create anoxia. Penecontemporaneously, the hydrological conditions of early burial control whether organics are to be preserved in its evaporitic matrix until any protokerogen is sufficiently buried to evolve into a source rock. Brine density increases with increasing salinity, so influxes of less dense brines into an evaporitic depression create a layered system where lower salinity waters tend to float on top of higher salinity waters. Depositional hydrologies in all modern and ancient evaporite systems are accordingly layered and, as will be demonstrated below, the stability, temperature and salinity range of this layering largely controls whether and where organic matter accumulates in an evaporitic depression.

Almost all primary organic matter in an evaporitic source rock was first photosynthesized in surface brines outcropping at the top of the active phreatic zone or its capillary fringe. An active phreatic flow regime encompasses the zones of seepage outflow, brine/seaway ponding, brine reflux and meteoric flow. The brine surface of a perennial brine lake or seaway is the outcropping expression of the regional water table, and in marine-drawdown basins is by definition lower than sea level. In the surrounds, where the regional water table comes near the landsurface, the top of a capillary fringe may be the outcrop expression of the same regional water table and so is the depositional area where sabkhas dominate (Warren, 2006). Solar evaporation concentrates waters in both ponded and vadose settings to form matrices of bottom-nucleated and sabkha salts, respectively. Depressions with surface and near-surface brines in arid settings indicate groundwater discharge zones and their long-term outcropping creates discharge playas and ancient evaporite seaways.

Where areas of strong topographic relief define the margin of a modern evaporite basin, both unconfined and confined meteoric waters typically discharge into the edges of a brine-saturated depression, as in modern continental rift valleys of the East African rift, or in a transtensional basin-and-range setting of the American southwest, or in the Dead Sea of the Middle East. Farther out, beneath the more central and topographically lowest parts of the evaporite depression, density-induced brine reflux, and not meteoric throughput, is the dominant process driving shallow-subsurface brine flow. The saline water mass driving this reflux may be an ephemeral or perennial holomictic surface water. Which hydrological style of surface water dominates in an evaporite basin (ephemeral versus perennial) is in part related to the steepness of the surrounding topography and the presence or absence of a hydrological conduit for water outflow (Warren, 2006).

In a large evaporite drawdown basin, such as in the Mediterranean in the Late Miocene, the basin typically had no surface connection to the ocean, and the level of the discharge zone and the water

surface of the perennial brine discharge lake was at times thousands of metres below sea level. Gravity-induced seepage and associated evaporation of surface waters cycled huge volumes of marine/meteoric waters through the depression's surrounds and into the drawdown depression. Reflux beneath a stratified perennial meromictic water mass is at its maximum when the brine column is holomictic (Warren, 2006).

Hydrologies in saline basins

Hydrological settings that allow most evaporitic carbonates and associated organics to accumulate can be divided into two end member situations: (1) a perennial seaway or a brine lake that at times is density stratified; and (2) an evaporitic mudflat (sabkha) with a surface defined by the top of the capillary fringe and its most saline water lying at or just below the sediment surface. A common intermediary stage is an evaporitic mudflat occasionally covered by thin sluggish brine sheets (salt pan). The hydrology of an evaporitic mudflat and its landward surrounds is controlled by the position of the water table in the sediments (Fig. 8A). Pores below the water table are filled by brine and make up the phreatic or saturated zone where the water-volume saturation is total (equal to 1 or 100%). The phreatic zone is the region where gravity-driven groundwaters seep down the potentiometric slope

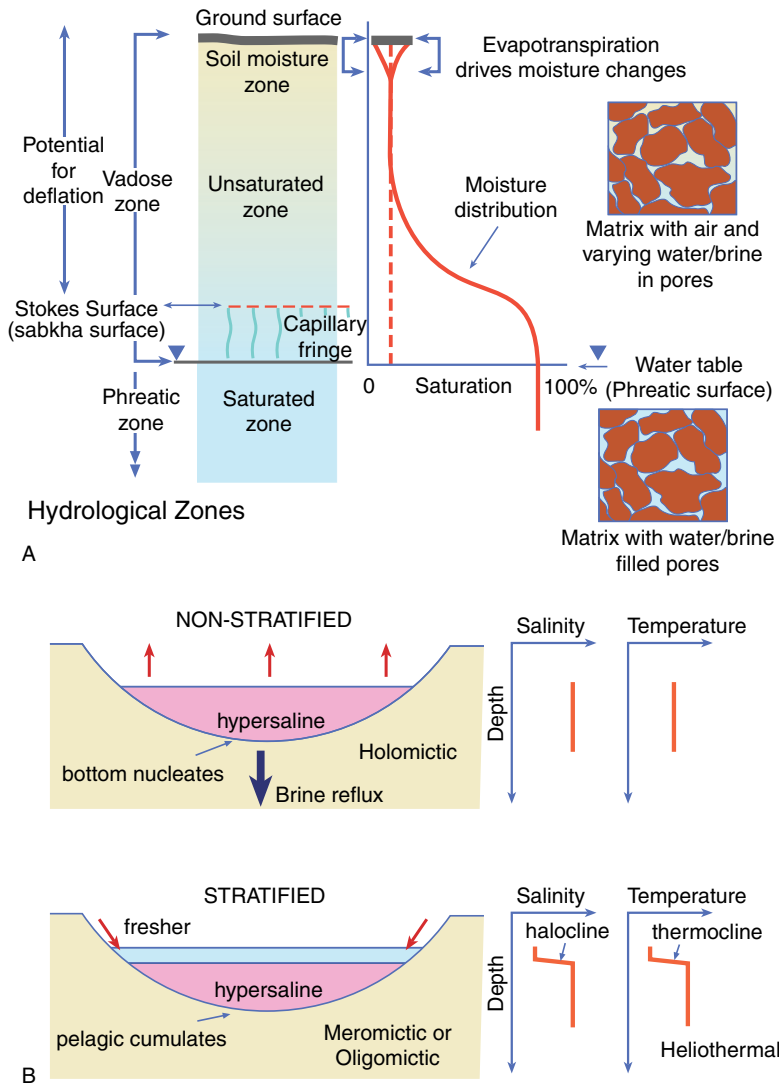


Fig. 8. Hydrological classification in saline settings. (A) Hydrological zonation in an evaporitic mudflat (sabkha) and its landward surrounds. (B) Water mass zonation in a perennial brine lake or seaway (after Warren, 2006).

toward discharge zones (forced-convection) and dense free-convecting brines sink into underlying strata. Above the water table is the vadose zone, where pores are filled by a combination of soil air and varying levels of water and brine and water-volume saturation is less than one.

Vadose hydrologies

The vadose zone in dry mudflats contains an uppermost interval where the water content and the oxygen/CO_2 content of the pore waters can vary considerably and is known as the soil moisture zone. Light rains on a dry mudflat typically penetrate the soil moisture zone but are not sufficient in volume to saturate the pore space of the whole vadose zone, and so are returned to the atmosphere via evapotranspiration without ever replenishing the water table (Wood *et al.*, 2002). Fluctuating evapotranspiration levels in this zone vary widely between storms, driven in part by the metabolic activities of the soil biota, by mean moisture contents, and by varying O_2 and CO_2 levels. Pedogenic carbonates and more soluble salts are precipitated as surface crusts and near-surface cements as a result of these fluctuations.

Ongoing and periodic oxidation of this vadose hydrology means any hydrogen-rich microbial material tends to be decomposed/oxidized prior to burial. Dry mudflats in saline depressions are not areas with any potential for long-term preservation of elevated amounts of hydrogen-prone organics. With the next heavy rain the less soluble carbonate precipitates remain, while the more soluble salts tend to be flushed through a now-saturated vadose profile to enter the water table. There they continue to flow as dissolved phreatic salts into the discharge depression where evaporative concentration once again reprecipitates them as wet sabkha and brine pool salts.

The lower part of the vadose zone beneath a dry mudflat is made up of the capillary fringe. In parts of an evaporitic mudflat (sabkha) depression that are actively accumulating displacive salts, the top of capillary fringe is at or above the land surface (Fig. 8A). This allows the concentration of pore brines to the attain hypersaline levels needed to precipitate the nodular and displacive salts that typify wet sabkhas and saline mudflats. Unlike the dry parts of a playa or mudflat, the inherently wet capillary surface facilitates long-term evaporative concentration of the near-surface pore brines and the ongoing crossflow of dense brine into sediments below the water table (sabkha-driven brine reflux). As long as brine can be supplied from an updip source, closed cellular flow beneath the wet sabkha flat is the result. In a capillary zone-bound system that is also subsiding, such wet sabkha hydrologies can retain continual hypersaline brine saturation with associated dysaerobia or anoxia, and so sequences of hydrogen-prone microbial organic matter can accumulate as mats and so be preserved into the burial environment.

Given enough time, waters in a brine plume beneath a wet sabkha or a periodically holomictic brine lake will reach the bottom of the basin fill or be dispersed back into the regional cross flow on top of any aquiclude it intersects on its way down (Wood *et al.*, 2002; Warren, 2006). In either case, the refluxed waters start to spread laterally and back out toward the basin fringes, so mixing with fresher forced-convection waters beneath the lake, playa or seaway margin. Ultimately this brine returns to the playa surface, usually in a diluted form as a component of water-edge spring or seep waters. This convective flow is an effective way of moving salt load through large volumes of the basin sediments beneath an accumulating salt bed, and yet still maintain anoxic pore waters beneath a wet sabkha or salt lake (see discussion of brine curtains in Warren 2006). Ongoing recycling of anoxic brine beneath a salt lake or seaway in-turn aids in the preservation of organic material. Thus, organics deposited in a perennial wet sabkha or saline mudflats with a long-term reflux curtain have the potential to be preserved as hydrogen-prone organics until the sediment passes into the zone of catagenesis.

Even so, outcropping capillary-fringe areas where brine-saturated microbial mats reside about the edge of a saline water body, can be subject to episodes of water table lowering or to flushing by fresh oxygenated meteoric waters. Then the microbial organic matter may be intermittently stripped of its hydrogen by aerobic decomposers that will flourish on top of and within the mats during times of exposure or pore-water freshening.

Perennial phreatic hydrologies

Permanent brine lakes and ancient epeiric seaways with variably holomictic water columns driving stable long-term reflux curtains or plumes, are much more likely than wet sabkhas to preserve hydrogen-rich organics into the zone of catagenetic burial. Surface water-masses within perennial

brine lakes or seaways routinely fluctuate between stratified and nonstratified conditions, while the bottom waters typically have a greater propensity to maintain long-term anoxia (Warren, 2006). An upper fresher (less dense) water layer sits on top of a more saline (denser) lower water mass in a stratified system in a perennially brine-filled depression (Fig. 8B). The narrow zone of transition in the brine column between the two waters is called a halocline or pycnocline. Often a stratified saline lacustrine/seaway system is also thermally stratified and heliothermic, with warmer waters constituting the lower water mass. The zone of transition separating the upper and lower water masses is the called the thermocline, or the chemocline, or the halocline, or the pycnocline. Thermal stratification of brine masses with a cool top and a hot base is opposite to that found seasonally in many temperate freshwater lakes and so is sometimes called reverse thermal stratification, but heliothermal is a more appropriate term.

Heliothermy is a result of the contrast in specific heat response between less saline and more saline waters. Specific heat of a brine decreases as the salinity increases (Kaufmann, 1960). Specific heat is the amount of heat needed to raise one gram of a substance by 1 °C. For a given amount of heat input, a unit volume of hypersaline water will show a greater increase in temperature than a less saline water. The resulting greater increase in temperature in a lower hypersaline water mass, compared to an upper less-saline water for the same degree of insolation, makes brine lakes and seaways heliothermic; independent of any salinity (osmotic) or oxygen stresses, heliothermy can induce pronounced heat stress in any benthic halobiota. Modern heliothermal lakes occur in appropriately stratified saline water bodies on all continents and include numerous saline lakes on the steppes of Russia, Siberia and Canada, Solar Lake in the Middle East (Fig. 11B), numerous coastal salinas in Australia, Lake Meggarine in Algeria, Hot Lake in Washington State and Red Pond in Arizona (Hammer, 1986). One of the more unusual examples is Lake Vanda in Antarctica, which has a maximum water temperature of 25 °C below the chemocline (at a depth of 64 m in the water column), yet the water surface remains ice-covered.

Dissolved gas levels and temperature changes associated with periodically heliothermal bottom waters create extreme levels of environmental stress in bottom communities attempting to cope with hypersalinity. For example, oxygen is supplied to any water body via exchange with the atmosphere and as a byproduct of photosynthesis of the biota living in the waters. In well-oxygenated water columns most of the organics produced by primary production the upper water mass are destroyed by microbial respiration and the conversion of organic matter back to CO_2. Much of the improved preservation potential associated with "higher than marine" bottom salinities in layered mesohaline to hypersaline settings reflects the effect on biotal diversity of increasingly low levels of dissolved oxygen and CO_2 in the bottom and pore waters on biotal diversity.

Oxygen levels in natural brines tend to decrease with increasing salinity, independent of biological respiration. If not enhanced by the activities of bottom-living photosynthesizers, natural bottom brines will be dysaerobic to anaerobic by the time salinities reach halite saturation (Fig. 9; Kinsman, 1973; Warren 1986). Dissolved CO_2 shows a similar depletion; dissolved CO_2 levels in marine-fed modern salt pans decrease to around 50% of the original value when the brine concentrations increase from 1.5 to 4 times that of seawater (Lazar & Erez, 1992). CO_2 concentration in brine is also pH dependent; at a pH of 9 (reached by concentrating seawater to around 70‰) the CO_2 content is near zero (Moberg *et al.*, 1932). Those algae and

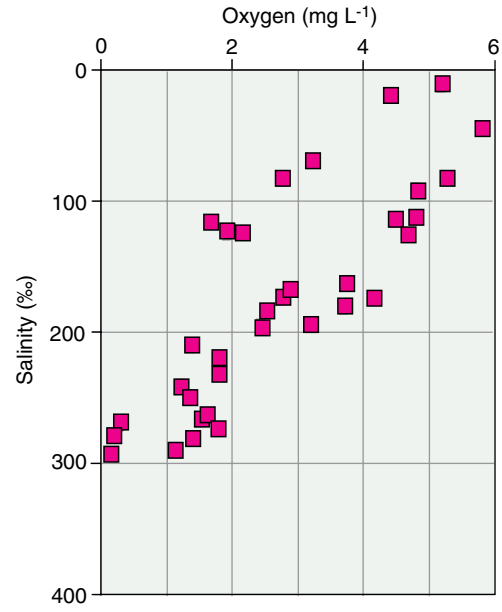


Fig. 9. Oxygen levels in present-day surface brines under increasing salinity. Oxygen content of modern seawater is ~5.4 mg L^{-1} (after Warren, 1986).

cyanobacteria, which are dependant on dissolved CO_2 for photosynthesis, will suffer or die at higher salinities.

Stability of brine stratification and anoxia in modern stratified brine lakes

Brine stratification occurs today in all perennial saline lakes, including many coastal salinas in Australia, rift valley lakes of the African Rift Valley and the Dead Sea, Israel and most are meromictic and oligomictic (Warren, 2006). Lake Hayward, a coastal salina in Western Australia, typifies such stratified brine system. It is a sub-sea-level water-filled marine seepage depression with bottom brines possessing ionic proportions similar to that of seawater (thalassic). The seawater seeps into the basin as groundwater and there is no hydrographic (at-surface) connection to the nearby ocean. Gypsiferous carbonate muds with organic contents of 1–5% accumulate on its microbially-bound floor beneath its small shallow perennial brine pool (0.6 km^2 and less than 2–3 m deep). In the permanently inundated centre of the lake, where waters are 1–2 m deep even in late summer, laminated benthic microbial mat communities flourish and are dominated by photosynthesizing cyanobacteria (mostly *Cyanothece sp.*). Filamentous *Microcoleus sp.*, along with coccoids, dominate the laminated to pustular mats in the seasonally-desiccated strand zone. Sediments in the lake centre accumulate under a limnology that is density-stratified and heliothermal for much of the year (Rosen *et al.*, 1995). Meteoric winter inflow creates a well-defined long-term mixolimnion (Fig. 10A) where an upper, less dense and cooler water mass has salinities ranging from 50 to 210‰. It exists from late autumn to early summer

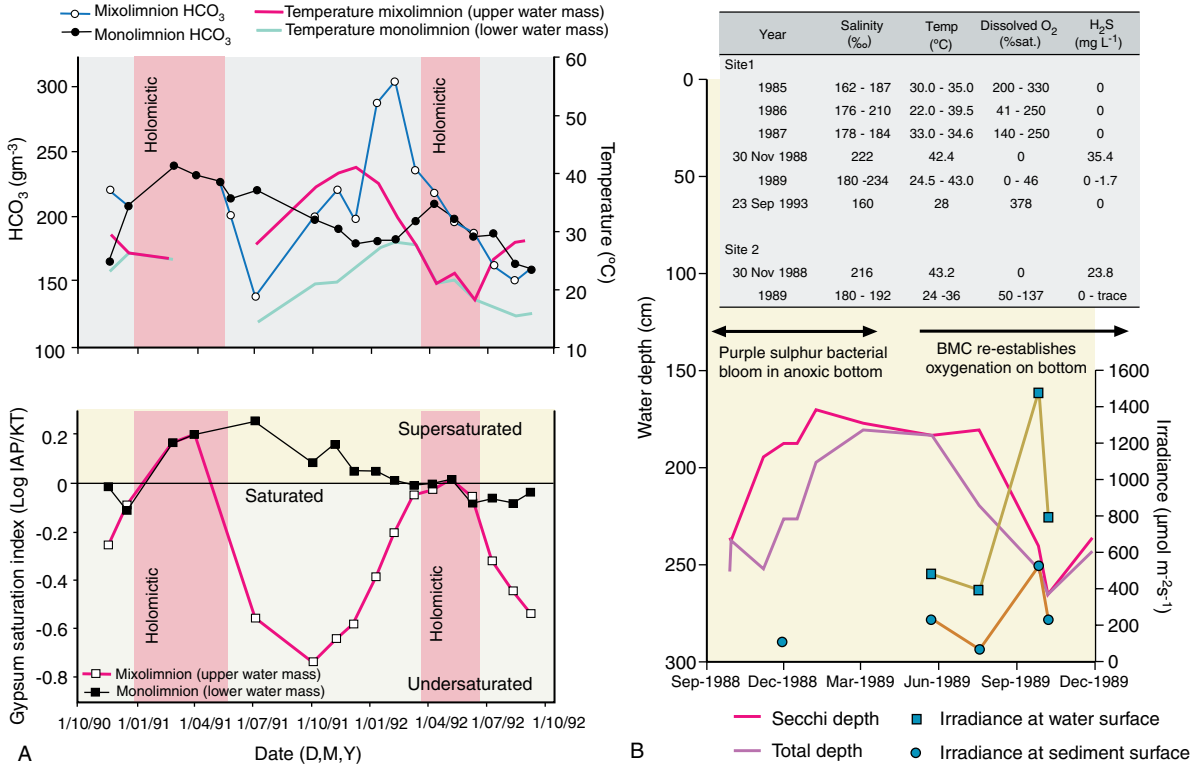


Fig. 10. Brine stratification in Lake Hayward waters, West Australia. (A) Seasonal hydrogeochemical evolution. Uppermost plot shows temperature regime in upper (mixolimnion) and lower (monolimnion) water masses and bicarbonate content. As the lake mixes, the thermal and density stratification disappears. Immediately prior to mixing the bicarbonate concentration decreases, suggesting precipitation of calcium carbonate (aragonite; after Rosen *et al.*, 1995). Lower plot shows saturation state of waters with respect to gypsum. The monimolimnion was saturated with respect to gypsum for summer 1991–1992 and was near saturation at the start of summer 1992–1993. The mixolimnion is only saturated when the lake water is homogeneous (after Rosen *et al.*, 1996). (B) Effect of gypsum precipitation on benthic microbial communities and associated oxygenation in Lake Hayward, West Australia (compiled from data in Burke & Knott, 1997).

(May to February) as it floats on top of a lower denser and warmer water mass (monolimnion) with salinities in the range 150 to 210‰.

Stratification disappears for a few months each year from mid-summer to mid-to-late-autumn. During summer the waters of the upper water mass evaporate and concentrate as their bicarbonate content steadily increases. From the onset of stratification in late autumn, across mid-winter and on into to early summer the temperature trends of the two water masses are parallel (Fig. 10A). They form a heliothermic system where the lower water mass is some 15–20 °C hotter than the upper water mass. By mid-summer (e.g. January 1992) lower water mass began to cool, while the temperature of the upper water mass continued to rise. Once the temperatures (and densities) of the two water masses equalize, they mix as the lake overturns (holomixis) and waters of the lower water mass (the monolimnion) came into contact with the atmosphere once more.

While the water masses are stratified, the chemocline and the thermocline are sharply defined across a 10 cm interface with a salinity contrast that may be as much as 135–140‰ and a temperature difference of up to 19 °C. The time of mixing is immediately preceded by a sharp fall in the level of bicarbonate in the mixolimnion, suggesting that from late summer to autumn the precipitation of pelagic calcium carbonate (mostly aragonite) then gypsum occurs in the upper water mass (Fig. 10A, upper plot; Rosen *et al.*, 1995). For example, the upper water mass in Lake Hayward was supersaturated with respect to gypsum and anhydrite from October 1991 to February 1992 (Fig. 10A, lower plot; Rosen *et al.*, 1996). When the lake mixed from March 1992 until early May 1992, the entire water body was at gypsum saturation, but slightly undersaturated with respect to anhydrite.

A 'whiting' (a cloudy white appearance to the water body) was observed in the lake in March, just at the time of first mixing of the lake waters. Analysis by scanning electron microscopy of the collected filtrate indicated that the "whiting" was composed of gypsum and silica from diatom tests. At that time, there was a thin (10–20 mm) crust of gypsum accumulating on the lake bottom. After the "whiting", when the water was unstratified (holomictic), both the monimolimnion and mixolimnion were near saturation with respect to gypsum. After mixing, with the next influx of meteoric waters building across the lake water surface, salinity stratification re-established itself. Prior to the long-term stratification that defined the winter months, brine layering in the transition to stratification was not stable as the upper and lower water bodies remixed a number of times extending over periods of days before stable stratification set in by mid-winter (Fig. 10A, May–June 1992; M. Rosen pers. comm., 2006).

