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Evaporites through time: Tectonic, climatic and eustatic controls in marine and nonmarine deposits

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ABSTRACT

Throughout geological time, evaporite sediments form by solar-driven concentration of a surface or nearsurface brine. Large, thick and extensive deposits dominated by rock-salt (mega-halite) or anhydrite (mega-sulfate) deposits tend to be marine evaporites and can be associated with extensive deposits of potash salts (mega-potash). Ancient marine evaporite deposition required particular climatic, eustatic or tectonic juxtapositions that have occurred a number of times in the past and will so again in the future. Ancient marine evaporites typically have poorly developed Quaternary counterparts in scale, thickness, tectonics and hydrology. When mega-evaporite settings were active within appropriate arid climatic and hydrological settings then huge volumes of seawater were drawn into the subsealevel evaporitic depressions. These systems were typical of regions where the evaporation rates of ocean waters were at their maximum, and so were centred on the past latitudinal equivalents of today's *horse latitudes*. But, like today's nonmarine evaporites, the location of marine Phanerozoic evaporites in zones of appropriate adiabatic aridity and continentality extended well into the equatorial belts.

Exploited deposits of borate, sodium carbonate (soda-ash) and sodium sulfate (salt-cake) salts, along with evaporitic sediments hosting lithium-rich brines require continental–meteoric not marine-fed hydrologies. Plots of the world's Phanerozoic and Neoproterozoic evaporite deposits, using a GIS base, shows that Quaternary evaporite deposits are poor counterparts to the greater part of the world's Phanerozoic evaporite deposits. They are only directly relevant to same-scale continental hydrologies of the past and, as such, are used in this paper to better understand what is needed to create beds rich in salt-cake, soda-ash, borate and lithium salts. These deposits tend to be Neogene and mostly occur in suprasedalevel hydrographically-isolated (endorheic) continental intermontane and desert margin settings that are subject to the pluvial–interpluvial oscillations of Neogene ice-house climates. When compared to ancient marine evaporites, today's marine-fed subsealevel deposits tend to be small sea-edge deposits, their distribution and extent is limited by the current ice-house driven eustasy and a lack of appropriate hydrographically isolated subsealevel tectonic depressions.

For the past forty years, Quaternary continental lacustrine deposit models have been applied to the interpretation of ancient marine evaporite basins without recognition of the time-limited nature of this type of comparison. Ancient mega-evaporite deposits (platform and/or basinwide deposits) require conditions of epeiric seaways (greenhouse climate) and/or continent–continent proximity. Basinwide evaporite deposition is facilitated by continent–continent proximity at the plate tectonic scale (Late stage E through stage B in the Wilson cycle). This creates an isostatic response where, in the appropriate arid climate belt, large portions of the collision suture belt or the incipient opening rift can be subsealevel, hydrographically isolated (a marine evaporite drawdown basin) and yet fed seawater by a combination of ongoing seepage and occasional marine overflow. Basinwide evaporite deposits can be classified by their tectonic setting into: convergent (collision basin), divergent (rift basin; prerift, synrift and postrift) and intracratonic settings.

Ancient platform evaporites can be a subset of basinwide deposits, especially in intracratonic sag basins, or part of a widespread epeiric marine platform fill. In the latter case they tend to form mega-sulfate deposits and are associated with hydrographically isolated marine fed saltern and evaporitic mudflat systems in a greenhouse climatic setting. The lower amplitude 4 and 5th order marine eustatic cycles and the greater magnitude of marine freeboard during greenhouse climatic periods encourages deposition of marine platform mega-sulfates. Platform mega-evaporites in intracratonic settings are typically combinations of halite and sulfate beds.

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1. Introduction

By definition, for an evaporite salt to precipitate, liquid water loss from a brine mass must exceed inflow and the brine concentration process should be driven by solar evaporation (Warren, 2006). Throughout time, evaporite salts have accumulated on the floors of standing brine lakes or seaways, in near-surface pore throats, and as capillary efflorescences atop exposed arid landsurfaces. Variation in the resultant textures (subaqueous versus sabkha versus burial salts) indicate both hydrological stability and mechanical energy level in the brine at the time of precipitation. The diversity and extent of ancient evaporite deposits is far greater than in the eustatically and time limited sample available for study in Quaternary evaporite deposits (Fig. 1).

All evaporites are ionic salts containing the major ions Na, Ca, Mg, K, Cl, SO_4 , and CO_3 in varying proportions, along with other less common ionic constituents such as B, Ba, Sr, Br, Li and I and varying amounts of bound or structural water (Appendix A lists chemical formulae). Mineralogy and order of salts precipitating in a concentrating brine is controlled by the ionic make-up of the parent water (Hardie and Eugster, 1970). Deposits of various evaporite salts can be classified according to the source of the mother brine; they can be marine (thalassic ionic proportions), nonmarine (athalassic) or a blend of the two brines, along with varying inputs from deeply circulated meteoric, basinal and hydrothermal waters. Throughout deposition and burial, evaporite beds subject to variable fluid crossflows show reaction rates and precipitative reversibilities (backreactions) that are an order of magnitude faster than for non-evaporite sediments.