Lake Hayward bottom sediments also illustrate an aspect of pelagic evaporite precipitation that is probably true for many ancient "deep water" density-stratified saline settings. Namely, that while precipitation of pelagic evaporitic sediment is seasonal, and it occurs in the surface water mass even as the lake waters are density stratified, bottom salts can only accumulate when the whole brine column is saturated and unstratified (holomictic). This is so even if the chemistry of the lower water mass is at gypsum or halite saturation almost all year round. Only pelagic sediments (including carbonates and organic residues) and terrigenous detritus (including eolian dust) make it to the bottom when a saline lake is perennially stratified, as was the case in the Dead Sea for the 400 years prior to 1979 (Warren, 2006).

Intensity of light penetration to the subaqueous bottom of an evaporite-accumulating depression is a significant control on how much photosynthetic oxygen can be generated by the bottom-living microbial community. In Lake Hayward a healthy mat of photosynthesizing halotolerant cyanobacteria drastically alters the levels of anoxia in shallow bottom brines. Photosynthesis, via its benthic microbial mat community, is normally sufficient to maintain supersaturation of the Lake Hayward bottom waters with dissolved oxygen, even during periods of brine column stratification (Fig. 10B).

Burke & Knott (1997) found that after an unusually dry year in 1987, the salinity of Lake Hayward increased to 260‰ as gypsum precipitated throughout the lake waters. Brine turbidity generated by the markedly increased pelagic crystallization of gypsum in the surface waters in that year was sufficient to obscure the benthos completely, despite the shallowness of the lake. As a result the amount of oxygenic photosynthesis and aerobic decomposition was greatly reduced in the benthic mats and they degraded. During brine stratification in the following winter (1988), bottom waters became anoxic and sulphurous. During the next few years, after each subsequent brine column overturn, healthy microbial mats were re-established across the lake floor and they

were able to again supersaturate the bottom waters with oxygen year round, as was seen in 1992, which was the time of the Rosen *et al.* (1995, 1996) study.

Development of a healthy mat community in the Lake Hayward salina prevents periodic bottom anoxia. Nearby lakes, that do not contain a healthy microbial benthos, tend to anoxia during stratification. Comparisons between Lake Hayward and nearby lakes clearly show that healthy microbial mats function as a strong homeostatic mechanism in the lake hydrology. Shallow meromictic but perennial salt lakes, with long-term stability of photosynthetically elevated oxygen levels in the bottom, tend to have lower levels of preserved TOC due to the higher efficiencies of halotolerant aerobic decomposers acting on the benthic organic matter. This can be seen when comparing TOC levels in the microbial laminites of Lake Hayward and Solar Lake (Fig. 5).

Solar Lake in the Middle East is another small meromictic hypersaline lake (coastal salina) with a well-documented heliothermal hydrology. It is located on the Sinai coast of the Gulf of Aqaba (Cytryn *et al.*, 2000) and is separated from the ocean by a narrow permeable sand barrier. The barrier allows seawater to seep into the sub-sea-level hydrographically-isolated lake depression and so replace waters lost to evaporation. Seepage-derived seawater can then pond on top of the lake floor, along with lesser volumes of waters supplied by occasional winter rains (Fig. 11A). Brine depth in the lake centre fluctuates between 4 and 6 m, driven by seasonal changes in the intensities of evaporation and the related levels of seawater seepage and brine reflux.

Thick cyanobacterial mats carpet much of the Solar Lake sediment surface and contain a highly diverse microbial community of cyanobacteria and haloarchaea. Unlike the microbial laminites of Lake Haywood, a structureless organic-rich gypsiferous mush constitutes the sediment across the m-deep bottom of the anoxic lake centre (Fig. 11A; see Warren, 2006 for geological detail). Fluctuating

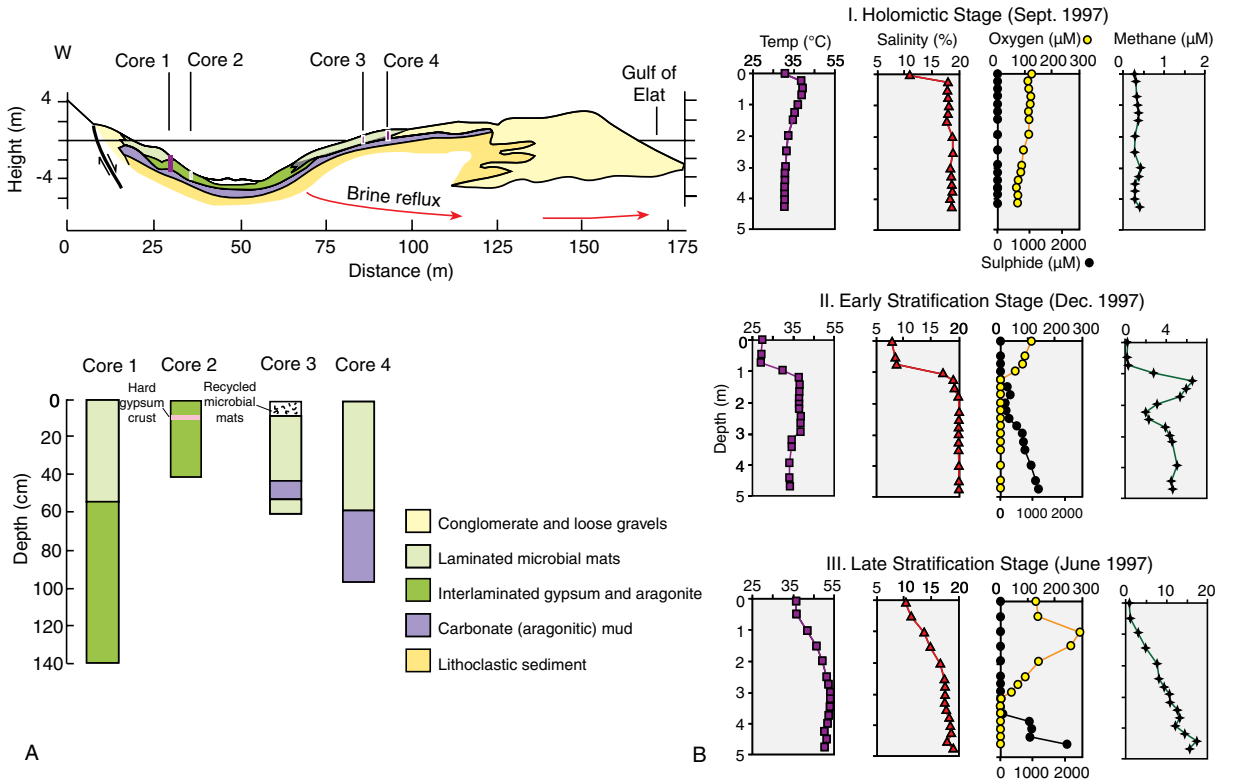


Fig. 11. Solar Lake, Sinai Peninsula, Middle East. (A) East–west topographic and lithological cross section based on cored sediments showing peripheral algal facies and a more central organic-rich gypsum zone (after Aharon *et al.*, 1977). (B) Effects of the seasonal development of heliothermic and oxic stratification in the water column of Solar Lake (after Cytryn *et al.*, 2000).

planktonic microbial activity mirrors seasonal changes in brine column layering by exporting varying volumes of oxygen, sulphide, and methane into the brine column as this mush accumulates (Fig. 11B).

High evaporation and aridity in the summer months raises Solar Lake salinity to 200‰. At that time the brine column is completely mixed (holomictic) and the entire water column is oxygenated (Fig. 11B, September, 1997). Temperature and salinity in the holomictic state vary little throughout the water column and sulphide and methane concentrations are very low. By autumn, the water column becomes stratified as a newly introduced seawater brine (50‰) layer overlies the residual, highly saline bottom water (180–200‰). A well-defined density gradient (halocline or pycnocline) separates an upper oxygenated cooler (16 °C) brine mass (epilimnion) from the lower hotter (45–55 °C) anoxic sulphide-rich brine mass (hypolimnion; Fig. 11b, December 1997). A high sulphide concentration develops in the anoxic waters below the halocline and comes from the activities of sulphate-reducing bacteria both in the water column and in the underlying degrading cyanobacterial mats. Crossing the halocline into the lower brine there is a rapid downward increase in sulphide concentration, which reaches a maximum value of 1240 mM near the sediment-brine contact (Cytryn *et al.*, 2000). At the same time a peak in methane concentration develops directly below the halocline, where a maximum value of 6.5 μM was measured in the December 1997 profile and was in-part a reflection of the decomposer activities of the methanogenic haloarchaea.

As winter passes into spring gradual heating, along with an increase in the salinity of the upper water mass, degrades the halocline (Fig. 11B). Thus the June 1997 data portray a transitional state between late stratification and the beginning of holomixis. Salinity and temperature gradients across the halocline are more gradual and deeper in the water column than those observed in the December 1997 profile. The deepening halocline of June 1997, when the chemocline was located 3.25 m below the water surface, allowed oxygen to penetrate much deeper into the brine column, and so extend farther out across the subaqueous lake bottom than it had in the earlier stages of stratification. Oxygen concentration in the upper water mass in June 1997 reached a maximum value of 300 μM at a depth of 1 m below the water surface. These supersaturated values of oxygen imply intense oxygenic photosynthetic activity at the brine surface and in underlying shallow salina waters. Deeper in the brine column, and well below the chemocline, a sharp rise in sulphide concentration occurs reaching a maximum value of 2150 μM at the water-sediment interface (Cytryn *et al.*, 2000). Methane concentration increases linearly below the brine surface and reaches a maximum value of 17 μM adjacent to the lake bottom, implying methane, like the bacterially derived H_2S, is escaping from the sediments. Increased evaporation rates in the mid- to later summer further increase the salinity of the surface layer and ultimately disrupt the stratification and so lead into summer holomixis (as seen in the September 1997 profile). Unlike Lake Hayward, conditions beneath the perennial lake floor of Solar Lake are anoxic for longer periods, oxygenic species, including cyanobacteria, tend not thrive in bottom waters for long periods, especially in the deep central parts of the lake, where levels of preserved organics tend to be higher (5–20% versus 1–5% TOC in Lake Hayward; Fig. 5).

Substantial density differences between the upper and lower masses in most density-stratified systems means diffusive mixing across any halocline is insignificant. When a hypersaline water mass is density stratified there is no mechanism to drive changes in saturation state and so there is no widespread bottom nucleation of salts. Sedimentation on the floor of the lower water layer (especially if it is below the euphotic zone) is mostly by a pelagic rain of organics and evaporite crystallites formed in the upper water mass at the halocline via brine mixing. There may also be local changes in brine chemistry and the associated mineral precipitation driven by local influxes of spring and seep waters. In contrast, when the upper and lower water masses equilibrate and homogenize, bottom nucleation of salts is possible even at the base of deep brine columns, as is occurring with the precipitation of coarsely crystalline halite at the base of the 350 m holomictic brine column in the Dead Sea today (Warren, 2006). In some perennial saline lakes in more temperate climates the holomictic stage is seasonal and so the sediment layers are varves (e.g. Lake Hayward, Solar Lake, Lake Van, Lake Urmia), in others, holomictic mixing of surface with bottom water masses occurs across a longer time frame (e.g. the 400 year stability of the lower water layer in the Dead Sea driving episodes of laminite versus coarse crystalline halite beds on the deep lake floor).

Whenever a homogenized brine mass restratifies, the lack of ongoing concentration in the lower water mass means the rate of brine reflux through bottom sediments beneath the sediment brine interface slows and ultimately stops. Hypersaline pore brines remain but in a stagnant condition as there is no ongoing mechanism to resupply brines denser than existing pore waters in the column substrate. High pore water salinities, a propensity for anoxia, anoxic pore brines and elevated bottom temperatures, all tend to exclude aerobic burrowing and grazing animals from evaporite bottom sediments beneath a stratified brine column. This minimizes the effects of oxygenic biota that would otherwise oxidize and destroy mesohaline microbial debris, as in sediments deposited in less saline settings.

Although the daily temperature/stratification records of Lake Hayward and Solar Lake are probably the best documented examples of the long-term hydrological cycling of a naturally stratified brine pool, they both have a number of limitations when attempting to use them as direct analogues for the hydrology of ancient stratified brine seaways. Unfortunately, neither lake can act as a same scale hydrological analogue for ancient evaporite seaways, intraplatform depressions or even some of the larger ancient evaporitic lakes. They suffer from the scaling limitations that enfeeble all modern marine-associated evaporite analogues (Warren, 2006). Although hydrographically isolated and marine-seepage fed, neither lake is situated in a hydrological setting where enough time or aerially extensive drawdown stability has transpired to allow substantial thicknesses of mesohaline carbonates, halite or gypsum to accumulate. Their small aerial extents ($\leq 0.6\,km^2$) and their centripetal meteoric inflow hydrologies (driven by winter rains, a marked seasonal lowering of evaporation intensity, and a high-relief hinterland immediately adjacent to the water body) means they cannot be directly compared to ancient mesohaline epeiric brine seaways where inherently low-relief topographies meant strandlines moved up to hundreds of kilometres in a wet-dry cycle, and where unfractionated meteoric runoff from the hinterland was much less significant in the freshening process.

Biological responses to layered hydrologies

Brines in modern evaporitic depressions are typically layered in terms of the annual or longer-term hydrological cycle, with denser more saline waters supporting an ephemeral mass of less dense inflow water. The lower, denser part of the water mass tends to be more stable and its physical conditions change less. In contrast, the conditions in the floating less-dense layer are much more variable and its physical chemistry tends to oscillate. This upper layer periodically freshens to where it supports a widespread planktonic bloom (feast). Then, as ongoing evaporation concentrates the upper layer, conditions become increasingly less suitable for life (famine) and a mass die-off occurs, first of the haloxene species, then the halotolerants, then the halophiles.

The die-back creates a pulse of organic matter that can swamp the abilities of the decomposers in the water column to strip it of its hydrogen, and so it can reach the sediment interface with its long-chain alkanes still intact. Even in conditions where light penetrates to the bottom of the brine column and the bottom waters immediately above the sediment surface are oxygenated, the halotolerant primary producers can be sufficiently productive and the underlying anoxic decomposers sufficiently inefficient that substantial volumes of hydrogen-rich microbial mater can be retained into burial. Some modern examples of hydrologically induced community layering in modern evaporitic settings will now be considered.

Halotolerant plankton and water column layering

The significance of periodic freshening on biomass in stratified waters in creating conditions of "famine or feast" for halotolerant and halophilic species is clearly seen in the present productivity cycle of the Dead Sea (Fig. 12; Oren 2005; Oren & Gurevich, 1995; Oren *et al.*, 1995). The main component of the halobiota in the Dead Sea waters is a unicellular green alga, *Dunaliella parva* being the sole primary producer in the lake. Several types of halophilic archaea of the family Halobacteriaceae then metabolize the glycerol and other organic compounds produced by the alga. As in all ecosystems, producers and consumers in the brine-stratified water columns are codependent. Halophilic archaea (*Halobacterium and Halococcus*) survive into much higher salinities than *Dunaliella parva* as they decompose the glycerol-rich remains.

Three distinct periods of organic productivity were seen in thirteen years of quantitative studies

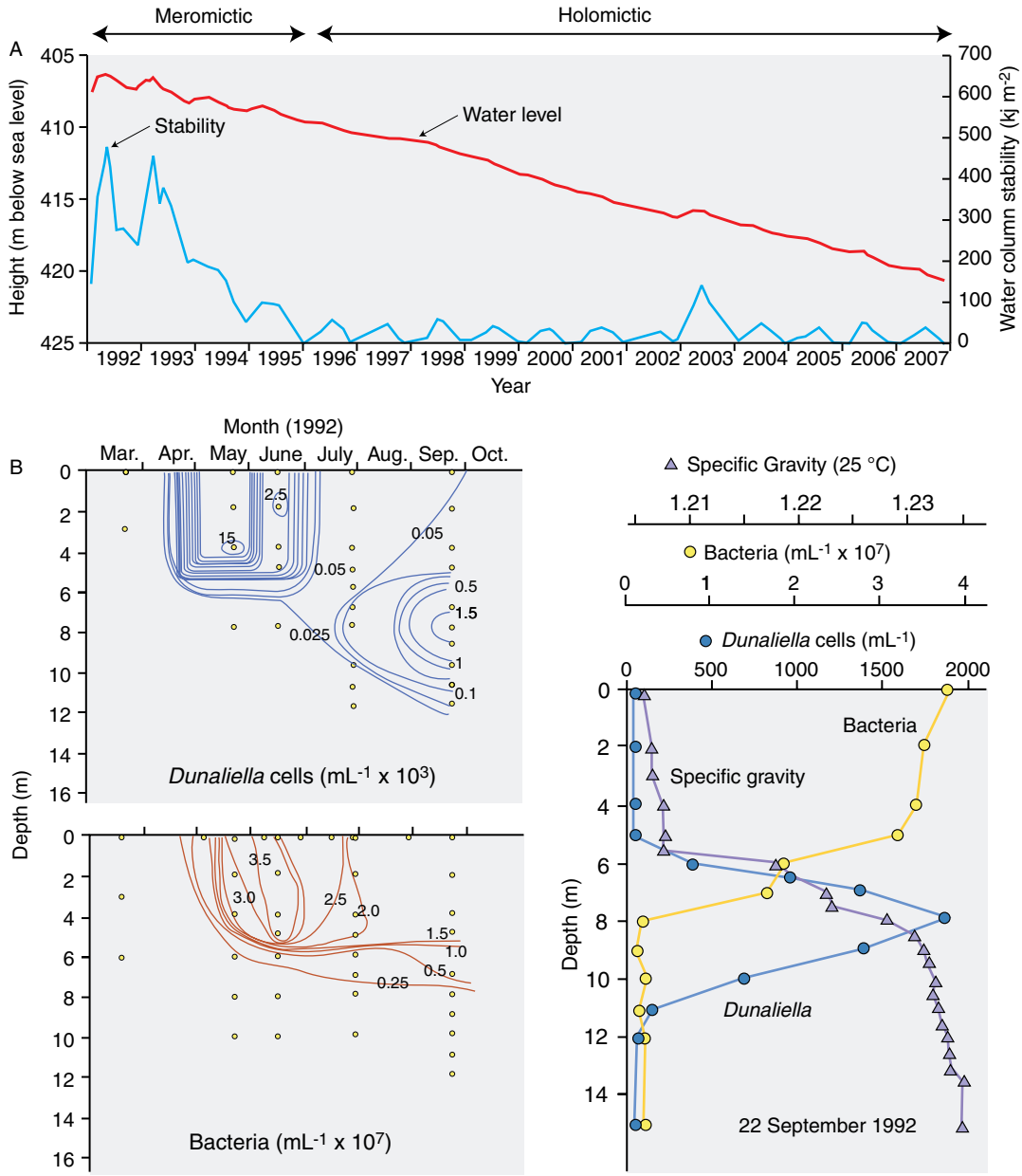


Fig. 12. Biodynamics in the Dead Sea, Middle East. (A) Long-term changes in quasi-salinity and temperature in the deep water body (below 100 m) of the Dead Sea in a meromictic to holomictic period (after Gertman & Hecht, 2002; with additional data from http://isramar.ocean.org.il/DeadSea, last accessed 29 September 2004). (B) Changes in the vertical distribution of *Dunaliella* and halobacteria during the rain flood-induced density stratification of the Dead Sea in 1992 (after Oren, 1993). Note the vertical distribution of *Dunaliella* and halobacteria relative to the halocline on 22 September 1992. See Warren (2006) for full discussion of long-term sedimentary dynamics of the Dead Sea and Lake Lisan depressions.

of Dead Sea microbiology starting in 1980 (Oren, 1993). Unlike more temperate lakes, organic blooms in the Dead Sea are not an annual event. Mass developments of *Dunaliella* (up to 8800 cells mL^{-1}) and red halophilic archaea (2×10^7 cells mL^{-1}) were observed in 1980, following a dilution of the saline upper water layers by rain floods and an associated rise in lake level of 1.5 m. This bloom had disappeared at the end of 1982, following complete mixing of the water column and the associated salinity increase in the upper water mass (holomixis).

During the period 1983–1991 the Dead Sea was holomictic, and no *Dunaliella* cells were observed.

Viable halophilic and halotolerant archaea were present during this period, but in very low numbers. Then heavy rain floods during the winter of 1991–1992 raised the lake level by 2 m and caused new salinity stratification as the upper five metres of the water column was diluted to 70% of the normal surface salinity (Fig. 12A). The meromictic phase lasted until 1996 when the current holomictic conditions with seasonal stratification were established, clearly illustrating the oligotrophic hydrology of the Dead Sea brine column. *Dunaliella* reappeared in the upper less saline water layer (up to 3×10^4 cells mL^{-1} at the beginning of May 1992, rapidly declining to less than 40 cells mL^{-1} at the end of July), while the bloom of the archaea (3×10^7 cells mL^{-1}) continued and imparted a reddish colour to the Dead Sea brines (Fig. 12B). The reddish hue of the surface waters at this time was due to elevated levels of the carotenoid pigment bacterioruberin, which absorbs light at wavelengths between 420–550 nm.

Archaeal numbers in the Dead Sea decreased only a little after the July 1992 decline of the *Dunaliella* bloom, and most of the haloarchaeal community was still present at the end of 1993. However, the amount of carotenoid pigment per cell decreased 2–3-fold between June 1992 and August 1993 (Fig. 12B; Oren & Gurevich, 1995). No new algal and archaeal blooms developed after the winter floods of 1992–1993, in spite of the fact that salinity values in the surface layer were sufficiently low to support a new algal bloom. A remnant of the 1992 *Dunaliella* bloom maintained itself at the lower end of the pycnocline (halocline) at depths between 7 and 13 m (September 1992–August 1993). Its photosynthetic activity was small, and very little stimulation of archaeal growth and activity was associated with this algal community (Fig. 12B). This pattern suggests that the photosynthetic activity of the algae may have been limited by a lack of nutrients in the upper brine column.

Colouration of the Dead Sea waters from the initial algal bloom allowed Oren & Ben Yosef (1997) to use Landsat images, collected in May 1991 and in April and June 1992, to plot the development of the *Dunaliella parva* bloom. In contrast, the carotenoids of the subsequent archaea bloom did not produce a recognizable signal in the Landsat images. The April 1992 image obtained at the time of the onset of the algal bloom, prior to its lake-wide spread, suggested it originated in the shallow areas near the shore of the lake, where light penetrated to the bottom of the brine column and a newly established freshened water layer intersected the lake floor. The resulting algal blossoming was instigated by resting cells that had survived near the sediment surface around the lake margin or in species refugia around freshwater springs.

The decline of the lake-wide bloom of halophilic archaea in the Dead Sea appears to be related to viral infection (Oren *et al.*, 1997). For example, in October 1994, there were between 0.9 and 7.3×10^7 virus-like particles per mL of brine during declension of halophilic archaea in the upper 20 m of the Dead Sea water column and virus-like particles outnumbered archaea by a factor of 0.9–9.5 (averaging 4.4). By 1995 all water samples contained low numbers of both archaea and virus-like particles; $1.9–2.6 \times 10^6$ and $0.8–4.6 \times 10^7$ mL^{-1} respectively in April 1995. Viral numbers declined even further so that by November 1995–January 1996 all samples contained less than 10^4 particles mL^{-1}. Oren *et al.* (1997) further suggested that viruses play a major role in the decline of halophilic archaeal communities in many other hypersaline settings at salinities where protozoa and fungi are absent.

Community layering in mesohaline microbialites

Laminated organic-rich sediments that typify many evaporitic microbial carbonates (possible petroleum source rocks) and described by sedimentologists using the general, and perhaps dated, terms algal mats and cryptalgal-laminites, are in effect microbial "high rises," as are many living stromatolites. They, and their entrained biomarkers, indicate the activities of an ecologically layered microbial community that can thrive in both subaerial and subaqueous settings. Like microbial layering in the Dead Sea brine column, layering in a microbial mat is divisible into an upper aerobic community and a lower layer of anaerobic decomposers (Fig. 13). As a microbial mat accretes, its organic constituents are buried. The biochemical make-up of the initial halobiota, which flourished in the hypersaline conditions (typically oxygenic) at or above the mat surface, is altered by the metabolic activities of various decomposers flourishing below.

In order to investigate early or syndepositional changes in the dominant organic constituents and the main diagenetic processes influencing organic character, Grimalt *et al.* (1992) studied organic profiles in cross sections through two different

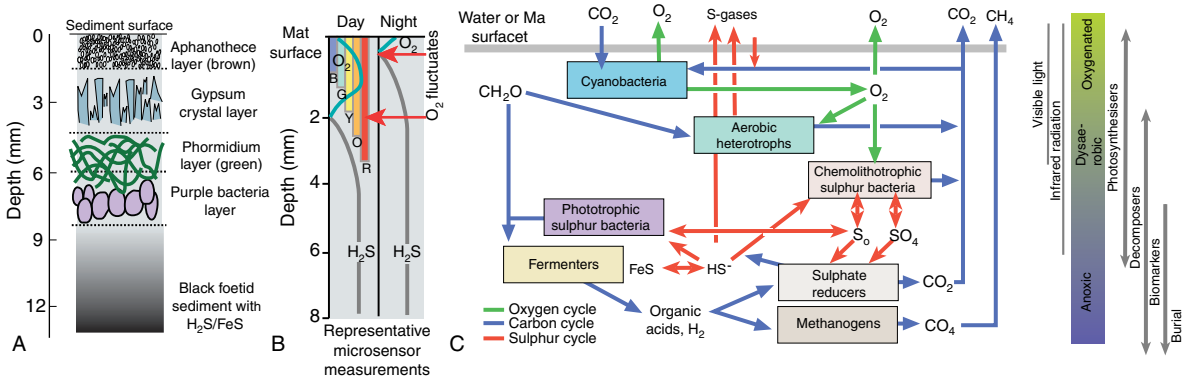


Fig. 13. Layering and metabolism in microbial mats. (A) Typical microbial community in an evaporitic laminite in a modern coastal salina with salinity in the range 130 to 200‰ (after Caumette, 1993). (B) Inter-relationships between microbes and the oxygen, carbon and sulphur cycles in the uppermost 5–10 mm of a microbial mat. The oxic-anoxic transition shifts lower in the mat in the daytime and higher in the mat at night (when photosynthesis has stopped). (C) Biogeochemical cycles operating within the mat versus depth.

subaqueous cyanobacterial mats in a modern coastal salina. Changes in lipid composition were compared with the vertical distributions of the various microbial populations. Vertical distributions in the lipid patterns were defined using enrichment cultures from typical species of cyanobacteria, diatoms, purple bacteria, sulphate-reducers and methanogens obtained from the layered mats. Cyanobacteria *Phormidium valderianum* and *Microcoleus chthonoplastes* were the dominant primary producers in the sampled mats, they occurred almost as monocultures in the upper 6 mm of the mats (Fig. 13A). Worldwide, these and other cosmopolitan filamentous cyanobacterial photosynthesizers are the most obvious organisms in most mesohaline algal mats. Their chlorophyll creates a green layer with a sticky or slimy surface and defines the upper few millimetres of the mat community. As layers of mucilaginous sheaths aggrade via periodic growth spurts, it creates biolamination.

Below the photosynthesizing cyanobacteria is a layer of aerobic heterotrophs (bacteria and archaea), which in the presence of oxygen break down organics produced by the cyanobacteria (mostly abandoned algal sheaths and slime). However, because oxygen is only produced by photosynthesis, these organisms can only perform this process during daylight. The next layer below is dominated by chemolithotrophic sulphur-oxidizing bacteria. These are life forms that use the redox energy contained in the biochemical gradient between reduced sulphur compounds produced by sulphate reducers (below) and oxygen produced by the cyanobacteria (above). They are anaerobic photosynthesizers that fix sugars by utilizing the infrared portion of the light spectrum as they convert H_2S to SO_4. Infrared radiation penetrates deeper into microbial sediment than the visible light used by the cyanobacteria (Fig. 13B). Utilizing the redox gradient these purple sulphur-oxidizing bacteria synthesize organic matter and create the characteristic purple-orange layer seen below the green layer in an aggrading microbial mat. The sulphur-oxidizing bacteria can only metabolize in a suitable redox gradient, and they need to locate themselves exactly within this gradient, so they are typically the most motile forms in a microbial mat. The redox gradient lies deeper in the mat community during the day due to oxygen production by the cyanobacteria, but it rises and can even reach the mat surface in the dark of night (Fig. 13B).

Below the phototrophic sulphur-oxidizing bacteria are the sulphate reducers, the fermenters and the methanogens (Fig. 13C). In saline settings they are relatively inefficient decomposers and tend to be active at salinities that are less than 150‰ (Figs 3 and 4; Ollivier *et al.*, 1994). During the day the sulphate-reducers metabolize organics deep in the microbial mat via anaerobic respiration, utilizing a variety of chemical constituents including manganese, nitrate, sulphate and even CO_2. At night they rise somewhat with redox gradient and at times of prolonged bottom-brine anoxia and brine-column turbidity can even reach the mat surface or enter the lower parts of a density-stratified brine column. They are very important decomposers in most mesohaline microbial mats and give the lower parts of a mat its characteristic "rotten egg" smell. They generally consume up to one third of the

organic carbon present in a typical mesohaline microbial mat and are most efficient at salinities that are less than 120–140‰.

Fermenters and reducers do not completely break down the organics but create alcohols, lactates and other organic compounds (Ollivier *et al.*, 1994). The other group of anaerobic decomposers deep in the mat is the methanogens. They are archaea and utilize simple compounds created by the fermenters (CO_2 and hydrogen, along with organic components such as methanol, acetic acid, formic acid and methylamines) to produce methane. This metabolic pathway produces little biochemical energy and is usually the "last resort" community that makes up the lowermost living layer in the microbial high-rise community that inhabits a microbial mat or a stratified brine column.

Stratification of the microbiota in response to, and in biofeedback with, oxygen levels has important implications in terms of the biomarkers found in preserved saline sediments (and source rocks). Grimalt *et al.* (1992) found that although the uppermost layers of saline microbial mats are dominated by cyanobacteria, they typically leave no more than minor traces in the solvent-extractable lipids (biomarkers) in the buried sediment. Rather, the predominant fatty acid distributions in the lower parts of mesohaline mat sediments parallel the compositions observed in the enrichment cultures of sulphur-oxidizing bacteria, and appear to be mixed with acids characteristic of heterotrophic bacteria, including purple bacteria and sulphate-reducers. In other words, the retained organic signatures, even as the mat lamina were accumulating a few millimetres above, were those of the decomposers, not the primary producers (Fig. 13C). This implies that many biomarkers used to typify organic production in modern and ancient hypersaline sediments typically do not come from organics of the primary producers but from the products of the decomposer community.

The overprinting effects of the decomposers in microbial laminites are clearly seen when molecular characteristics of recent hypersaline sediment from the Ejinur salt lake (northern China) are compared to Tertiary (Eocene) core samples from the Qianjiang Formation (hypersaline lacustrine) of the Jianghan Basin, central eastern China (Fig. 14; Wang *et al.*, 1998). N-alkanoic acids in sediments from both areas (Ejinur and Jianghan) show a pronounced even-over-odd predominance and a bimodal distribution. In the lower molecular

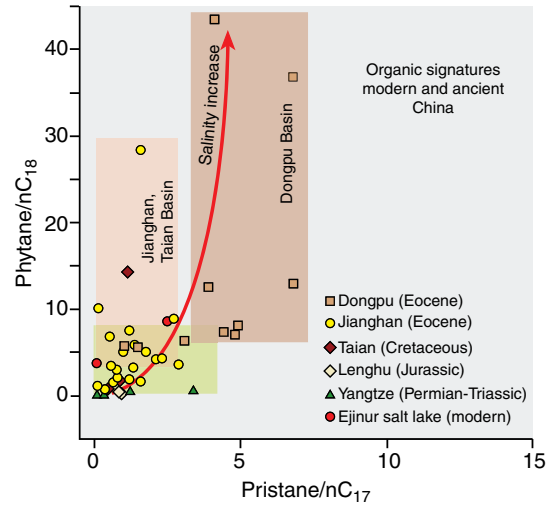


Fig. 14. Crossplot of pristane/nC_{17} versus phytane/nC_{18} ratios for various saline/hypersaline settings in China (after Wang, 1998).

weight range, the C_{16} and C_{18} components are prominent, with the former dominant. For higher homologues (greater than or equal to C_{20}), docosanoic (C_{22}) and tetracosanoic (C_{24}) acids dominate the n-alkanoic acid homologues for the Jianghan and Ejinur samples, respectively. Alkanoic acids with an isoprenoid skeleton are more abundant in Jianghan samples, including C_{20}, C_{21}, C_{24}, C_{25} and C_{30} homologues, with a C_{25} component (3,7,11,15,19-pentamethyleicosanoic acid) most pronounced in the lower part of the Qianjiang Fm. The carbon skeletons of these isoprenoid acids are attributed to archaeal decomposers. *Iso* and *anteiso* branched carboxylic acids are prevalent in both the Lake Ejinur samples and the upper portion of the Qiangiang Formation. (Wang, 1998). They derive from bacteria, probably sulphate-reducing bacteria, and their abundances clearly show again the importance of bacterial decomposers, along with haloarchaea as contributors to the biochemical signature of organic matter in both modern and ancient saline lake sediments. The presence of hopanoid acids and a 3-carboxy steroidal acid in both further attest to contributions from bacterial and eukaryotic sources, respectively. The occurrence of particular carboxylic acids in the Jianghan samples illustrate these compounds, indicators of halotolerant and halophilic decomposers, can survive as biomarkers in source rocks deposited in hypersaline settings.

Defining where ancient halotolerant and halophilic decomposers lived ("in brine column" or "in mat") is not possible from an analysis of sediment

biomarkers. It requires sedimentological interpretation of the rock matrix, which typically is a laminite. As discussed in Warren (1986), any assumption of "lamination indicating deeper brines" is fraught with difficulty, as ancient evaporitic laminites and biolaminites were subaqueous sediments with near-identical mm-scale textures accumulating beneath stratified and unstratified perennial brines columns at depths ranging from less than one metre to hundreds of metres. Determination of water depth requires sedimentary analysis of evaporitic sediments that are intercalated with the laminites.

ORGANIC ENRICHMENT

At the broader scale of petroleum source rock creation, the amount of organic matter preserved in evaporitic sediment, which becomes a potential source rock, is a function of three factors that can be expressed in the equation (Bohacs *et al.*, 2000):

$$\text{Organic Enrichment} = (\text{P-De})/(\text{Di}) \quad (3)$$

where P is production, De is destruction (oxidation and biodegradation and Di is dilution (detrital influx and matrix precipitation). Maximum enrichment occurs when production is maximized and destruction and dilution are minimized.

Production at mesohaline salinities is mostly via photosynthetic fixation of CO_2. It includes autochthonous organic matter, formed at or near the site of accumulation and derived from algae, bacteria and aquatic plants, as well as allochthonous organic matter carried in during floods (Bohacs *et al.*, 2000). Katz (1990) showed that varying levels of solar input and water chemistry/stratification exert the largest effects on overall primary production in mesohaline settings. Initial destruction of organic matter is mostly a function of the efficiency of the various scavengers and grazers, which is typically a function of the availability of oxygen (Demaison & Moore, 1980). In higher salinity settings the scavenger/decomposer population is dominated by bacteria and archaea, while the density of the metazoan grazers is largely inhibited by the same higher salinities. Dilution by an influx of mineral precipitates to possible areas of organic enrichment can limit levels of organic enrichment by decreasing the proportion of organic matter relative to inorganic matrix. The source of dilution can be detrital siliciclastics or precipitates of gypsum and halite.

Salinity controls on organic productivity: the flamingo connection

When biodiversity is low and salinity is high, a proliferation of well-adapted mesohaline species can generate organic productivity levels in surface waters that are much higher than those observed in most non-evaporitic settings. These saline systems are indicative of general principles seen in stressed ecosystems, namely, as the harshness or abiotic stress in a system increases, the biotic stress decreases on a few well-adapted species (as there are fewer predators and grazers). The total biodiversity (number of species) decreases, while at the same time the biomass (total mass of organisms in the system) initially increases (e.g. Garcia & Niell, 1993). Ultimately, as salinity rises further, biomass declines as conditions become unsuitable for any life. One of the most visually impressive indications of periodic very high levels of organic productivity in a modern salinity-stressed water body resides in the "flamingo connection", a connection between flamingos, mesohaline planktonic blooms and saline lakes, well documented in Lake Nakuru by Vareschi (1982) and first noted in the geological literature by Kirkland & Evans (1981).

Flamingos are filter feeders thriving on the dense cyanobacterial blooms in the shallows of saline lakes around the world. For example, two species of flamingo intermittently occur in huge numbers in the various East African rift lakes. These are the greater and the lesser flamingo (*Phoenicoptus ruber roseus* and *P. minor*); the lesser flamingo is the bird with the spectacular pink-red colouration. These bright pink birds feed and breed in rift lakes where cyanobacterial blooms can be so dense that a secchi disc disappears within a few centimetres of the lake's water surface (Warren, 1986). Lake Natron is a major breeding ground for flamingos in East Africa and is the only regular breeding site for the lesser flamingo in Africa (Simmons, 1995). In fact, Lake Natron has the highest concentration of breeding flamingos of any lake in East Africa. Both the greater and the lesser flamingo are found there, with the lesser flamingo outnumbering the greater by a hundred to one. Lesser flamingos bred at Lake Natron in 9 out of 14 years from 1954 to 1967. While Lake Natron (a trona lake) is an essential breeding site, it is not a focal feeding site for flamingos. Major feeding sites in the rift valley are Lakes Nakuru and Bogoria in Kenya, which are somewhat less saline than Lake Natron and so have a greater abundance of mesohaline plankton.

The main phytoplankton component in Lake Nakuru waters is the cyanobacterium, *Arthrospira platensis* (previously known as *Spirulina platensis*), it forms the main food component of the lesser flamingo. In Nakuru it is also consumed by one species of tilapid fish and one species of copepod and a crustacean. Rotifers, waterboatmen, and midge larvae also flourish in the waters of Lake Nakuru. The mouth-breeding tilapid fish *Sarotherodon alcalicum grahami* was introduced to the lake in the 1950s to control the mosquito problem and they have flourished ever since, at times displacing the flamingos as the primary consumers of planktonic algae. Their introduction also increased the number of fish-eating birds residing in the lake (Vareschi, 1978).

In a good year more than a million flamingos consume more than 200 tons of plankton per day from Lake Nakuru, a shallow saline soda lake with a pH ~10.5 and a typical annual salinity range of 10–120‰. The lake measures some 6.5 km by 10 km, with waters up to 4.5 m deep in the lower parts of the lake during a "lake-full" period. Lake levels are subject to change, both annually and on a longer time scale, with permanent eutrophic waters developed in the lake centre during times of higher water (Fig. 15A and B; Vareschi, 1978–1982).

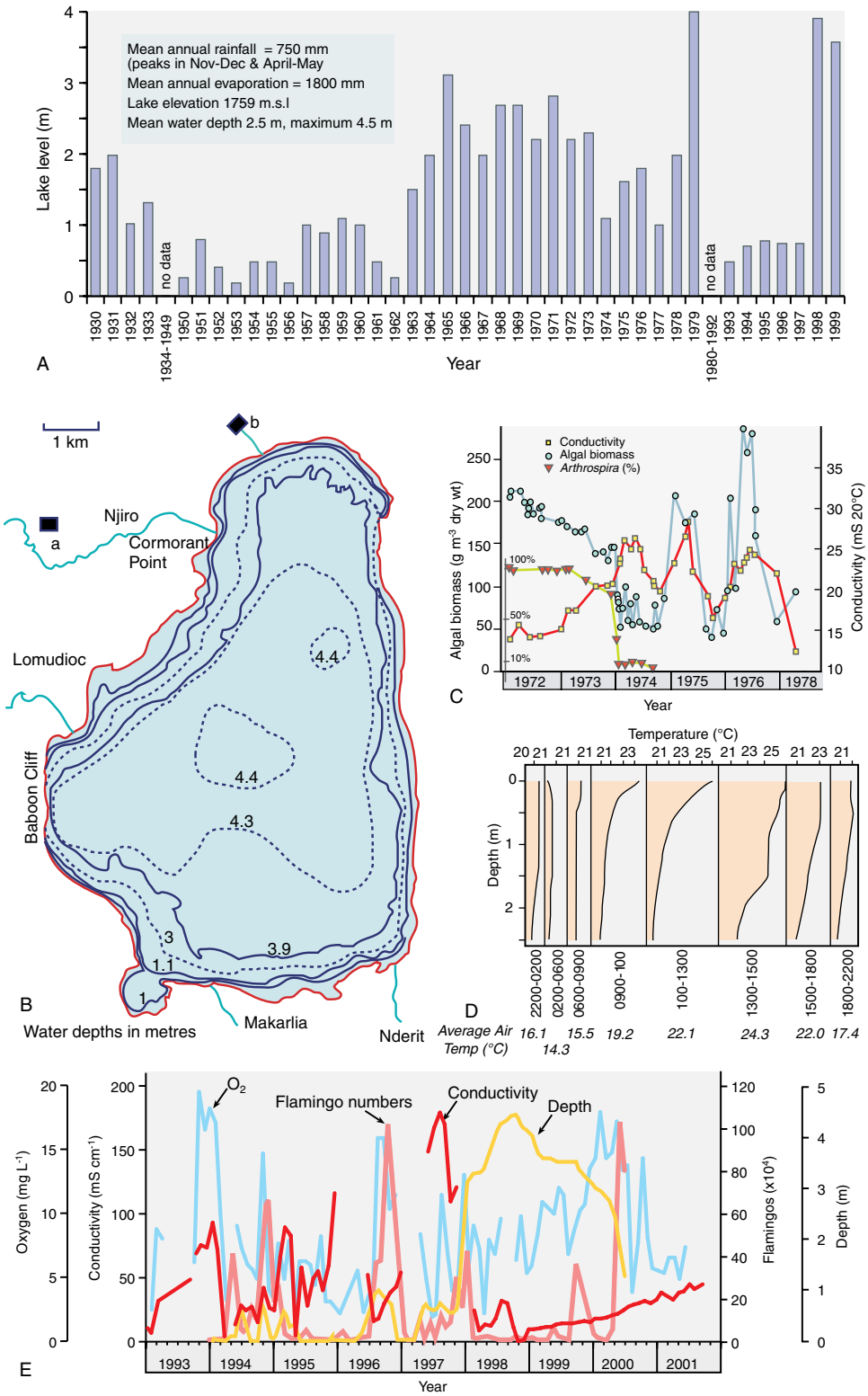
The feeding style of the birds is to wade through the shallows, with heads upside down and beaks waving side to side across the water surface. Flamingo beaks have evolved to skim plankton from saline to brackish surface waters and are equipped with a filter-feeding system unlike any other bird on Earth and more akin to feeding apparatus of the krill-ingesting Great Whales. Flamingos siphon the lake water through the beak filters to trap *A. platensis* and other plankton by swinging their upside-down heads from side to side and using their fat tongues to swish water through their beaks. They can filter as many as 20 beak-fulls of plankton-rich water in a second. Spacings of the filters in the beak of the greater flamingo are wider than those in the beaks of the lesser flamingo. Greater flamingos feed mostly on zooplankton, while lesser flamingos feed almost solely on *Spirulina*, thus in any saline lake where the two species co-exist they do not compete for the same food source.

Arthrospira platensis provides high levels of the red pigment phycoerythrin to the food chain and it accumulates in flamingo feathers to give the birds their world famous colouration (hence the "flamingo connection"). This is the same pigment that turns waters red in Lake Natron and Lake Magadi, but in this case it comes mostly from the halophilic archaea. Lesser flamingos, with their narrower spacings of beak filters, survive solely on *Arthrospira* and so have a more intense pink colour than greater flamingos, a species that sits higher in the lake food chain and get its feather colour second-hand from the lake zooplankton.

As well as possessing very high levels of phycoerythrin in its cytoplasm, *Spirulina* is also unusual among the cyanobacteria in its unusually high protein content. In Lake Chad and in some saline lakes in Mexico it accumulates as a lake edge scum that is harvested by the local people and used to make nutritious biscuits. In the 16th century it was mentioned in the diary of one of Cortez's soldiers who described how the Aztecs sold hard flat cakes made from the dried remains of *Arthrospira*. The Aztec word for it was Tecuitlatl, which translates literally as "excrement of stones." The lack of cellulose in the *A. platensis* cell wall means it is a source of plant protein readily absorbed by the human gut, making it a potentially harvestable food source in water bodies in regions of desertification and it has become a popular alternative protein source in the developed world.

In 1972, Lake Nakuru waters held a surface biomass of 270 g m^{-3} and an average biomass of 194 g m^{-3} but, as in most hypersaline ecosystems, Nakuru's organic production rate varies drastically from year to year as water conditions fluctuate (Fig. 15C; Vareschi, 1978). *Arthrospira platensis* was in a long-lasting bloom in 1971–1973, and accounted for 80–100% of the large phytoplankton biomass in those years. In 1974, however, it almost disappeared from the lake and was replaced by coccoid cyanobacteria such as *Anabaenopsis sp., Chroococcus sp.* and by diatoms, all species that dealt better with elevated salinities. This change in biota was tied to a serious reduction in biomass, which in 1974 was down to 71 g m^{-3} in surface waters, and averaged 137 g m^{-3} in the total water mass. As a result, the flamingo population in the lake declined from 1 million to several thousands (Vareschi, 1978).

The lower salinity limit for *Arthrospira platensis* growth is ~5‰ and in terms of water conductivity it does best in the range 10–50 mS cm^{-1}. The driving mechanism for the change in biomass in Lake Nakuru in the mid-1970s was not clearly documented. It was thought to be related to increased salinity and lowering of lake levels, along with


Mean annual rainfall = 750 mm
(peaks in Nov-Dec & April-May
Mean annual evaporation = 1800 mm
Lake elevation 1759 m.s.l
Mean water depth 2.5 m, maximum 4.5 m
Lake level (m)
no data
1934-1949
1980-1992
Year
A
1 km
b
a
Njiro
Cormorant
Point
Lomudioc
Baboon Cliff
4.4
4.4
4.3
3
3.9
1.1
1
Makarlia
Nderit
B
Water depths in metres
Conductivity
Algal biomass
Arthrospira (%)
Algal biomass (g m3 dry wt)
Conductivity (mS 20°C)
100%
50%
10%
C
Temperature (°C)
Depth (m)
2200-0200
0200-0600
0600-0900
0900-100
100-1300
1300-1500
1500-1800
1800-2200
Average Air Temp (°C)
16.1
14.3
15.5
19.2
22.1
24.3
22.0
17.4
D
O2
Flamingo numbers
Conductivity
Depth
Oxygen (mg L-1)
Conductivity (mS cm-1)
Flamingos (x10³)
Depth (m)
E
Year

the growth and bottom shading by planktonic algal species that were better adapted to higher salinity. These better adapted were present in lesser volumes and with lower per cell protein cells (Fig. 15C; Vareschi, 1978).

During the mid- to late 1970s and in the 1980s Lake Nakuru returned from a relatively saline dry phase to more typical annual schizohaline oscillations in water level and salinity (Fig. 15A). Seasonally, in the 1980s, the *A. platensis* and flamingo populations returned to impressive numbers. From the 1990s more reliable long-term data on physical lake condition and flamingo numbers have being compiled (Fig. 15E). In 1995 and 1998 feeding flamingo populations in Lake Nakuru were once again at very low levels and the remaining population was stressed (Fig. 15E). In 1998, unlike 1974, the stress was related to freshening driving a decrease in *A. platensis* biomass, not increased salinity and desiccation. This freshening of the lake waters favoured a cyanobacterial assemblage that also produced toxins (see Cyanobacterial toxins in Glossary). In the preceding bountiful year (1996), the *A. platensis*-dominated biomass had bloomed at times when salinities were favourable, and died back at times of elevated salinities and lake desiccation, as in 1974. By 2000, the somewhat lower salinity cycles had once again increased, making surface waters suitable for another widespread *A. platensis* bloom and the associated return of high numbers of feeding flamingos.

It seems that breeding flamingos come to Lake Nakuru to feed in large numbers when there is water in the lake with appropriate salinity and nutrient levels to facilitate an *A. platensis* bloom. In some years when heavy rains occur, lake levels rise significantly and the lake waters, although perennial, stay in the lower salinity tolerance range for *A. platensis*, as in the El Niño period between October 1997 and April 1998. Once lake levels start to fall, salinities and rates of salinity change return to higher levels, then water conditions once again become appropriate for *A. platensis*. Environmental stress on the flamingos also comes with drier periods that elevate lake salinities into the upper end of *A. platensis* tolerance. Ongoing drought ultimately leads to lake desiccation and the complete loss of the food supply in the lake.

One of the reasons why Lake Nakuru is so suitable for cyanobacterial growth at times of *A. platensis* bloom, is the maintenance of suitable temperatures and associated oxygenation in the upper water mass. The lake develops a remarkable daily thermocline in the upper 1.5 m of the column that dissipates each day via wind mixing in the late afternoon, and so recycles nutrients back to the oxygenated surface waters to facilitate the ongoing plankton bloom of the next diurnal cycle (Fig. 15D).

Some environmentalists have argued in the popular press that lower numbers of flamingos in Lake Nakuru, such as occurred in 1995 when more than 50,000 birds died, are an indicator of: uncontrolled forest clearance; an uncontrolled increase in sewerage encouraging eutrophication; an increase in heavy metals from increasing industrial pollutants in the lake; and general stress on the bird population from tourists and the drastic increase in local human population centered on the town of Nakuru (now the third largest in Kenya). Numbers of people in the town, which is the main city in the rift valley, have grown by an average of 10% every decade for the past 30 years.

Like many environmental doomsday arguments, the above are more based on opinionated prediction than on scientific fact. Rise and fall of lake levels, drastic changes in salinity, a periodically stressed biota, and a lack of predictability in water characteristics are endemic to saline ecosystems (cycles of "famine or feast"). Oscillations in one or more of these factors are not necessarily

Fig. 15. Physical and chemical characteristics, algal biomass and flamingo numbers of Lake Nakuru, Kenya. (A) Lake levels from 1930 to 1999. Data are not sufficiently detailed to record times of complete lake drying or drought, and there are also substantial times when no data were collected/published (1934–1949 and 1978–1992). (B) Lake bathymetry (December 1979) and strand-zone changes. Solid isopleths are actual shorelines at different lake levels over a 20-year period; from margin to centre these are: December 1979; January 1969; January 1967; and January 1961. Dashed isopleths are based on soundings taken in December, 1971. Two sewage plants are located at a and b. (C) Trends of algal biomass and conductivity of lake water during 1972–1978. The percent contribution of *Arthrospira platensis* (formerly *Spirulina platensis*) to the total algal biomass is also shown. (D) Mean water temperature profiles at different times of day from 1972–1973. (A–D) after Vareschi (1982). (E) Monitored water depths, conductivities, oxygen levels and flamingo numbers at Lake Nakuru for the period 1993 to mid-2001. Water depth and flamingo data only available from 1994 to mid-2000 (data are digitized and replotted to a common time scale from a number of figures and pdf reports downloaded from http://www.worldlakes.org on 2 February 2004).

anthropogenically induced. For example, the amounts of most heavy metals (Cd, Cr, Cu, Hg, Ni, Pb, Zn) in the lake sediments were found to be in the typical range of metals in natural lakes worldwide (Svengren, 2002). The exception was cadmium, which is elevated in the lake sediment and could perhaps be assigned to anthropogenic pollution. All other metals are present at low levels, especially if one considers that Lake Nakuru lies within a labile catchment where bedrock is an active volcanogenic-magmatic terrane. At the present time, sufficient base a scientific data are not yet available in Lake Nakuru, and so scientifically accurate determinations cannot be made of the relative effects of humanity verses natural baseline environmental stresses on bird numbers in this schizohaline ecosystem.

Nearby lakes Magadi and Natron have extensive trona platforms covered with brine sheets that are characterized by short periods of high productivity and times of bright red waters. In this higher salinity ecosystem, the dominant producers of the brine colour are haloalkaliphilic bacteria and archaea. Archaeal species belonging to the genera *Natronococcus, Natronobacterium, Natrialba, Halorubrum, Natronorubrum and Natronomonas*, all occur in the lakes. Lake centre brines when this biota flourishes are at trona/halite saturation, with a pH ~12. Stratified moat waters around the trona platform edge are at times almost as chemically extreme, and the moat bottom sediments are made up of aragonite/dolomite/detrital laminites that can preserve elevated levels of organics (~6–8%). As well as algae and cyanobacteria, Lake Magadi and Natron moat waters also harbour a varied anaerobic bacterial community including cellulolytic, proteolytic, saccharolytic, and homoacetogenic bacteria (Shiba & Horikoshi, 1988; Zhilina & Zavarzin, 1994; Zhilina *et al.*, 1996). When the homoacetogen *Natroniella acetigena* was isolated from Lake Magadi its pH growth optimum was found to be 9.8–10.0, and it continued to grow in waters with pH up to 10.7, making it an exemplary alkaphile (Zhilina *et al.*, 1996).

Regionally, salinities in the East Africa rift-valley lakes range from around 5‰ total salts (w/v) in the more northerly lakes (Bogoria, Nakuru, Elmenteita, and Sonachi) to trona and halite saturation (>200‰) in lakes to the south (Lakes Magadi and Natron). Yet across this salinity range, a combination of high ambient temperature, high light intensity and a continuous resupply of CO_2, makes these soda lakes amongst the highest in the world in terms of their seasonal planktonic biomass (Grant *et al.*, 1999) and also places them among the world's most productive ecosystems (Melack & Kilham, 1974). As demonstrated above, the less saline soda lakes are dominated by periodic blooms of cyanobacteria, especially *Arthrospira platensis*, while the hypersaline lakes, such as Magadi, can on occasion support blooms of both cyanobacteria and alkaphilic phototrophic bacteria belonging to the genera *Ectothiorhodospira* and *Halorhodospira* (Jones *et al.*, 1998).

The halotolerant and halophilic biota living in the layered water columns of these soda lakes constitute small-scale "famine or feast" ecosystems, which at times of "feast" are far more productive than zones of marine upwelling (Fig. 16A). A general observation of short periods of enhanced organic productivity between somewhat less and somewhat more saline episodes in schizohaline lake waters worldwide, reflects the general ecological principle that increased environmental stress favours the survival of a few well-adapted halotolerant species, to the detriment of others better suited to life in a less saline environment (see inset in Fig. 16A). Ultimately, abiogenic stresses associated with more elevated salinity means all life, including the halophiles, ceases to function.

The same general principle that schizohaline ecosystems encourage dominance by a few better-adapted species can be clearly seen in the decrease in invertebrate species (grazers and predators) with increasing salinity in the carbonate lakes of the Coorong of Southern Australia, where only brine shrimp remain alive in waters with salinities in excess of 200‰ (Fig. 16B). It reflects a general trend of decreasing faunal biomass with increasing salinity (Fig. 16C). A decreased level of biomass in a mesohaline system does not necessarily mean less source rock potential in the resulting sediments. Preservation levels of organic matter and suitability of the protokerogen (type I to type III) depends on what biotal contributors constitute the biomass preserved in the sediment.

Examples of "famine or feast" productivity have so far focused on continental salt lakes. Similar enhancements of primary productivity can occur in modern coastal salinas during episodes of periodic freshening as blooms of haloxene and halotolerant microbes (oxygenic photosynthesizers) take place across formerly exposed mats. For example, a study of biolaminites collected from a modern salina (Storr's Lake in the Bahamas) showed that a reduction in brine salinity from 90 to 45‰

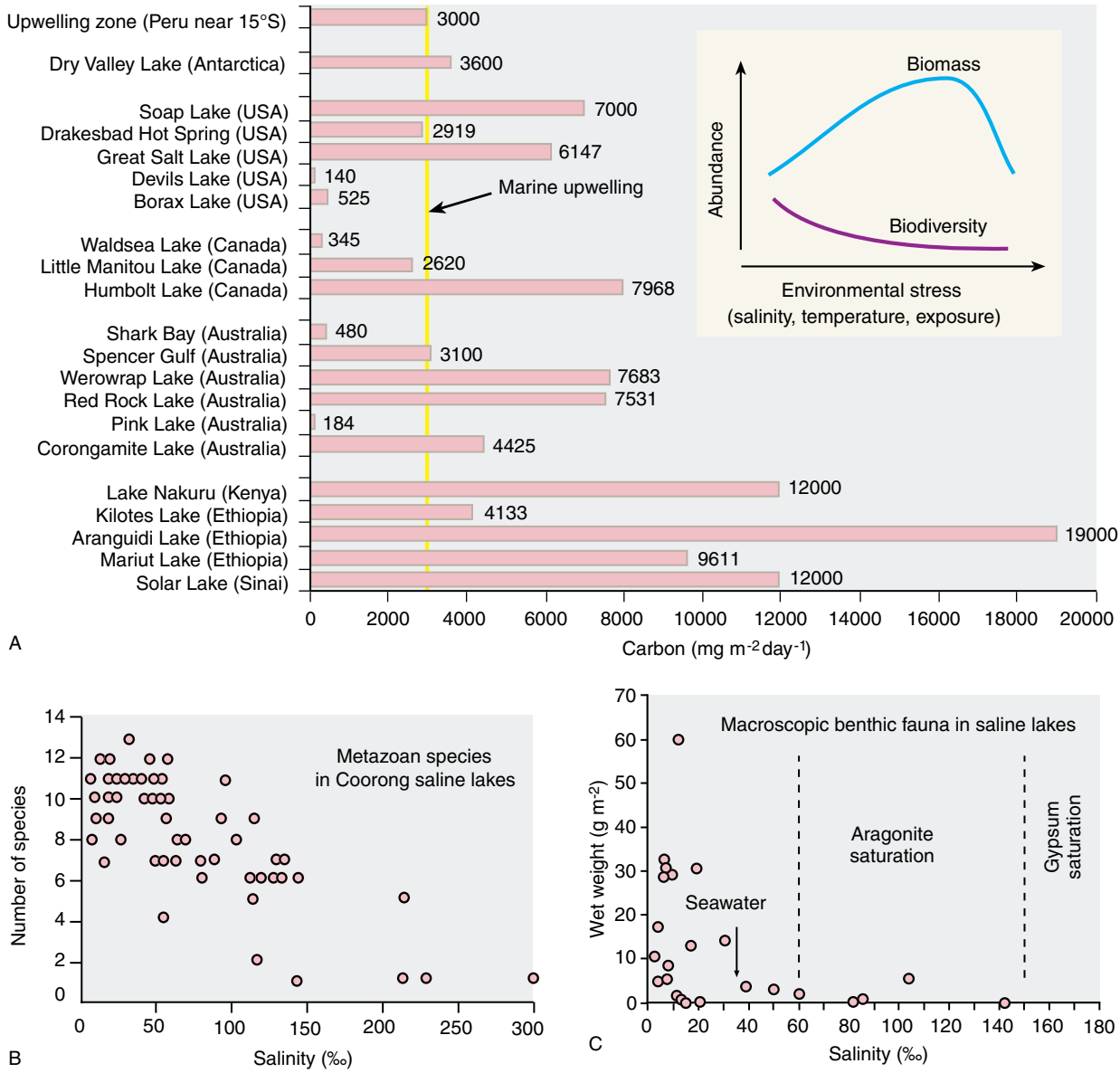


Fig. 16. Productivity and biodiversity in saline ecosystems. (A) Organic productivity in various saline ecosystems. Typical marine upwelling zone (offshore Peru) is ~2000–3000 mg C m^{-2} day^{-1} (yellow line), open-marine waters average 20 mg C m^{-2} day^{-1} and coastal waters 40–50 mg C m^{-2} day^{-1}. Preservation is more important than production rate in terms of source potential. Compiled from sources listed in Warren (1986, 2006). (B) The effect of increasing salinity on metazoan species diversity in the saline lakes of the Coorong region, South Australia (after de Decker & Geddes, 1980). (C) Standing crop (g m^{-2}) of the macroscopic benthic fauna in selected athalassic (non-marine) saline lakes of the world (after Hammer, 1986).

significantly enhanced CO_2 and N_2 fixation rates, but additions of inorganic nutrients and dissolved organic carbons did not show any significantly enhanced rates compared with the salinity controls (Pinckney *et al.*, 1995). That is, dissolved organic carbon/dissolved organic nitrogen uptake was not influenced over the entire range of salinities (45–90‰) seen in this study of mesohaline mat growth.

In other words, abiotic stress, induced by hypersaline conditions in the Bahamian lagoons, created lower productivity in the saline-tolerant microbial mats, even when nutrient levels were high. Once the osmotic stress on the biota was relieved by a lowering of salinity, mats underwent enhanced primary production and nitrogen fixation as haloxene producers could once again photosynthesize. Changing nutrient levels were far less significant

than changing salinity levels as controls on mat productivity in this stressed setting. Salinity-induced stress in these halotolerant microbial mats outweighs typical limiting factors regulating primary production in phototrophic communities at the lower salinities that typify marine and brackish waters.

Organic production in saline waters

When surface water salinities are suitable, evaporite basins have some of the highest measured rates of organic productivity in the world (Fig. 16A; Warren, 1986). Times of elevated primary production ("feast") in density-stratified hypersaline brine lakes and evaporitic seaways appear to be controlled by two factors: (1) the ephemeral presence of a less saline surface water; and (2) a supply of nutrients (nitrate/ammonia and phosphate) from the lower hypersaline water mass. The biota contributing the organics that ultimately reach the bottom sediments to form organic-rich laminae (and so control their future biomarker signature) are largely dependent on the timing of photosynthetic activity. Perennial saline lakes subject to an annual freshening of surface waters will deposit varved carbonates (e.g. Lake Tanganyika with up to 7–11% TOC in deep bottom laminites; Cohen, 1989), while other saline lakes and seaways with less predictable stratification may form similar carbonate laminites, but the organic layering may not be annual, and the resulting organic biomarkers contain elevated levels of isoprenoids due to the greater contribution from the haloarchaea. Microbial mats in some shallower saline lakes may be subject to short periods of photosynthetic oxygenation and even subaerial exposure, yet still preserve elevated levels of hydrogen-prone organics (Warren, 1986).

Once brine moves into the gypsum precipitation field and beyond, the amount of organics accumulating on the bottom is diluted by inherently rapid rates of crystal precipitation and accumulation, especially if the bottom brine is photosynthetically oxygenated by its microbial community. Hypertrophication, in combination with shading by pelagic crystallites, can overwhelm the delivery of oxygen to the bottom, as in Solar Lake and in Lake Hayward in the late 1980s. Evaporitic systems subject to longer-term eutrophication can facilitate high levels of pelagic organic delivery to bottom sediments, even beneath shallow penesaline waters (Horsfield *et al.*, 1994; Warren 1986). In a study of eutrophication in man-made saltfields, Javor (2000) found that in shallow gypsum and pre-gypsum ponds there was an interesting inverse relationship between the level of nutrients (nitrates and phosphates) in the brine column and the development of microbial mats on the water covered pan floor. In a high-nutrient brine system (eutrophic or "well-nourished pan") the algae and bacteria flourished as planktonic forms and the biomass buildup in the upper parts of the brine column tended to shade the sediment surface. There was little or no development of an oxygenated microbial mat and bottom waters were dysaerobic to anoxic. In a low nutrient system (oligotrophic or "poorly-nourished pan") there was little or no planktonic development of algae or bacteria and microbial mats tended to flourish on the perennial pond floor. Benthic mats formed from salinities of 50‰ to gypsum saturation in the poorly-nourished pans. In pans at even lower salinities the benthic mats were destroyed by the feeding activities of invertebrates and fish.

Preservation of microbial mats into early burial in hypersaline systems depends, in large part, on the efficiency of nutrient recycling by the bacterial and archaeal decomposers that making up the underside of the living part of a mat. Even if nitrogen and phosphorus levels are low in the overlying brine, there may be sufficient recycling of nutrients within the mat community to allow the benthic mat to continue to grow. Javor (1989) found that once a gypsum crust becomes well established over the floor of a crystallizer pond, there was little recycling of nutrients from beneath the crust to the uppermost photosynthesizers, and from this point downstream in the crystallizer pans, nitrate and phosphate nutrients were concentrated by evaporation and recycled into the biomass living in the brine column. In oligotrophic gypsum ponds the gypsum crust is stable and the bottom waters are oxygenated. In eutrophic gypsum ponds at the same salinities, the bottom waters become anoxic and sulphate-reducing bacteria flourish. In these systems, gypsum dissolves and a black slimy organic-rich carbonate/detrital mud (a potential source rock in ancient counterparts) covers the bottom and contains no more than a few embayed and dissolved gypsum remnants. If portions of this slimy bottom become suspended and are flushed into the next stage of crystallizer they create a problem in the final salt product known as "black spot".

The difference in organic levels between oligotrophic systems such as Lake Hayward and

perennial eutrophic systems like Solar Lake probably explains why the latter retains much higher levels of hydrogen-prone organic material in its preserved bottom sediments (Fig. 5). Javor's work also demonstrated that as higher salinity brines tend to concentrate nutrients, they will supply these nutrients at times or at interfaces where supersaline waters in a natural schizohaline system are subject to periodic freshening or mixing.

Proximity of organic-rich mesohaline laminites to bedded evaporites in ancient successions has led some geologists to postulate that bedded salts are potentially also organic-rich sediments, with the same level of source potential as mesohaline carbonates. This is not borne out by TOC analysis of evaporitic salts; total organic matter levels in ancient $CaSO_4$ and NaCl lithologies tend to be normal or depleted (Katz *et al.*, 1987), although levels of dissolved organic matter and volatile fatty acids may be high in the entrained brine inclusions (Hite & Anders, 1991). The typically low organic matter levels in bedded gypsum and halite may reflect the higher depositional rates of evaporitic salts when compared with evaporitic carbonates (dilution effect). Only in settings where bottom waters are anoxic in the gypsum stage can the build up of H_2S from sulphate reduction become high enough to remove $CaSO_4$ minerals and so allow preservation of elevated levels of partially degraded organics (as in Solar Lake today).

That organic enrichment mostly occurs in the mesohaline carbonate stage in an evaporite basin is clearly seen in organic contents of the evaporitic marls and salts of the Oligocene Mulhouse Basin (Fig. 17; Hofmann *et al.*, 1993a, b). This deposit is one of a few ancient evaporites where organic chemistry has been studied in a logical and detailed fashion. Organic matter occurs mostly in finely laminated carbonate marls (varves), which can contain up to 7% TOC, anhydrite beds contain 0.08–0.78% TOC, halite beds 0.01–0.25% TOC and the potash beds <0.1% TOC. The marls are characterized by thin, continuous bedding parallel laminae that are not disturbed by any bioturbation. They are interpreted as seasonal varves with the clay and carbonate forming alternate layers in the couplet (Fig. 17, inset). In spring and summer the increased temperature in surface waters favoured precipitation of micritic carbonate, in autumn and winter the phytoplankton died back and rainfall/runoff transported siliciclastic debris into the basin. On the basis that the laminar couplets are varves, Hofmann *et al.* (1993a) were able to plot the relationship between sedimentation rate and TOC content in the marls (Fig. 17). Marls deposited during times of low sedimentation tend to be organic-rich, while marls deposited with higher sedimentation rates tend to contain lower amounts of organics. They extrapolated that the even lower levels of organics in the more saline salt beds (anhydrite and halite) indicate greater dilution because of the inherently higher sedimentation rates of halite and gypsum compared to mesohaline carbonate.

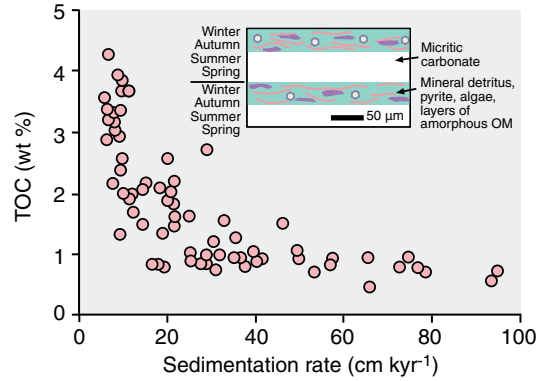


Fig. 17. Sedimentation rate versus percent of total organic carbon (TOC) in laminite marls from the Oligocene evaporites of the Mulhouse Basin, France. Inset shows the scale and mineral/organic distribution in the laminae (varve couplets) of the sampled intervals (after Hofmann *et al.*, 1993b).

Salinity-induced environmental stress ("famine or feast") facilitates organic preservation

Organic matter in modern saline systems tend to accumulate in bottom sediments beneath density-stratified saline water and sediment columns in evaporitic settings where layered hydrologies are subject to oscillations in salinity and brine level. Organic matter is not produced at a constant rate in such systems, rather, it is produced as pulses by a halotolerant community in response to relatively short times when less stressful conditions occur in the upper part of the layered hydrology (Fig. 18A). This happens when an upper less-saline water mass forms on top of nutrient-rich brines or within wet mudflats when waters in and on top of the uppermost few millimetres of any microbial mat freshen. The resulting bloom (a time of "feasting") by halotolerant algae and cyanobacteria is a time characterized by very high levels of organic productivity. In mesohaline waters where light penetrates to the bottom, the organic-producing

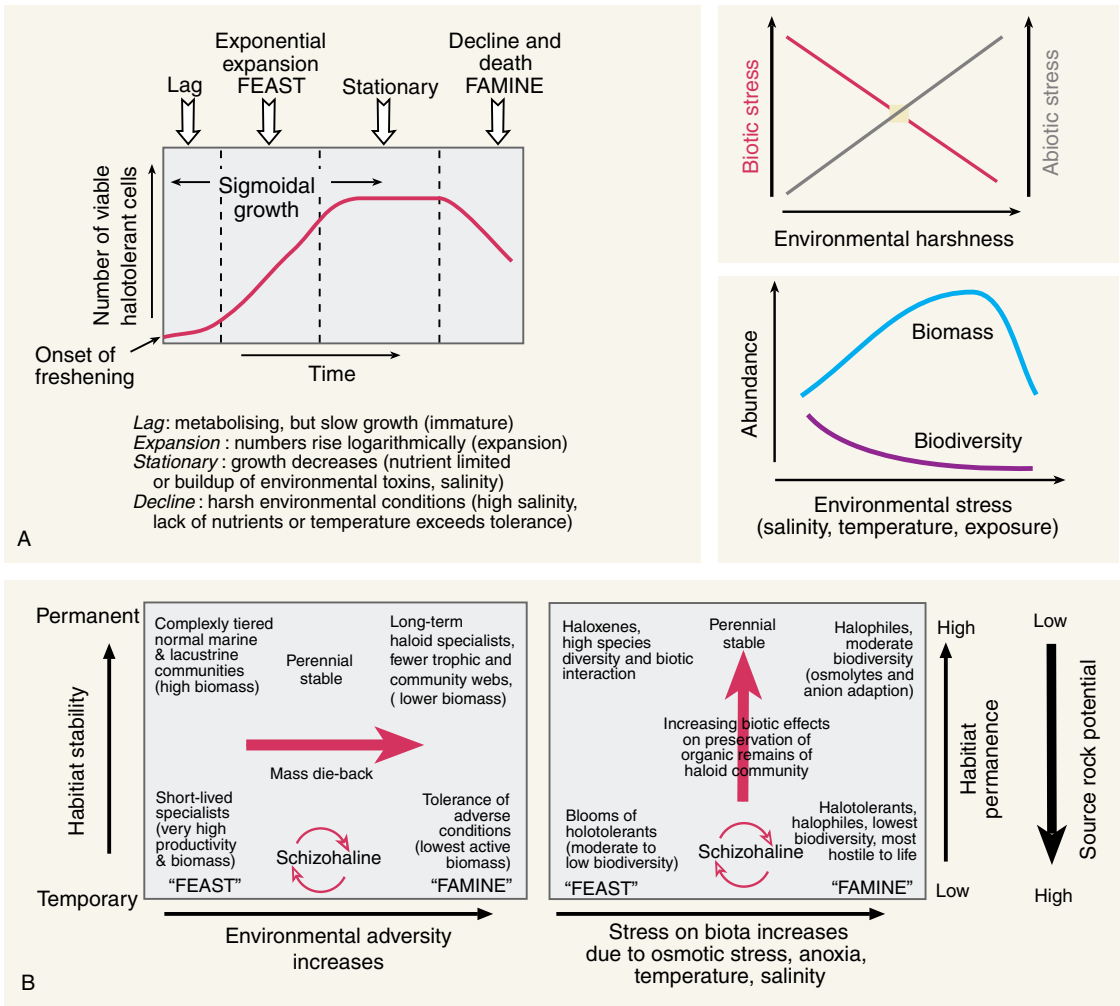


Fig. 18. Life in saline systems. (A) General ecological principles in stressed saline ecosystems. Sigmoidal growth curve of life moving into a newly created niche (as created by a freshening event setting up a layered brine). As environmental harshness increases due to abiogenic stress factors (such as increasing salinity, osmotic stress and temperature) the level of biogenic stress (predation or grazing decreases, allowing a few well-adapted species to flourish, leading to a decrease in biodiversity and a short-term increase in biomass. (B) Schematic summary of the inter-relationships between habitat stability, environmental stress or adversity, biodegradation, anoxia and source rock potential in an evaporite basin, showing why schizohaline environmentally stressed mesohaline systems tend to favour the accumulation of organic matter in bottom sediments.

layer is generally the upper algal and bacterial portion of benthic laminated microbialites (typically characterized by elevated numbers of cyanobacteria). In stratified brine columns, the typical producers are the planktonic algal or cyanobacterial community inhabiting the upper water mass. Halotolerant autotrophic microbial communities, living off the remains of this plankton, float midwater at the halocline of the density-stratified brine columns. Similar aerobic decomposers can also constitute bottom-layer communities in zones of oxygenated oligotrophic waters.

Short pulses of extremely high organic productivity during times of freshened mesohaline surface waters in-turn create a high volume of organic detritus settling through the water column and/or construction of benthic microbial mats. Then, with the end of the freshening event, the ongoing intensely arid climate that characterizes evaporitic depressions means that salinities, temperatures and osmotic stresses increase rapidly in the previously freshened water mass. This leads to a time of mass die-off, in the once flourishing mesohaline community ("famine;" Fig. 18B). First, these

increasingly salty waters can no longer support haloxene forms. Then halotolerant life dies back and finally, by the halite precipitation stage, only a few halophilic archaea and bacteria remain in the brine column (typically acting as heterotrophs and fermenters). Repeated pulses of organic matter created during a freshening event in a stratified brine column thus create laminated bottom sediment.

Hydrogen-rich algal and eubacterial debris is best preserved within sediments where pore waters are anoxic and remain so until the resulting kerogen is sufficiently buried for it to generate liquid and gaseous hydrocarbons (Demaison & Moore, 1980). Thus the preservation of organics with long-chain hydrocarbons intact is most likely in settings characterized by long-term anoxia (less efficient decomposers). This tends to occur beneath stratified eutrophic saline brine columns with a permanent anoxic mesohaline bottom water mass and a transiently freshened upper water mass. Preservation is also possible in benthic mats in shallow oligotrophic systems with permanently hypersaline pore waters, but the propensity for periodic bottom oxygenation means preservation potential of oil-prone mats is less likely in this setting, as is also the case in mats of the strandzone.

Increasing rates of mineral precipitation at higher salinities means levels of hydrogen-prone organics are highest in sediments deposited in schizohaline waters that remain in the mesohaline field. Once ambient salinities pass into the penesaline and supersaline, the proportion of organics in the sediment becomes insignificant as it is rapidly diluted by large volumes of gypsum and halite (or trona and glauberite in some continental penesaline/supersaline waters).

Feast and famine cycles are a biotal response to environmental salinity conditions that at first are eminently suitable and then increasingly adverse to life. It reflects the typical biological response to rapid niche creation and expansion as the freshened water layer sets up in the evaporitic depression, and is known as the sigmoidal growth response (Fig. 18A). Freshening of surface waters creates a vacant ecological niche into which microbial life rapidly expands, flourishes and then once more dies back as drying or brine concentration shrinks suitable niche space.

Long-term stability in any ecosystem leads to domination by "specialist" species that are well adapted, diverse and efficient in terms of energy flow-nutrient utilization (Fig. 18B). This biodiverse community takes up and recycles carbon very efficiently through the system and the potential for large volumes of carbon passing into the burial realm is low and hence source potential is also low (a good example in the marine realm is a tropical coralgal reef).

In contrast, a schizohaline system is one defined by high habitat instability, its lack of habitat permanence encourages opportunistic lifestyles (cycles of "famine or feast"). Opportunist species expand rapidly into any suitable niche space, but then just as quickly die back or encyst as conditions become adverse. Such systems are characterised by high biomass pulses and low species diversity, leading to pulses of organics accumulating in the evaporitic depression, with the remains likely to be buried and "pickled" beneath anoxic bottom brines and pore waters, giving such systems a higher source rock potential (Fig. 18B).

Some hypersaline settings are intermediates in that their waters are constantly hypersaline, stressful to most life, but suitable to a few well-adapted species. These regions are usually populated by a few very specialized species (e.g. "high-salt-in" halophiles) that can survive and flourish in conditions where most life dies. They photosynthesize and metabolize successfully in these hypersaline conditions (often for example living near haloclines), but do so at rates that are much slower than the growth rates attained by halotolerant "opportunists" at times of "feast." The long-term cycling of organic materials means bottom sediment layers tend to have lower levels of entrained organics preserved compared to the schizohaline-mesohaline.

To take an understanding of community and controls from the modern into ancient saline systems, it is necessary to account for changes in both scale and diversity when comparing the style and setting of "famine or feast" in modern saline settings to those of the past. Put simply, there are no modern same-scale analogues for ancient marine-fed evaporite depressions, and so there are no modern same-scale marine-fed evaporitic source rocks (Warren 2006, 2010).

ANCIENT EVAPORITIC SOURCE ROCKS

The common theme to deposition of all prolific source rocks, both evaporitic and non-evaporitic, is that they require anoxic conditions to accumulate and preserve their organics (Demaison &

Moore, 1980). This in-turn requires some way of restricting the influx of oxygenated waters and is usually accomplished by thermal or density stratification of a water body, in a setting where planktonic-producers flourish periodically in the upper water mass. This is why so many ancient evaporitic settings are also places where organics tend to accumulate. By definition, evaporites require restricted inflow conditions to accumulate, they are also typically areas of density-stratified waters with long-term elevated salinities in the lower denser water mass. Levels of dissolved gases are negligible to non-existent in the lower brine body, as it does not easily exchange with the atmosphere, so encouraging long-term bottom anoxia.

This does not mean that all of the world's anoxia-associated source rocks were deposited in evaporitic settings, only that the restricted conditions that favour the accumulation of evaporites are in their early stages similar to conditions that favour the accumulation of organics. In arid climates any minor changes in inflow conditions can easily force a transition from one into the other. Hence the common association of source rocks with the freshened, typically early phases of the onset of evaporitic sedimentation in many modern and ancient lacustrine settings (Table 5). In the marine realm, the same need for tectonic or eustatic restriction to create basins suitable for source rock accumulations (intrashelf, circular or linear sags) also explains why, if further restriction and isolation from surface connections to the oceans ensue, the same regions are easily covered by a sequence of salts (Fig. 19).

Tectonic and eustatic styles in ancient evaporitic basins

Almost all of the information that has been gathered and analyzed so far in this paper comes from organic accumulations in saline Quaternary lacustrine and marine-margin settings. Likewise, all the largest and thickest examples of Quaternary sabkhas, saline pans and salinas are continental deposits (Warren, 2006). Quaternary saline systems only define same-scale analogs for ancient continental lacustrine deposition and are not same-scale analogues for ancient marine-fed epeiric and basin-centre salt basins, or their entrained source rocks (Fig. 19; Warren 2006, 2010). Yet compared to lacustrine sediments, these ancient marine-associated deposits entrain and seal far greater volumes of evaporitic source rocks (Table 5).

Most ancient marine-fed evaporite deposits are one or two orders of magnitude larger than today's marine-fed hypersaline systems and accumulated in huge marine-seepage fed sub-sea-level tectonic depressions with no surface connection to the ocean (Fig. 19). Well-documented source rock-entraining ancient basinwide evaporite deposits include the Jurassic Hith, Permian Zechstein and Miocene Messinian evaporites, but none have a same-scale modern counterpart. Likewise, no widespread marine-fed platform evaporites have accumulated since the Eocene. The Mediterranean Messinian salts (~5.5 Ma) are the youngest known basinwide evaporite. Well-documented marine-fed platform evaporites include the evaporite-capped cycles of the Jurassic Arab Formation in Saudi Arabia and the United Arab Emirates, the Permian Khuff Formation in the same region, and the evaporite-capped Permian backreef strata of Guadalupian age in West Texas and New Mexico.

Although platform and basinwide evaporites may have no Quaternary counterpart in terms of scale or thickness, they can be interpreted using process models that are combinations of the hydrologies of Quaternary sabkhas, saline pans and salinas. Accumulations of thick evaporite accumulations (continental or marine) and associated mesohaline stages require a stable long-term brine curtain (~100 kyr–1 Myr) to accumulate to substantial thicknesses and lateral extents (Warren, 2003, 2006). The hydrological position of the active top of an aggrading brine curtain, with respect to the evaporite depositional surface, in both platform and basinwide settings, defines the dominant textural signature of the resulting salt sequence (saline-pan, evaporitic mudflat/sabkha, saltern, deeper slope and basin).

High amplitude, high-frequency 4th-order sea-level oscillations of the current "icehouse" climate do not allow the set up of stable brine curtains behind laterally-continuous seepage shoals in present-day carbonate platforms, and so there are no Neogene examples of platform evaporites with stable intrashelf depressions. Platform evaporites require greenhouse eustacy to form. Nor are there suitable sub-sea-level rift-induced intracratonic sags or soft-collision belts in arid marine-fed settings where conditions are suitable for the creation of basinwide marine drawdown deposits (Warren, 2006).

The need for sub-sea-level tectonically-induced basins explains why times of worldwide continent-continent collision followed by continental

Table 5. Characteristics and settings of evaporitic source rocks. Basin styles: 1 = basin centre; 2 = intrashelf; 3 = lacustrine. See Warren (2006) for further detail on the significance of different basin styles

Formation/Group locality and age	Basin Style	Characteristics and depositional setting	Reference
Messinian carbonates Lorca Basin, Spain Upper Miocene	1a Basinwide evaporite marginal basin	Organic-rich laminated mudstones deposited in pre-evaporitic mesohaline marginal basins with density- and salinity-stratified brine columns. The basin underwent sporadic phases of circulatory restriction with marked production and preservation of organic matter, culminating in evaporative sedimentation (latest Miocene). As the water in this basin evolved toward evaporative conditions, a number of organic-rich depositional phases (>25 wt% TOC) occurred. During the early parts of these phases, the upper water was nutrient rich and comparatively normal marine, and the bottom water was anoxic and more saline. This was followed by rising salinities in the surface waters, holomixis and short phases of evaporite formation.	Benali *et al.*, 1995 Russell *et al.*, 1997 Rouchy *et al.*, 1998
Gessoso-Solfifera Formation, Sicily Upper Miocene (Messinian)	1a Basinwide evaporite marginal basin	Biomarker compositions from immature organic sulphur-rich marl samples from 10 of the 14 evaporite cycles in an Italian Messinian evaporitic basin (Vena del Gesso) indicate large variations in the composition of species in the water column (e.g. dinoflagellates, diatoms and other algae, cyanobacteria, methanogens, green sulphur bacteria and bacterivorous ciliates) and in contributions from the continent (i.e. land plants) within each marl bed and between marl beds. The marl beds were deposited within a stratified lagoon where anoxic conditions extended into the photic zone for much of the time.	Damste *et al.*, 1995 Keely *et al.*, 1995 Lugli *et al.*, 2007
Organic-rich marls, Rudeis, Kareem and Belayim Fms. Gulf of Suez Miocene	3 Rift basin continental to transitional marine	Inclusion studies show evaporitic environment of deposition (reducing conditions and high salinities), favoured oil-generating kerogen. Carbonate minerals and inclusions trapped in gypsum indicate possible mixing of marine water with a brine of restricted occurrence at the time source rocks were deposited.	Kholief & Barakat, 1986 Rouchy *et al.*, 1995 Barakat *et al.*, 1997 Alsharhan, 2003
Bresse and Valence salt basins, France Paleogene	3 Rift basin continental to transitional marine	Organic matter is mostly immature and occurs in intercalated non-halite beds. Type-III kerogen is tied to terrigenous deposition. Type-I kerogen is abundant in mesohaline evaporitic laminites of Valence basin. Type-II is more abundant in Bresse Basin. Organics accumulated beneath a perennially stratified brine column of up to tens of metres. Syndepositional dissolution of halite may have aided the accumulation of significant amounts of oil-prone organic matter in non-soluble brecciated residues.	Curial *et al.*, 1990

(*continued*)

Table 5. (*Continued*)

Formation/Group locality and age	Basin Style	Characteristics and depositional setting	Reference
Salt IV Formation, Mulhouse Salt Basin, Europe Lower Oligocene	3 Rift basin continental to transitional marine	Biomarker assemblages are dominated by acyclic isoprenoids, especially phytane ($0.13 < Pr/Ph < 0.52$), n -alkanes with specific distribution patterns, and steranes. Large differences in distribution indicate changes in paleoenvironment. The largest changes are in desmethyl- and methylsterane distributions and are probably linked to occasional reconnection of the stratified evaporite basin to the sea, leading to a dinoflagellate bloom in the upper waters of a density-stratified brine column.	Damste *et al.*, 1993 Hofmann *et al.*, 1993a, b Hollander *et al.*, 1993 Keely *et al.*, 1993
Eocene Qianjiang and Lower Eocene-Paleocene Xingouzhui Formations of Jiangling-Dangyang area, Jianghan Basin, Northwest China Eocene-Paleocene	3 Foreland flexure basins, mountain-front fault depressions	Anoxic evaporitic lacustrine source rocks generated most of the crude oils. High salinity and low Eh enhanced preservation of oil-prone organic matter and facilitated incorporation of sulphur. Anoxia and the unusual presence of abundant sulphate as gypsum resulted in microbial reduction of sulphate to sulfide and incorporation of this sulphur into the kerogen. Biomarkers in Qianjiang Formation show that some source rocks (Sha 13 well -1322 m) was deposited under more saline, lower Eh conditions than others) Ling 80 well - 1808 m). Sha 13 sample is more organic-rich (6.62 vs 1.27 wt% TOC), has a higher hydrogen index (794 vs 501 mg HC g^{-1} TOC) and faster reaction kinetics. Kerogen from the Sha 13 sample is Type I.	Jiang & Fowler, 1986 Huang & Shao, 1993 Peters *et al.*, 1996 Ritts *et al.*, 1999 Hanson *et al.*, 2001
Green River Formation, Wyoming and Utah Eocene	3 Foreland flexure basin from Laramide orogeny	Laminated organic mudstones and oil shales deposited in deeper anoxic bottom waters of a perennial saline and density-stratified alkaline lake. Gilsonite and tabbyite bitumens are associated with Parachute Creek Member, deposited during a major expansion and freshening of ancient Lake Uinta. Compound specific isotopic analyses of β-carotene and phytane ($\delta^{13}C = -32.6$ to $-32.1‰$) from these bitumens reflect input from primary photosynthetic producers such as cyanobacteria. Sterane $\delta^{13}C$ values (-34.5 to $-29.2‰$) reflect contributions from lacustrine algae, while extremely depleted $\delta^{13}C$ values for methylhopanes (-58.1 to $-61.5‰$) suggest input from methanotrophic bacteria/archaea. Variations in the $\delta^{13}C$ values of the α−β-hopanes (-51.4 to $37.7‰$) imply additional input from other bacterial sources. The wurtzilite bitumen generated from the saline facies of the Green River Formation was deposited during a later regression of Lake Uinta. Compound specific isotopic analyses of phytane ($\delta^{13}C = -30.1‰$) and steranes ($\delta^{13}C = -29.6$ to $-26.7‰$) from this bitumen indicate continued input from primary producers and eukaryotes. The higher relative concentrations of gammacerane ($\delta^{13}C = -26.9‰$) indicate increasing input from aerobic species. Slight enrichment in $\delta^{13}C$ in the wurtzilite extract (and several biomarkers) suggests sulphate-reducing bacteria outcompeted methanogens, thereby, eliminating the influence of methanotrophs in this later saline stage of deposition.	Ruble *et al.*, 1994 Katz, 1995

Kongdian Formation (Ek) and Es4 member of the Shahejie Formation Zhaolanzhuang field, Jizhong depression, Bohai Bay Basin, China Eocene–Oligocene	3 Continental half-graben Palaeogene rift with Neogene subsidence	Natural gas contains the highest proportions of H_2S (40–92%) among the sour gases encountered in China. The sedimentary sequence consists of halite, anhydrite, carbonate, sandstone and shale interbeds deposited in the evaporative brackish water lacustrine- salt lake setting. In the deepest part of the Jinxian sag, the total thickness of evaporites is more than 1000 m, of which halite accounts for over 40%. Various organic-rich mudstones intercalated with the evaporites are currently within the conventional hydrocarbon window (with a depth of 2500–3500 m), and likely the source for the oil and sour gas in the Zhaolanzhuang field. The temperatures of the gas reservoirs range from 75 to 100 °C, too low for significant thermochemical sulphate reduction. The co-occurrence of abundant elemental sulphur with the sour gas and the $\delta^{34}S$ values of the various sulphur-containing compounds indicate that the H2S gases were most likely derived from much deeper source kitchens where significant thermochemical sulphate reduction has occurred.	Chen *et al.*, 1996 Zhang *et al.*, 2005
Bucomazi Formation, Cabinda, offshore Angola Cretaceous	3 Rift basin continental to transitional marine	The Lower Congo hydrocarbon habitat is dominated by the Pre-Salt Bucomazi petroleum system. These lacustrine, often super-rich, laminated evaporitic sediments reveal considerable organofacies variations between their early lacustrine basin fill and later sheet drape development with three major depositional regimes reflecting salinity and water depth control. ^{13}C depleted basal sediments, showing strong gammacerane/4-methyl sterane signatures, were segregated as seen by a major isotopic excursion. This event represents the transition from an early saline playa lake to a deeper water salinity-stratified mesohaline lake supporting a high level of bottom anoxia. For the intermediate sediments, sterane and tricyclic diterpane abundances, plus sterane/hopane ratios, had marine connotations and can be interpreted as the result of intermittent marine incursions. Foreshadowing irreversible oceanic ingression, a resurgence of gammacerane abundance in the uppermost sediments typified littoral-shallow marine depositional conditions.	Burwood *et al.*, 1995, 1992 Burwood & Mycke, 1996 Schoellkopf & Patterson, 2000
Lagoa Feia Formation, Campos Basin, Brazil Lower Cretaceous	3 Rift basin continental to transitional marine	Rift-stage lacustrine sediments are the source rock of all petroleum so far discovered in the Campos Basin, the most prolific oil province in Brazil. These organic-rich shales were deposited in anoxic brackish to saline lakes. Petroleum migration pathways involve direct contact between source and reservoir rocks within the rift sequence. Later migration to the marine sequence reservoirs is related to windows in the halokinetic salt layer connected to growth faults and unconformities.	Trindade *et al.*, 1995 Mello & Maxwell, 1991

(*continued*)

Table 5. (*Continued*)

Formation/Group locality and age	Basin Style	Characteristics and depositional setting	Reference
Muribeca and Maceió Formations, Sergipe Basin, Brazil Lower Cretaceous	3 Rift basin continental to transitional marine	Most hydrocarbon accumulations discovered in the Sergipe subbasin are sourced by the protomarine Aptian marls and calcareous shales of the Muribeca and Maceió formations both below and above the Aptian salt (Ibura Member). These source rocks average about 6% TOC and are composed mainly of hydrogen-rich type II kerogen.	Mello *et al.*, 1988
Kimmeridgian Shale, North Sea Upper Jurassic	1b Sediment-starved deep marine basin centre generated by ongoing Permian-Mesozoic rifting and surrounded by Purbeck evaporite-carbonate platform	Seawater flowed southwards from Boreal Ocean into Tethyan Ocean but evaporation in the shallow waters of the archipelago of islands and shoals created waters of increased salinity and in some cases local strong brines and evaporites, which sank and flowed as saline bottom currents (from 34–42‰) into deeper water. Areas of ponded deeper mesohaline water were commonplace in the more rapidly subsiding grabens, separated by sills, denser waters accumulated until they were able to spill over the sills. In this way more saline waters migrated along the seabottom depressions, their paths being determined by local tectonic features, but mostly in a north to south direction. A stable water stratification ensued, the halocline being at about 50 m water depth and periods of widespread increased salinity are marked by "hot" shales.	Cooper *et al.*, 1995 Miller, 1990
Purbeckian lacustrine beds, Dorset coast UK, Lower Cretaceous,	3 Continental lagoons and lakes in sea-margin position at edge of carbonate platform	Within these beds, which immediately overlie the Purbeck evaporites, a large OM accumulation is recorded, with total organic carbon (TOC) of up to 8.5 wt%. High hydrogen index (HI) values (up to 956 mgHC g^{-1} TOC) point to a Type I OM, generally considered as derived from algal-bacterial biomass. This contrasts with the OM present in the underlying and overlying intervals, displaying in general lower TOC and HI values, and consisting of degraded algal-bacterial material with higher proportions of terrestrial OM. This organic-rich accumulation can be interpreted as a period of enhanced primary productivity within coastal lagoonal/lacustrine settings at times of low sea level and has strong affinities to modern Coorong Lakes in Australia.	Schnyder et al., 2009
Shelf margin laminites, Arabian Gulf from NW Iraq through the Arabian Gulf to central Oman (e.g. Diyab, Tuwaiq and Hanifa Formations) Upper Jurassic	2 Density-stratified intrashelf basins surrounded by evaporitic platform. Some lows are possibly tied to salt withdrawal	Organic-rich laminated mudstones and wackstones deposited in pre-salt intrashelf, mesohaline basins on a gently downwarped epeiric platform. Intrashelf basins that retain organics all have a density and salinity stratified water column with mesohaline bottom carbonates. These basins source more than 90% of the hydrocarbons in the Middle East. They are argillaceous dolomitic limestones that feed the most prolific petroleum system in the world and underlie the world's richest reservoir: the Arab D in the Arab Formation. One of the most prolific source units is the Hanifa Fm. in the Arabian Basin of Saudi Arabia. In the deeper parts of the intrashelf Arabian Basin (waters ~30 m deep) the Hanifa is composed of laminite muds and marls, while	Ayres *et al.*, 1982 Palacas, 1984 Evans & Kirkland, 1988 Droste, 1990 Beydoun, 1993 Carrigan *et al.*, 1995 Whittle & Alsharhan, 1996 Ibrahim *et al.*, 2002

		in the surrounding shelf it is dominated by grainstones and packstones. Within the Hanifa laminites there are discrete but minor primary laminae of anhydrite (originally gypsum), as well as early diagenetic anhydrite nodules, both indicators of occasional hypersalinity. There are also laminae of fibrous calcite, which some authors have interpreted as another indicator of hypersalinity. The Hanifa is a widespread and prolific source, it can entrain more than 30 metres of laminites; total organic carbon exceeds 1%, with some sections having more than 5%. The kerogen is predominantly hydrogen rich, the generated oils have a high sulphur content, a Pr/Py < 1, and a predominance of even-numbered normal alkanes.	
Smackover trend of Mississippi, Alabama and Florida, northeastern Gulf of Mexico Upper Jurassic	2 Shallow restricted-circulation salinity stratified intrashelf basin on a broad carbonate platform	Oil and gas in this trend are generated from algal-rich light-brown to black laminated lime mudstones (argillaceous content <6%) of the Lower Smackover Formation. Deposition occurred in intraplatform depressions surrounded by a broad carbonate platform. Bottom waters were stratified with slightly saline waters supplied from the broad platform surrounds and the shoaling carbonate system was sealed by the sulfate evaporites of the Buckner Anhydrite.	Oehler, 1984 Sassen, 1990 Mancini *et al.*, 2003
Todilto Formation Todilto Basin, USA Middle Jurassic	3 Foreland flexural basin (lacustrine?)	The Limestone Member of the Todilto Fm. is a widespread carbonate laminite up to 3 m thick, overlain in the subsurface by up to 30 m of $CaSO_4$ known as the Gypsum Member, although it is mostly anhydrite. The Limestone Member is the source rock for 6 known hydrocarbon accumulations in the sands of the underlying Entrada Fm, while it and the overlying $CaSO_4$ are the seal. The quantity of TOC is low (~1%) for such a thin source rock and it has some unusual characteristics compared to most evaporitic source rocks. Laminite couplets are 0.15 mm thick yet are laterally continuous for up to 3.7 km and form widespread cohesive "sheets", which invariably contain remnants of vascular plants. The Todilto is probably lacustrine with a marine seep hydrology, similar in hydrology to the coastal salinas of southern Australia. The organics reflect the growth of a healthy conifer cover in its surrounds and its waters were density-stratified lacustrine, probably fed via a marine seepage inflow and periodic seasonal runoff. This maintained a density-stratified brine column, first at carbonate saturation during deposition of the Limestone Member, then at gypsum saturation during the deposition of the Gypsum Member.	Vincelette & Chittum, 1981 Evans & Kirkland, 1988
Organic mudstones intercalated with evaporites, Mandawa Basin, Tanzania Triassic	3 Rift basin continental to transitional marine	Total organic carbon (TOC) values range from 1.23 to 7.41 wt% of kerogen Type II/III. The evaporite (hypersaline) influence is indicated by the presence of C-24-tetracyclic terpanes, gammacerane and C-35- homohopanes. The relative abundance of tricyclic terpanes (C-19-C-28 +) with respect to pentacyclic terpanes (C-27-C-35,) seems to change with depth, whereby	Kagya, 1996

(*continued*)

Table 5. (*Continued*)

Formation/Group locality and age	Basin Style	Characteristics and depositional setting	Reference
		the tricyclic/hopanes ratio apparently increases with depth. The mixed organic input from marine and terrestrial precursors are indicated by mixed abundances of C-27-, C-28-, C-29- steranes.	
Sub salt-allochthon oil seeps, Windsor Group, Nova Scotia, Canada Carboniferous	3 Rift basin continental to transitional marine	The oil seeps are either associated with upper Horton Group (Ainslie Formation) or basal Windsor Group (Macumber Formation) sediments. The biomarker distributions of the samples are similar to Stoney Creek oils and their lacustrine carbonate source rock (Albert Shale) of the Moncton Sub-basin, New Brunswick, as are oils from seeps in the Pugwash Salt mine.	Fowler *et al.*, 1993
Black shales in the Paradox Member of the Hermosa Formation, Paradox Basin, USA Carboniferous (Pennsylvanian)	1a Foreland flexural basin	Organic-rich black shales (informally known as the Cane Creek, Chimney Rock, Gothic shales) form a carbonate laminite basal sequence to a number of salting-upward evaporite cycles in the Paradox Member. Mineralogically the shales are between 30–50% calcite or dolomite with clays and quartz sand forming the remainder of the matrix. TOC values of 5% of hydrogen-prone organics in the black shales are usual, with values of 10% not uncommon and the highest values more than 20%. The organics are mixtures of halotolerant debris and marine-style organics formed when surface waters were at marine salinities, as well as occasional terrestrial organics washed into the basin from the surrounding hinterland.	Evans & Kirkland, 1988 Hite *et al.*, 1984
Oil Shales, Junggar Basin, NW China Upper Permian	3 Controversial, with tectonic interpretations ranging from foreland flexure to regional transtensional basin	Junggar Basin is one of the largest oil-producing basins in China, its Upper Permian oil shales are among the thickest and richest lacustrine source rocks in the world. Together the Jingjingzigou, Lucaogou, and Hongyanchi Formations of the southern Junggar Basin comprise over 1000 m of organic-rich lacustrine facies. They record an evolution from relatively shallow, evaporative lakes to freshwater lakes with fluvial systems. Jingjingzigou Formation was deposited in a perennial saline lake characterized by low TOC and HI, and biomarker features (such as abundant β-carotane) consistent with a specialized saline or hypersaline biota. Biomarker distributions in Jingjingzigou Formation extracts most closely resemble oils from the giant Karamay oilfield. Overlying Lucaogou Formation represents one of the richest and thickest lacustrine source rock intervals in the world, yet it contradicts conventional lacustrine source rock models in at least two important aspects. First, deposition occurred at middle palaeolatitudes (39–43°N) rather than in the tropics. Second, limited nutrient supply in a drainage basin dominated by intermediate volcanic rocks appears to have caused low to moderate primary productivities. Stable salinity stratification and low inorganic sedimentation rates in a deep lake nonetheless resulted in deposits with up to 20% TOC and HI near 800.	Carroll, 1998 Carroll *et al.*, 1992 Tang *et al.*, 1997

		Overlying Hongyanchi Formation has 1–5% TOC but low HI, and was deposited in freshwater oxic to sub-oxic lakes.	
Ravnefjeld Formation, East Greenland Upper Permian	3 Rift basin continental to transitional marine	The Ravnefjeld Formation is subdivided into five units that can be traced throughout the Upper Permian depositional basin. Two of the units are laminated and organic rich, and were deposited under anoxic conditions. They are considered good to excellent source rocks for liquid hydrocarbons with initial average TOC (total organic carbon) values between 4 and 5% and HI (hydrogen index) between 300 and 400. The cumulative source rock thickness is between 15 and 20 m. The source rocks are separated and enclosed by three units of bioturbated siltstone with a TOC of less than 0.5% and an HI of less than 100. These siltstones were deposited under relatively oxic conditions. The organic geochemistry of the source rocks is typical for marine source rocks with some features normally associated with carbonate/evaporite rift environments [low Pr/Ph (pristane/phytane), low CPI (carbon preference index), distribution of tricyclic and pentacyclic terpanes]. The establishment of anoxic conditions and subsequent source rock deposition was controlled by eustatic sea level changes.	Christiansen *et al.*, 1993
Phosphoria Formation, Little Sheep Creek, Montana Permian	1b Foreland flexure basin	Correlations between biomarker indicators of anoxia and salinity suggest that anoxia was in part the result of a chemocline separating normal marine waters above from more saline bottom waters. Anoxia and salinity in the bottom waters increased with time making conditions in the basin progressively more hostile to benthic organisms.	Dahl *et al.*, 1993
Kupferschiefer Formation, NW Europe Permian	1a Rift basin, restricted marine	Thin, widespread organic-rich laminated mudstone deposited in shallow mesohaline marginal sea-lakes with waters which were <100m deep and mostly 10–30 m deep. Surface exchange with Zechstein ocean was restricted by palaeohighs.	Bechtel & Puttmann, 1997
Anhydritic lacustrine beds, East Shetland Platform, North Sea Middle Devonian	3 Rift basin, restricted marine	The UKCS well 9/16-3 drilled on the western flank of the Beryl Embayment indicates local development of hypersaline environments equivalent to the Achanarras/Sandwick fish bed. Shows close affinity with contemporaneous Middle Devonian source rocks of the Inner Moray Firth and crude oil in Beatrice oil field.	Duncan & Buxton, 1995
Muskeg Formation and Lower Keg River Member, Alberta, Canada Devonian	1a Rift basin, restricted marine	Laminated organic-rich bituminous mudstones deposited in pre-evaporitic density stratified water columns. Vertical migration from the Muskeg formation to the Muskeg Reservoirs may have occurred through local fracturing of anhydrites driven by the dissolution of Black Creek Halite.	Clark & Philp, 1989 Stasiuk, 1994; Chen *et al.*, 2005
Laminated evaporitic A-1 mudstones, Michigan Basin Silurian	1a Rift basin, restricted marine	Biomarker characteristics indicate a carbonate/evaporite source rock deposited under hypersaline conditions in a strongly reducing environment. The source rocks occur in the basin centre in organic-rich laminites of the inter-reef A-1 Salina	Gardner & Bray, 1984 Obermajer *et al.*, 1998, 2000

(*continued*)

Table 5. (*Continued*)

Formation/Group locality and age	Basin Style	Characteristics and depositional setting	Reference
		Formation, a mesohaline carbonate deposited beneath a density stratified brine column.	
Chandler Formation, Amadeus Basin, Australia Lower Cambrian	1a Foreland flexure, Restricted marine	Thin bituminous pre-evaporitic carbonate mudstone deposited subaqueously in a restricted basin immediately prior to the deposition of the thick halites of the Chandler Formation.	Bradshaw, 1988
Hormuz Series, Arabian Gulf and counterparts in Oman, India and Pakistan Neoproterozoic to Early Cambrian	1 Foreland flexure, restricted marine	Almost all the Persian Gulf and large areas of southern Iran and northeastern Arabia are underlain by a thick sequence of sediments, known as the Hormuz Series, or the Huqf Group in Oman. It is made up of interbedded salt, anhydrite, dolomite, shale and sandstone. It is not only the cause of many salt-dome-related oil and gas fields but is also considered to have been a major source rock for hydrocarbons in Ordovician, Devonian, Carboniferous, Permian and perhaps younger reservoirs. These oils have characteristic biomarkers and highly depleted carbon isotopes signatures indicative of their prokaryotic precursor.	Amthor, 2000 Edgell, 1991 Grantham *et al.*, 1988 Peters *et al.*, 1995 Terken & Frewin, 2000 Schoenherr *et al.*, 2007, 2009

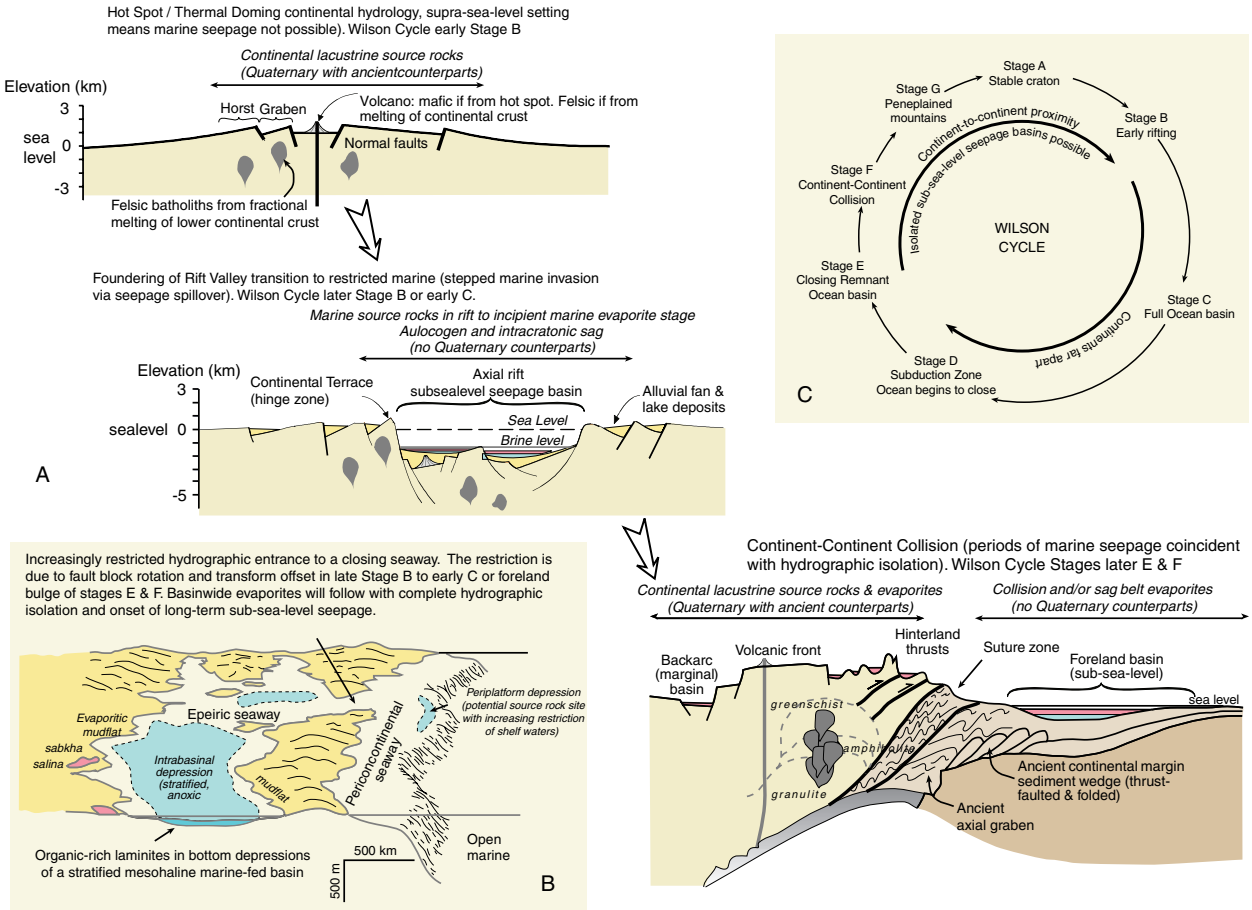


Fig. 19. Tectonic settings of ancient evaporate source rocks. (A) Ancient evaporite source rocks and regions with Quaternary counterparts (in part after Warren, 2006). (B) Styles of intrashelf and platform depressions where anoxic mesohaline bottom brines tended to accumulate in an ancient evaporitic platform. (C) Characteristics of the Wilson Cycle.

rifting ("zip then split") tectonics encourage the accumulation of substantial volumes of salts and organic-rich evaporitic sediments in sub-sea-level tectonic depressions (Fig. 19). In the past 800 Myr there have been two such tectonic cycles defined by supercontinent accretion and disaggregation (i.e. the accretion and disaggregation of Phanerozoic Pangea and Neoproterozoic Rodinia). Marine-fed evaporitic source rocks tend to form at times when the tectonic depression is undergoing hydrographic isolation from the open ocean. The basin still has a surface (hydrographic) connection to the ocean, but inflow is restricted and the basin is typically surrounded by widespread salty platforms with sheets of salterns and evaporitic mudflats (Fig. 19). When the surface connection to the open ocean is completely cut-off, the basin becomes a marine-fed sub-sea-level seepage depression and widespread thick salts precipitate in the lower parts of the basin floor in waters ranging from hundreds of metres deep to ephemeral.

Ancient mesohaline source rocks

Worldwide, studies of ancient evaporitic basins have shown that organic-rich mesohaline sediments accumulate in ephemeral surface brines, saltern sediments, or basin and slope settings in both marine and continental regimes (Evans & Kirkland, 1981; Oehler, 1984; Warren, 1986; Busson, 1988; Kirkland & Evans, 1988; Rouchy 1988). The most prolific accumulations of organics in ancient evaporitic sediments tend to have been deposited as laminated micritic carbonates that accumulated beneath density-stratified moderately-saline (mesohaline) anoxic water columns of varying brine depth. There are three, possibly

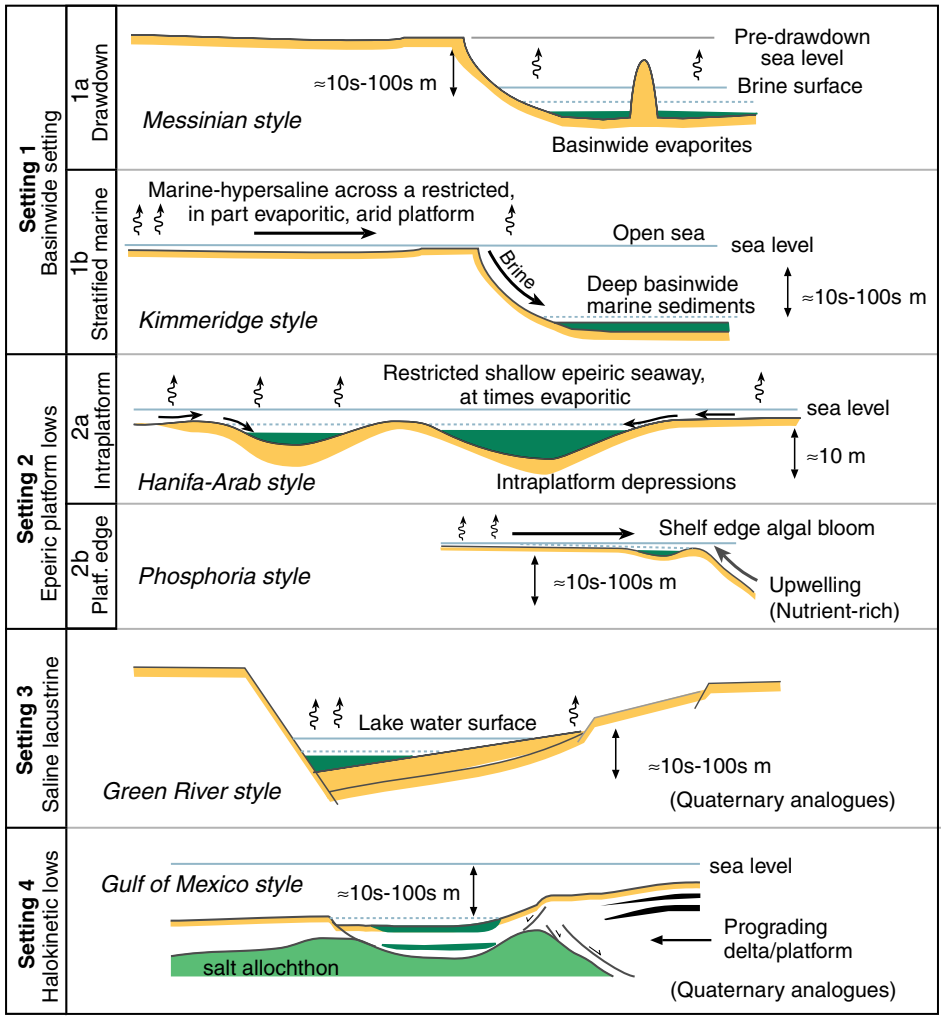


Fig. 20. Dominant depositional styles for evaporitic source rocks (dark green). All the water bodies show evidence of salinity-related density stratification (indicated by dashed line); this is also reflected in an associated heliothermic stratification (after Warren, 2006).

four, major mesohaline density-stratified settings where organic-rich laminites (source rocks) accumulate in saline settings that are also associated with, or evolve into, evaporite deposits (Fig. 20; Table 5). These are:

(1) Basin-centre lows in marine-fed evaporitic drawdown basins:
  (a) evaporite-plugged mesohaline basin centre;
  (b) evaporite platform rim surrounding restricted and stratified slightly-mesohaline carbonate basin centre.
(2) Mesohaline intrashelf lows on top of epeiric evaporitic platforms;
  (a) intraplatform depressions with layered mesohaline brines;
  (b) shelf-edge depressions with layered mesohaline brines.
(3) Saline-bottomed lows in perennial underfilled saline lacustrine basins.
(4) Closed seafloor depressions in halokinetic deep-water marine slope and rise terrains.

Basin Setting 1

There are two depositional styles for basin-centre or basinwide mesohaline source rocks: (a) basin-centre drawdown laminites intercalated and often sealed by basinwide salts; (b) basin-centre laminites where the basin margin is a shallow, restricted, at times evaporitic platform that surrounds a slightly mesohaline deep-water starved-

basin centre. Bottom waters in this deeper part of the basin were never drawndown or concentrated to salinities where basinwide salts precipitated. Matrices in Setting 1b basin-centre laminites range from limestones through marls to siliciclastics (Fig. 20).

Basin Setting (1a) In this setting the basin is largely isolated from a surface marine connection and high levels of organics accumulate as "black shales" (typically carbonate laminites), which are intercalated with, and overlain by, basinwide evaporite salts (typically gypsum/halite). These laminites accumulate on the bottom of mesohaline density-stratified pools in topographically closed parts of the basin floor during the early stages of isolation and drawdown. Inactive, typically subaerial, shelf margin reefs and pinnacles typically lay updip or encircled the basin-centre lows (Warren, 2006). Subsequent encasement of these platform buildups and other potential reservoirs by "fill and spill" evaporites means these basins easily become highly focused hydrocarbon flow systems. Hydrocarbons accumulate in the reefs or shelf margin shoals beneath basinwide evaporite seals. Such systems typify the marine-fed Silurian reef/salina salt association in the Michigan Basin, USA (Gardner & Bray, 1984), the Devonian Rainbow Reef reservoirs of the Black Creek/Muskeg Basin of Alberta (Clark & Philp, 1989), and the Messinian marls of the Lorca Basin, Spain (Russell *et al.*, 1997).

Expulsion efficiencies suffer from encasement and widespread salt plugging of the potential source rocks in many evaporite-rich Setting 1a basins. This style of deposit tends to retain volatiles in the source beds until the whole system becomes overmature. For example, in the Gibson Dome No. 1 well in the Paradox Basin, almost all of the black shales in the Upper Carboniferous Paradox Member are mature enough to have generated oil (Hite *et al.*, 1984), but the hydrocarbons have been largely retained in this mature source rock, reflecting the highly efficient sealing effect of the intercalated evaporite beds and salt plugs (mostly halite). Only where the black shales are intercalated with porous carbonates have the hydrocarbons escaped. The source potential of these shales is very high; the "Gothic shale" member is capable of generating almost 5000 barrels per acre. But that potential is never more than partially realized. Paradox "shales" are responsible for an accumulative production of a little more than 400 million barrels of oil and about 1 TCF of gas in the Paradox Basin in fields such as Ismay and Aneth (Peterson & Hite, 1969).

The problem of evaporite plugging plagues many basinal source rocks where the basin centre evolved to accumulate basinwide evaporates, and is one of the main reasons for the dearth of large onshore oilfields beneath bedded salt or within intrasalt carbonates in the Zechstein Basin of NW Europe. Organic-rich source intervals such as the Stinkdolomit, Stink-kalk, and Stinkscheifer are widespread, but the associated oil accumulations are never more than localized and are small scale. This setting also created the salt-encased self-sourced low-permeability reservoirs in the Cambrian Ara Group platform carbonate stringers and basin centre silicilytes of the South Oman Salt Basin (Al-Siyabi, 2005; Amthor *et al.*, 2005; Schoenherr *et al.*, 2007, 2009). Very rich organic source beds can characterize Setting 1a sediments, but the intercalated seals prevent most of the volatiles from ever escaping into a reservoir. Sometimes, as in the silicilytes of Oman, the source beds can become self-reservoiring. In later burial diagenesis the trapped hydrocarbons can play an important role as a reductant and metal fixer as ongoing burial dissolution of salt interbeds focuses long-term contact with basinal waters carrying Cu, Pb and Zn (Warren, 2000).

Basin Setting 1b Basin-centre mesohaline accumulations in this setting are much more efficient petroleum producers than Setting 1a as they lack intercalated beds of basinwide gypsum or halite, which otherwise create salt-plugged and salt-cemented source intervals. Setting 1b source rocks develop where dense mesohaline bottom-waters pond on the bottom of a deep density-stratified restricted-marine basins. Slightly elevated bottom-brine salinities are maintained by a series of dense brine underflows, fed from nearby shoalwater evaporitic platforms (Fig. 20). Such basins are typified by a deep-water "marine" centre and the presence of widespread evaporitic and shoal water carbonate sediments in the surrounding platforms and shelves. Setting 1b basins are best thought of as stunted or underdeveloped basinwide evaporite systems. Development of the basinwide evaporite hydrology was suspended prior to the basin centre drawdown reaching the state of sea-surface (hydrographic) isolation, which is needed for widespread salt precipitation across the basin centre. Nonetheless, evaporitic conditions dominated

in isolated platform depressions about the basin margin. Typical examples of this style of association are the Upper Jurassic Kimmeridge shales of the North Sea (Miller, 1990; Cooper *et al.*, 1995), the organic-rich laminites of the Cherry Canyon Formation in the Permian Delaware Basin of West Texas (Jones, 1984), and possibly the Jurassic Lower Smackover Formation in the Proto-Gulf of Mexico (Sassen, 1990).

In Setting 1b, the deep-water basin centre remains "sediment starved" and density-stratified, with the upper less-saline part of the water column typified by normal marine water, maintained through surface connections to the open ocean. The little sediment matrix that does accumulate in the basin centre settles into an anoxic thermally/density stratified bottom, so that the sediment matrix of the source laminites is dominated by a planktonic or nektonic biota and a more or less constant elevated organic content. Carbonate banks or reefs in the surrounding platform grade landward through lagoonal and evaporitic platform facies into terrestrial siliciclastics. At times of slightly lowered sea-level these epeiric platforms can go evaporitic and so deposit widespread platform salts (Warren, 2006). Such basins show a centrifugal salinity gradient where the highest salinity areas are the shallow evaporite platforms, which supply dense saline waters that trickle and seep basinward to pond in seafloor lows at the anoxic base of a density-stratified water column.

With Setting 1b, the formation of evaporites and saline waters about the basin edge is not typically followed by the deposition of basin-centre evaporites. At the time the deep-water organic laminites are accumulating, the deep basin-centre waters lie at the bottom of the thick density-stratified water column in a semi-enclosed seaway, and bottom brines may be no more than 3–5‰ more saline than the normal marine waters. For example, at the time the Upper Jurassic Purbeck evaporites were accumulating on the platforms of northern Europe, the anoxic bottom waters in the marine basin centre where the Kimmeridge Clay was accumulating had salinities around 42‰, temperatures ~30°C and densities ~1.027. The overlying near-normal marine waters had salinities of 34–39‰, surface temperatures of 26°C in the south and as low as 6°C farther north in the region of the Boreal Ocean inflow, and densities around 1.0267 (Miller, 1990). As the Kimmeridge Clay source rocks accumulated, halokinesis and salt solution of Zechstein mother salt probably also played a role in generating local briny anoxic bottoms on the deeper parts of the basin floor (Clark *et al.*, 1999).

Basin Setting 2

Upper Jurassic source rocks of the Middle East are well-studied examples of the epeiric shelf or marine evaporitic platform settings and typify Setting 2a source rocks, which are deposited within local somewhat deeper, density-stratified mesohaline intrashelf lows (Figs 19, 20 and 21; Table 5; Ayres *et al.*, 1982; Evans & Kirkland, 1988; Droste, 1990; Warren, 2006). In the Tethyan of the Middle East this style of source rock feeds a petroleum system that is probably the most efficient in the world. It evolved from Upper Jurassic source rock accumulators (typically with TOC's ~1%, occasionally up to 13%) into evaporitic mudflats sealing the mostly bioclastic carbonate reservoirs of the Arab Formation cycles, into the regional Hith Anhydrite seal, which was deposited on a saltern-covered platform.

The laminite source rocks in the various intrashelf depressions were deposited at times of widespread epeiric carbonate deposition and stagnant oceanic circulation. It was a time when a warm shallow greenhouse sea covered much of the Arabian platform and was precipitating carbonates and evaporites over much of its extent. Denser warmer waters, generated by evaporation of these epeiric waters, along with waters supplied by the surrounding evaporitic mudflats, were concentrated to where they were somewhat more saline than normal seawater. These dense brines then trickled and seeped over the shallow seafloor into the lower parts of restricted intrashelf basins to create density-stratified bottom waters that were not more than tens of metres deep and no more than 10–30‰ more saline than seawater (Ayres *et al.*, 1982). Ongoing mixing and dilution of the bottom-hugging brines during their passage to the lows meant that the basal waters on the intrashelf lows, although saline, rarely attained gypsum saturation (mostly mesohaline anoxic brines). The overlying column was typically at near-normal marine salinities. Salt withdrawal and dissolution of salt diapirs and allochthons, sourced in the Precambrian Hormuz salt, perhaps helped create the intrashelf depressions and may also have played a role in generating a portion of the bottom brines.

One of the most prolific intrashelf source rocks in the Middle East is the Upper Jurassic Hanifa

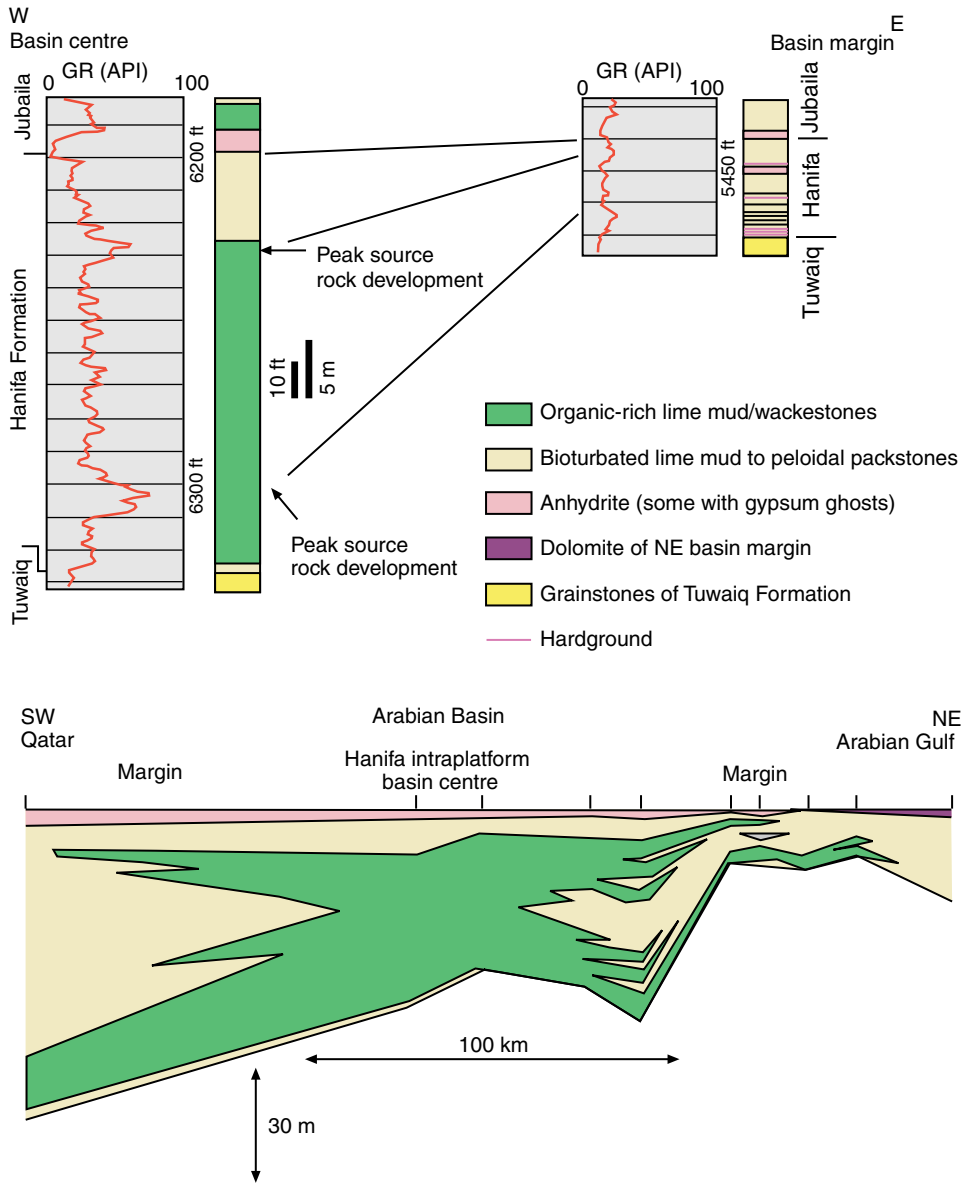


Fig. 21. Correlation and lithofacies of the Upper Jurassic Hanifa Formation, Saudi Arabia. This Setting 2 intraplatform basin source rock was deposited beneath relatively shallow and anoxic mesohaline bottom waters in a slight depression on the shelf and was surrounded by epeiric evaporitic sedimentation, as indicated by the presence of anhydrite in the Hanifa Formation (after Droste, 1990). Peaks in the organic content of these carbonate mudstones are indicated by peaks in the gamma curve. Cross section redrafted from Carrigan *et al.* (1995).

Formation deposited in the intrashelf Arabian Basin of Saudi Arabia (Fig. 21; Droste, 1990; Carrigan *et al.*, 1995). It sources most of the hydrocarbons reservoired in the Arab cycles of Saudi Arabia and is regionally sealed by the Hith Anhydrite. The organic-rich portions of the Hanifa and its equivalents elsewhere in the Middle East were deposited in the "deeper" parts of a number of Jurassic intrashelf basins (waters ~30 m deep). Sediments accumulating beneath the slightly mesohaline layered bottom waters are composed of organic-rich laminite muds and marls, while sediments of the surrounding Arabian shelf are dominated by grainstones and packstones. As the various intrashelf depressions filled with laminites they shallowed to where the stratification was lost and the sediment became an open-marine packstone-wackestone equivalent to sediments deposited over the rest of the Arabian Platform.

Successive platform isolation, via buildups of a transgressive platform rim and a slight fall in sea level, then drove deposition of anhydritic saltern or mudflat caps of the various Arab cycles (Cycles A–D; Warren, 2006). Within the Hanifa laminites, there are discrete laminae and thin beds of primary anhydrite, as well as early diagenetic anhydrite nodules, both indicators of periodic hypersalinity even as the laminites were accumulating. Likewise, the evaporitic cap to each of the source cycles in the Hanifa Formation in the Arabian Basin preserves aligned gypsum ghosts indicating a subaqueous gypsum precursor. Similar, but volumetrically less prolific, intrashelf source rocks characterize the Lower Smackover Formation (Upper Jurassic) of the northeastern Gulf of Mexico (Oehler, 1984; Sassen, 1990) and the Cretaceous Sunniland Formation of Florida (Palacas *et al.*, 1984).

A variation on this density-stratified mesohaline platform-depression style of source rock accumulation is the phosphate and organic-rich Setting 2b source rocks sediment of the Phosphoria Formation in the USA (Stephens & Carroll, 1999). This unit sources much of the oil in Wyoming and was deposited in somewhat-saline shelf-edge depressions of the Phosphoria Sea adjacent to an area of marine upwelling. The nutrient-rich waters facilitated algal blooms near and above the shelf edge, while bottom-hugging brines, seeping seaward from the evaporitic hinterland, ponded in stagnant shelf-edge depressions. Overlap of the two systems created local anoxic bottom-waters in the shelf-edge depressions that preserved the organics fed by the detritus of the overlying algal blooms (Fig. 20).

Basin Setting 3

These source rocks accumulated in sediment-starved or underfilled saline lakes in arid climates. The laminites typically accumulated in the early continental stage of infill in an opening rift, prior to its opening into a marine-fed marginal evaporite basin (Figs 19 and 20), or in the restricted lacustrine stage of a foreland flexure in a collision belt. Modern underfilled saline rift lakes have some of the highest rates of organic productivity known and can accumulate high levels of organics within carbonate laminites. Some of these lacustrine laminites accumulate beneath deep density-stratified water columns, while others accumulate as "moat facies" or microbial mudflats around lake margins (Fig. 20; Table 5).

The likelihood of numerous water level changes during the life of a saline lake especially affects laminites deposited in shoal-water moats and margin mudflats and so can lower their preservation potential (Bohacs *et al.*, 2000). Most oil-prone Setting 3 lacustrine source rocks were deposited at the bottom of perennial salinity-stratified hydrologies, with water column depths measured in metres to tens of metres, not as subaerially exposed algal mudflats. Examples include the Wilkins Peak Member of the Eocene Green River Formation, USA, the Lower Cretaceous Lagoa Feia Formation of the Alagoas portion of the Campos Basin in Brazil, and the Permian Jingjingzigou Formation in the Junggar Basin, China (Table 5).

Desiccation needed to form an underfilled lacustrine succession typically means that saline lacustrine phases have lesser aerial extents compared to units deposited at times of fresher water in the lake depression. This does not necessarily mean the evaporitic lacustrine source rocks are less prolific than their freshwater counterparts. Within the Green River Formation there are two associations (fresh and saline) of lacustrine organic laminites exemplified by the Luman Tongue and the Laney Member (Fig. 22; Horsfield *et al.*, 1994). The Luman Tongue consists of organic matter-rich mudstones deposited as profundal sediments at a time when lake waters were relatively fresh (Fig. 22A). Proximal organic matter-poor sediments, as well as coals and thin sandstones, were deposited on the lake plain. The highest levels of TOC in the Luman Tongue occur in lake-margin deposits, which contain a mixture of alginite and vitrinite, but they have a low hydrogen index and a low petroleum generation potential (Fig. 22B, C). In fact, the petroleum generation potential of these freshwater deposits is no more than moderate.

In contrast, the organic percentages of the carbonate laminites of the evaporitic Laney Shale are much higher (6–22%) and these are hydrogen prone (Fig. 22B, C). The most organic-rich samples were deposited in the lowest parts of the lake and are composed mostly of alginite with relatively minor contributions from higher plants. The much higher petroleum potential of the Laney Shale reflects the marked density stratification of Lake Gosiute waters at the time the Laney was accumulating. At that time bottom anoxia was stabilized by the perennial highly saline bottom waters (Boyer, 1982; Fischer & Roberts, 1991). The dissolution of underlying evaporites to create density-stratified lacustine waters also characterized the

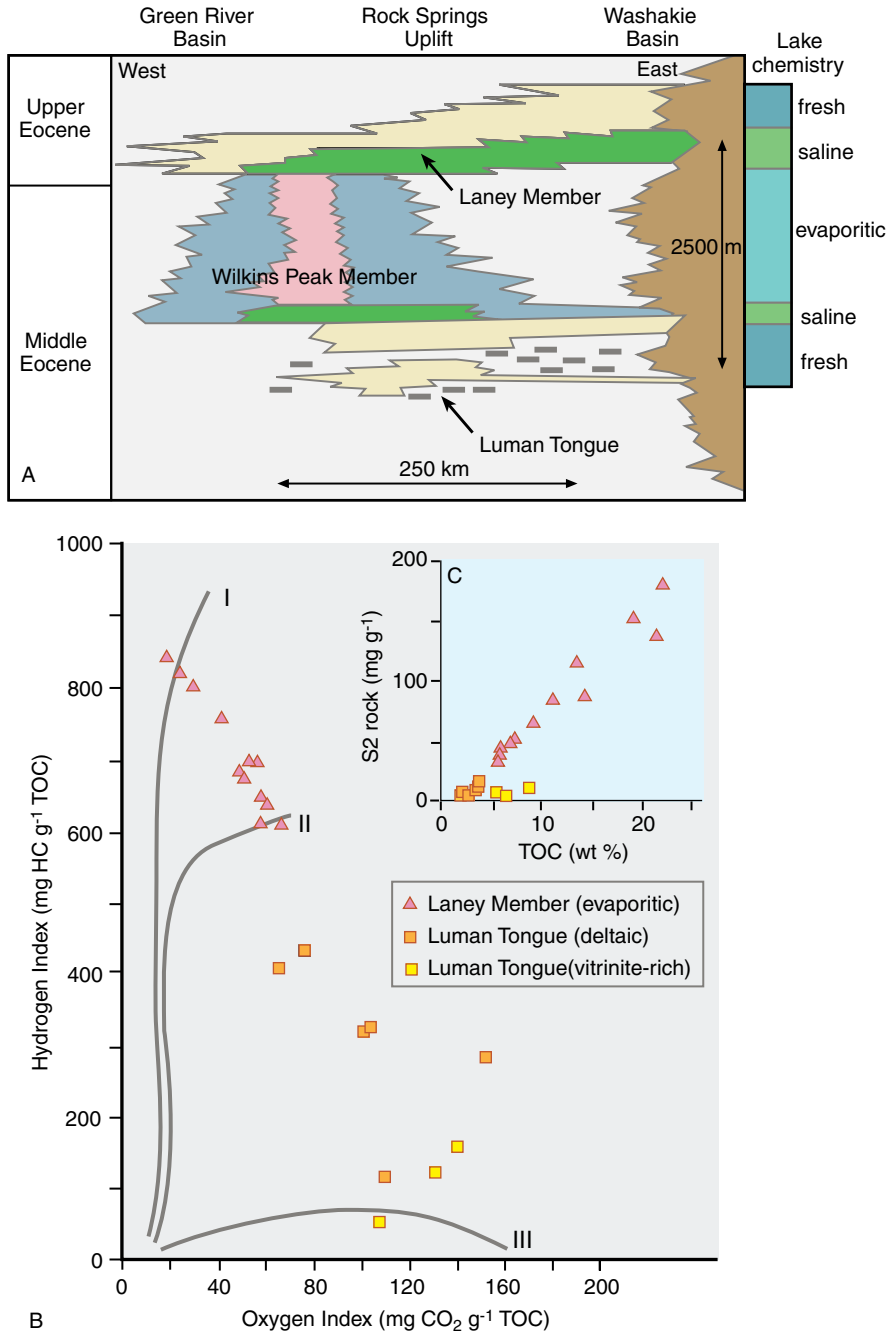


Fig. 22. Lateral variation and kerogen character of the Laney Member and the Luman Tongue of the Eocene Green River Formation, USA. (A) Schematic E–W cross section showing lateral extent and thickness of various lacustrine units (after Bohacs *et al.*, 2000). (B) Hydrogen and oxygen indices. (C) Pyrolysis yields of hydrocarbon-equivalents (mg g^{-1} rock) plotted against organic carbon percentages. (B and C) after Horsfield *et al.* (1994).

Cretaceous Purbeck strata of Dorset, although in this case the underlying evaporites were marine and the depositional setting was akin to the sea-margin meteoric lakes of today's Coorong region of Australia (Schnyder et al., 2009).

Basin Setting 4

This is an increasingly documented open-marine evaporite-associated source rock setting where density-stratified saline bottom brines and

organic-enriched laminites accumulate in brine-bottomed depressions on top of and adjacent to shallow and dissolving salt allochthons (Fig. 20). With burial these laminites may act as source rocks, but unlike the restricted settings of the preceding three styles, deposition typically occurs in open-marine waters in continental slope and rise environments. The laminites accumulate on the floor of deep brine pools that form on or near the margins of actively flowing and dissolving shallow salt allochthons (Warren, 2006). This is also a significant setting for the formation of base metal-hosting laminites as in Tunisia and the Red Sea (Warren, 2000). As yet it is not a widely documented environment for hydrocarbon source rocks, but it may in-part explain the higher than expected source potential of many prodelta and slope muds in the passive margin fill of evaporite-floored halokinetic rifts.

Source rocks of settings 1a, 2 and 3 are typified by the accumulation of mm-scale layers of oil-prone organics typically in a matrix of fine carbonates. Setting 1b typically contains higher levels of siliciclastic fines and in many cases the host to the organics is a basinal marl or less often a laminated calcareous shale. The matrix of Setting 4 laminites tends to be composed of whatever detrital sediment is accumulating above the salt allochthon. In many situations, such as the Gulf of Mexico and the Mediterranean allochthon terranes, this matrix is a siliciclastic mud/clay laid down at the distal ends of prodelta wedges. In others, such as the Jurassic and Cretaceous of the Arabian Gulf and the Triassic of Tunisia, the matrix is carbonate.

CONCLUSION

It seems that there are no same-scale "famine or feast" analogues for modern and ancient saline lacustrine settings (Table 6, Setting 3). Organic-rich carbonate laminites forming in the African rift valley lakes have been documented and similar-scale counterparts exist in the Mesozoic source rocks found for example in the Cabinda Basin of Angola and the lacustrine basins of South America (Table 5). Likewise, Quaternary examples of supra-allochthon brine lakes with anoxic bottoms rich in organics are now being documented (Table 6, Setting 3).

However, there are no modern counterparts for most ancient large-scale marine evaporite depressions with mesohaline "famine or feast" laminites (Table 6, settings 1 and 2). These Pre-Quaternary evaporitic source rocks generated far greater hydrocarbon volumes than all lacustrine source rocks combined, yet many source rock models for evaporitic mesohaline carbonates still draw strong comparisons to underfilled Quaternary lacustrine settings. Such "strict" uniformitarian comparisons lead to the conclusion that evaporitic mesohaline source sources are probably not all that significant as contributors to the volume of exploitable hydrocarbons in the world.

It is the author's opinion that depositional settings in arid environments are still being considered in the same way that Lotze (1957) viewed the abundance of life in modern deserts. Organic accumulations in ancient evaporitic source rocks should be seen as biological responses to the "feast or famine" cycles that still characterize life in arid depositional settings. Formation of ancient marine-fed mesohaline depressions required varying combinations of greenhouse eustacy (epeiric seaways) and tectonics-climate, which are also needed to create huge sub-sea-level depressions filling with evaporites (epeiric platform evaporites, marine-seepage rifts, soft collision belts and far-field intracratonic sags). These systems do not have same-scale Quaternary counterparts (Warren, 2010). Yet, it was in salinity-layered intraplatform epeiric depressions and restricted tectonically induced mesohaline basin centres where the requisite schizohaline water columns and stable long-term brine bottoms occurred. They did so across time scales and across areas that not only allowed widespread periodic halotolerant blooms in the surface waters of whole mesohaline-floored seaways, but also formed in settings that facilitated long-term stable anoxic bottom brines. This anoxic brine-soaked bottom in-turn allowed widespread mesohaline source rocks to accumulate and to be preserved across the areally-extensive depressions (Figs 19 and 20; Table 5).

As for most ancient evaporite styles, the present is not a suitable time for studying scales of marine mesohaline source rock development. However, process and texture relevant to these ancient mesohaline source rocks can be seen in "famine or feast" cycles in small-scale Quaternary continental deposits. Rather than the words of Lotze (1957), a more apt aphorism to describe life in modern and ancient saline systems is found in the words of John Morley, a 19th Century Scottish statesman (1838–1923), agnostic, and the First

Table 6. Summary of evaporitic source rock associations

Setting	Other significant characteristics	Some ancient examples	Quaternary counterparts	Tectonic/eustatic associations
Setting 1. Basin-centre lows in marine-fed evaporitic drawdown basins, typically with evaporite platform rim	1a. Drawndown evaporite-sealed and plugged mesohaline basin centre carbonates	Cambrian Ara stringer and silicilytes, Oman; Silurian reef/Salina Salt, Michigan Basin, USA; Devonian Rainbow Fm of the Black Creek/ Muskeg Basin, Canada; Permian Stinkdolomit Zechstein Basin, Europe; Carboniferous Gothic Shales, Paradox Basin, USA; Messinian marls, Lorca Basin, Spain	None	Rifts, collision belts and intracratonic sags with complete hydrographic isolation of marine-seepage basin centre
	1b. Density-stratified restricted-marine slightly-mesohaline basin centres with no immediately overlying evaporite seal	Permian Cherry Canyon Fm, Delaware Basin, USA: Jurassic Kimmeridge shales, North Sea; Jurassic Egret Member, Jeanne d'Arc Basin, offshore Canada; Cretaceous Sirte Shale, Sirte Basin, Libya	Partial	Often tied to early opening stages of rifts in semi arid climatic settings in greenhouse climate mode. Some aspects of Red Sea/Gulf of Suez are similar, but high aridity and icehouse eustacy do not allow a direct comparison
Setting 2. Mesohaline intrashelf lows within an epeiric evaporitic platform	2a. Intraplatform lows with adjacent epeiric mesohaline shoals	Hanifa Formation in the intrashelf Arabian Basin, Saudi Arabia and its equivalents throughout the Middle East; Lower Smackover Formation (Upper Jurassic) of the northeastern Gulf of Mexico; Cretaceous Sunniland Formation of Florida	None	Greenhouse eustacy creates continuous shelf- or ramp-edge rim, the dissolution of the crests of nearby active halokinetic structures may contribute brines to the seafloor lows
	2b. Platform edge low with epeiric mesohaline hinterland	1b: Phosphoria Fm, USA	None	Greenhouse eustacy creates continuous shelf- or ramp-edge rim
Setting 3. Mesohaline-upper column in perennial saline lacustrine basins.	Underfilled stages alternating with balanced fill stages in response to tectonic/climatic changes	Permian Jingjingzigou Formation in the Junggar Basin, China: Eocene Green River Formation, USA; Cretaceous Lagoa Feia Formation, Campos Basin in Brazil; Tertiary saline lacustrine basins, China	East African Rift Valley lakes; Lake Van, Turkey; Lake Urmia, Iran	Enhoheic basins in rift or continent-continent collision settings
Setting 4. Closed mesohaline-bottomed deep seafloor depressions in halokinetic belts	Brine seeps that create the stratified brine lakes are tied to ongoing salt dissolution and shallow subseafloor salt flows	Possible explanation for the enhanced source potential of marine deep-water shales in various circum-Atlantic halokinetic basins	Poorly documented stratified brine lakes in suprasalt allochthon provinces	Halokinetic provinces in the deep waters of the passive margin slope and rise of the Gulf of Mexico and the Mediterranean Ridge collision belt

See Fig. 20.

Viscount of Blackburn, who once said: "The great business of life is to be, to do, to do without, and to depart."

GLOSSARY

Aerobes are organisms that can survive and grow in an oxygenated environment.

Aliphatic hydrocarbons are any chemical compound belonging to the organic class in which the atoms are not linked together to form a ring. They are divided into three main groups according to the types of bonds they contain: alkanes, alkenes, and alkynes. Alkanes (n-alkanes) have only single bonds and a continuous chain structure, alkenes contain a carbon-carbon double bond, and alkynes contain a carbon-carbon triple bond. Aromatic hydrocarbons are classified as either arenes, which contain a benzene ring as a structural unit, or non-benzenoid aromatic hydrocarbons, which are characterized by stability in burial but lack a benzene ring as a structural unit.

Anaerobes are organisms that do not require oxygen for growth and may even die in its presence. Obligate (or strict) anaerobes are unable to live in even low oxygen concentrations. Facultative anaerobes are able to live in low or even normal oxygen concentration as well. All anaerobes are simple microorganisms such as bacteria, archaea and some fungi. Archaea are usually strict anaerobes.

Autotrophs (literally "self-feeders") are organisms capable of producing organic compounds from simple inorganic compounds.

Basinwide evaporites are one of the two major styles of ancient marine-fed salt accumulations known as: (1) marine-fed basinwides and (2) marine-fed platform evaporites. Neither setting is active anywhere on the world's current landsurface. Basinwide salt fills tend be thick (>100 m) and relatively pure with deposits accumulating rapidly across time frames of less than one million years. Basinwide evaporites are most likely to accumulate on the floors of isolated sub-sea-level depressions at times of close proximity of drifting landmasses (Warren 2006, 2008, 2010).

Catabolism is the breakdown in living organisms of more complex substances into simpler ones together with a release of energy.

Cellulolytic bacteria decompose cellulose; proteolytic bacteria breakdown proteins into simpler, soluble substances such as peptides and amino acids; saccharolytic bacteria breakdown sugars, while homoacetogens are obligately anaerobic bacteria that make acetate from either (H_2 + CO_2) or from the fermentation of sugars.

Chemoautotrophs use endogenous light-independent reactions to obtain energy, these reactions involve inorganic molecules and an electron donor other than water and do not release oxygen.

Cyanobacterial toxins. Intoxication of lesser flamingo flocks by cyanobacterial toxins, and sometimes even mass fatalities have occurred in nearby Lake Bogoria when the birds ingest detached cyanobacterial cells from cyanobacterial mats flourishing in the vicinity of hot springs (Krienitz *et al.*, 2003). This is because the flamingos feeding at night on plankton blooms in a saline lakes need to drink fresh or brackish water after feeding, and to wash their feathers daily. They tend to do this in waters in the vicinity of the hot springs, where salinities are lower than in the main waterbody of the lake where they have been feeding. Mycosystin heptatoxins can characterize the benthic microbial community in those hot spring mats and waters can be dominated by the potentially toxic cyanobacterial association of *Phormidium terebriformis, Oscillatoria willei, Spirulina subsalsa and Synechococcus bigranulatus.*

Denitrification is the microbial process by which nitrates are removed from an aqueous liquid.

Dissimilatory metabolic processes drive the conversion of food or other nutrients into products plus energy-containing compounds.

Dissimilatory sulphate reduction. Sulphate-reducing bacteria gain energy for cell synthesis and growth by coupling the oxidation of organic compounds or molecular hydrogen to the reduction of sulphate to sulphide (H_2S, HS^-). This process is called "dissimilatory sulphate reduction", to allow clear differentiation from assimilatory sulphate reduction. Assimilatory sulphate reduction generates reduced sulphur for biosynthesis (e.g. of cysteine). It is a widespread biochemical capacity in prokaryotes and plants and does not lead to the excretion of sulphide. Only upon decay (putrefaction) of the biomass is the assimilated reduced sulphur released as sulphide.

Endosymbionts are organisms that live within the body or cells of another organism without deleterious effects.

Extremophiles are organisms that thrive in extreme conditions including: extremely saline (halophile), extremely hot (thermophile), extremely dry (xerophile), extremely acid (acidophile), extremely alkaline (alkaliphile), and extremely cold (psychrophile) environments.

Fermentation is of a series of anaerobic transformation processes whereby organic matter is broken down into compounds of smaller size, which are more reduced or more oxidized and eventually more assimilatable by living matter. When fermentation leads to organic acids and a lowering of pH, it is called acidogenesis. The microorganisms responsible for this are called acidogens.

Gram-negative and *Gram-positive* are responses to the Gram staining technique whereby micro-organisms are first stained with crystal violet, then treated with an iodine solution, decolourized with alcohol, and counterstained with safranine. Gram-positive bacteria retain the violet stain; Gram-negative bacteria do not.

"Halobacteria". Prior to hybridization studies and genome mapping, classification was based on morphology and staining, the evolutionary relationships among various members of the bacterial and archaeal domains were contradictory and poorly defined. Today some of these contradictions and confusions remain in microbial taxonomy of the group of microbial organisms broadly known as halobacteria, as distinct from the archaeal group Halobacteriales.

Halophilic organisms thrive at very high salt concentrations and can be killed by lower salinities.

Halotolerant (aka halovariant) organisms can tolerate high salt concentrations but grow better at somewhat lower salinities.

Haloxene organisms cannot tolerate high concentrations of salts.

Heterotrophs (literally "feeders on others") use organic molecules synthesized outside their body as a source of energy and carbon.

Holomixis indicates the entire mixing of the water column. Meromixis indicates partial or incomplete mixing.

Hopanoids are group of compounds (triterpenoids) produced by prokaryotic organisms, and the diagenetic alteration products of these compounds (found in oils, rock extracts and sediment extracts). Just as steroids (steranes) are a useful group of biomarkers for identifying input from various eukaryotic organisms (e.g. plants and animals), an analogous group of compounds, hopanoids, are a useful group of biomarkers for identifying input from various bacteria. Hopanoids serve the same function in bacteria as sterols do in eukaryotes: they act as cell wall rigidifiers. In petroleum and their source rocks, hopanoid biomarkers exist as a subset of a group of compounds called triterpanes (isoprenoids).

Hypersaline encompasses all waters more saline than seawater (mesohaline, penesaline and supersaline).

Hypertrophication describes the presence of excessive nutrients in a water body.

Isoprenoids are a major class of nonsaponifiable lipids that occur in plants, animals, and bacteria and are characterized by chains of modular groups of five carbon atoms in which the typical pattern has four of the carbon atoms in a linear chain and a single carbon attached at the carbon one position removed from the end of the chain. The term isoprenoid is derived from the name of the five-carbon, doubly unsaturated branched hydrocarbon isoprene, which could in principle be the simplest monomeric chemical precursor for this class of compounds. Isoprenoids are also known as terpenes. Terpenes are usually grouped according to the number of isoprene (C_5H_8) units in the molecule: monoterpenes ($C_{10}H_{16}$) contain two such units; sesquiterpenes ($C_{15}H_{24}$), three; diterpenes ($C_{20}H_{32}$), four; triterpenes ($C_{30}H_{48}$), six; and tetraterpenes ($C_{40}H_{64}$), eight. The carotenoid pigments are the best known tetraterpenes.

Lithotrophs are organisms that use an inorganic substrate (usually of mineral origin) to obtain reducing equivalents for use in biosynthesis (e.g. carbon dioxide fixation) or energy conservation via aerobic or anaerobic respiration.

Meromixis indicates partial or incomplete mixing. The term *meromictic* is used to describe a permanently stratified water mass where surface layers may mix, but the bottom layer does not. Many modern brine lakes are meromictic, the upper water mass comes and goes.

Mesophiles are organisms that grow best in moderate temperatures, neither too hot nor too cold, typically between 15 and 40 °C.

Mixolimnion. An upper water mass that periodically mixes is the mixolimnion, it sits atop the monolimnion.

Monolimnion. A lower, permanent unmixed water mass.

Neutrophilic organisms are not stained strongly or definitely by either acid or basic dyes, but are stained readily by neutral dyes.

Oligomictic or *oligotrophic* is used to describe stratified water masses that mix or homogenize for short irregular periods every few years.

Photoautotrophs use light as a source of energy and CO_2 as a source of carbon. Term comes from *autotrophs* (literally "self-feeders"), which describes organisms capable of producing organic compounds from simple inorganic compounds.

Photophosphorylation is the production of ATP using the energy of sunlight.

Platform evaporites are the other major type of ancient marine-fed evaporite. They formed on continental margins throughout much more of Phanerozoic time than basinwides. Salt fills are 10–50 m thick, mostly $CaSO_4$ and typically interbedded with normal-restricted marine carbonates. Stacked platform sections characterised by this style of accumulation encompass time frames of ~1–10 Myr and are largely tied to times in earth history when climate was in greenhouse mode and the associated eustacy favoured widespread epicontinental seaways subject to periodic restriction (Warren, 2006, 2010).

Red waters and brines. The pink to purple colours that typify many hypersaline water bodies come mostly from concentrations of carotenoid pigments present in the cytoplasm of various halotolerant and halophilic microorganisms. Most haloarchaea are red due to a high content of C-50 carotenoids of the bacterioruberin series. Photosynthetic cyanobacteria and eukaryotes (e.g. unicellular green algae of the genus *Dunaliella*) contribute to the pigmentation of the hypersaline waters thanks to the presence of chlorophylls and C-40 carotenoids (mostly all-*trans*- and 9-*cis*-β-carotene). Chlorophylls absorb red and blue wavelengths much more strongly than they absorb green wavelengths, which is why chlorophyll-bearing cyanobacteria appear green (Fig. 2B). The carotenoids and phycobiliproteins, on the other hand, strongly absorb green wavelengths. Algae and microbes with large amounts of carotenoid appear yellow to brown (such as carotene-rich forms of *Dunaliella sp*.), those microbes with large amounts of phycocyanin appear blue, and those with large amounts of phycoerythrin appear red. Pigment levels can indicate the stratification of the microbial community in any photoresponsive biomass in a brine column. Red wavelengths (long wavelengths) are absorbed in the first few metres of a brine column or the uppermost millimetre or two of a microbial mat (where chlorophyll utilizers flourish). Blue and green wavelengths (shorter) reach deeper into the brine column or into the sediment.

Saprophytes obtain nourishment by absorbing dissolved organic material; especially from the products of organic breakdown and decay.

Schizohaline describes waters subject to substantial ongoing salinity changes and periodically pass from brackish to hypersaline.

Third domain of life. In the late 1970s, Professor Carl Woese proposed, on the basis of ribosomal RNA affiliations (gene mapping), that life be divided into three domains instead of two, namely; Eukaryota, Eubacteria, and Archaebacteria (Woese, 1993). He later decided that the term Archaebacteria was a misnomer, and shortened it to Archaea and Eubacteria to Bacteria. Since the 1970s, DNA base-pair studies (aka genomic studies or gene sequencing) have shown that Archaea are as different from Bacteria as from *Homo sapiens*. This new approach to taxonomy is still working its way through the scientific community and some books and articles still ocassionally refer to archaea as types of bacteria. Prior to genomic studies, and based on their morphology and staining response, the archaeal Halobacteriaceae were grouped with the bacterial Gram-negative rods (a gram positive or gram negative description indicates whether or not the bacterial cell wall reacts with Gram's stain).

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