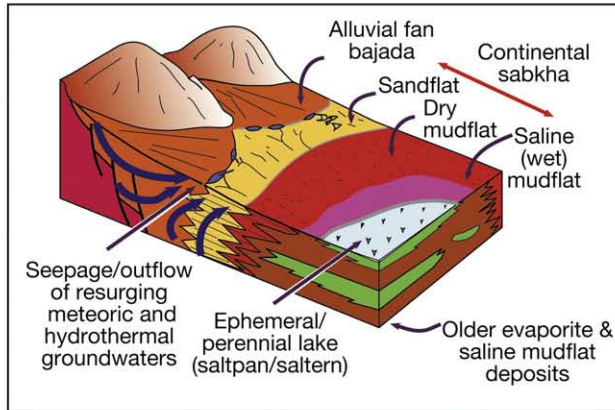
Mineralogically, most bedded ancient evaporites are varying combinations of 1) alkaline earth carbonates, 2) gypsum or anhydrite and 3) halite, with or without 4) the potash-entraining salts or bitterns such as sylvite, carnallite, polyhalite and epsomite. These 4 mineralogical groupings constitute more than 95% by volume of the world's Phanerozoic and Neoproterozoic evaporites, with anhydrite (typically with a gypsum precursor) and halite being the two dominant evaporite minerals. Varying combinations of sodium carbonate (soda-ash), sodium sulfate (salt-cake), and sodium borate salts constitute much of the remainder of the world's evaporitic sediments. Borate, salt-cake and soda-ash salts, which are all economically exploited, mostly precipitate in continental tectonically-active arid lacustrine, rather than marine, settings.

Most exploited evaporite salts and their associated brines are used in the manufacture of various chemical feedstocks, especially in the chloralkali industries, with lesser volumes supplying feedstock to the fertiliser industry (Table 1). Volumetrically, halite (rock-salt) is the most utilised evaporite salt, principally as feedstock to the chemical industry for the manufacture of a wide range of industrial chemicals (Table 2). In cold climates substantial volumes of crushed rock-salt are used for road de-icing. Next after rock-salt is gypsum, which is chiefly used in the manufacture of wallboard, plaster and cement for the world's construction industries. Next in terms of extracted volume is soda-ash, which is used in the manufacture of glass and detergent; then the potash salts, primarily used to manufacture agricultural fertilisers; then the borates and the sodium sulfates, all with a variety of industrial usages. Lithium (as lithium carbonate) is increasingly extracted from a brine rather than a solid mineral source.

Throughout the Phanerozoic the largest nonmarine evaporite deposits typically accrued at depositional scales that were more than an order of magnitude smaller than the larger of the ancient marine-fed evaporite (Fig. 2). This dichotomy in scale reflects the simple aphorism that the hydrology needed to form a huge mass of halite-dominant evaporites requires a huge volume of brine inflow, along with high levels of Na and Cl in the inflow. Such long-term reliable brine supply volumes and ionic proportions are simply not available in meteoric-fed saline lacustrine settings.

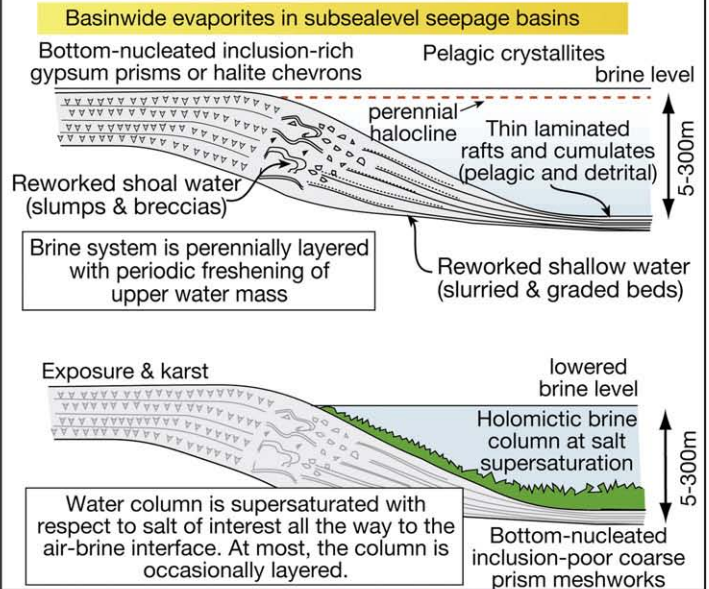
As long ago as 1877 the need for a marine brine supply to form large volumes of halite-dominant evaporites was recognised by Oschenius and by the middle of last century it was considered a truism by workers such as Borchert and Muir 1964; Holser and Kaplan, 1966; Kinsman, 1974. In the 1980s and 1990s the widely accepted axiom of a dominantly marine source for ancient evaporites was questioned by workers, such as Eugster, 1980 and Hardie, 1991, who were studying Quaternary lacustrine salts in nonmarine settings that were locally rich in halite-dominant deposits. These authors tended to be more focused on understanding controls to variations in the geochemistry of nonmarine brines and where and why ionic proportions in continental groundwaters could sometimes mimic seawater. For example Hardie (1991; p 138) stated, "...the dominance of sodium chloride brines in modern continental saline lakes offers a tangible contradiction of this dogma" (*of a marine source for large evaporite deposits*). Hardie (op, cit; p. 139) goes on to note that some

Depositional spectrum of ancient evaporite systems across deep time



CONTINENTAL (NONMARINE FEED)
sabkhas, saline pans, salt lakes

Quaternary analogues in texture, scale and hydrology (borates, salt cake, soda ash with halite and variable CaSO_4)

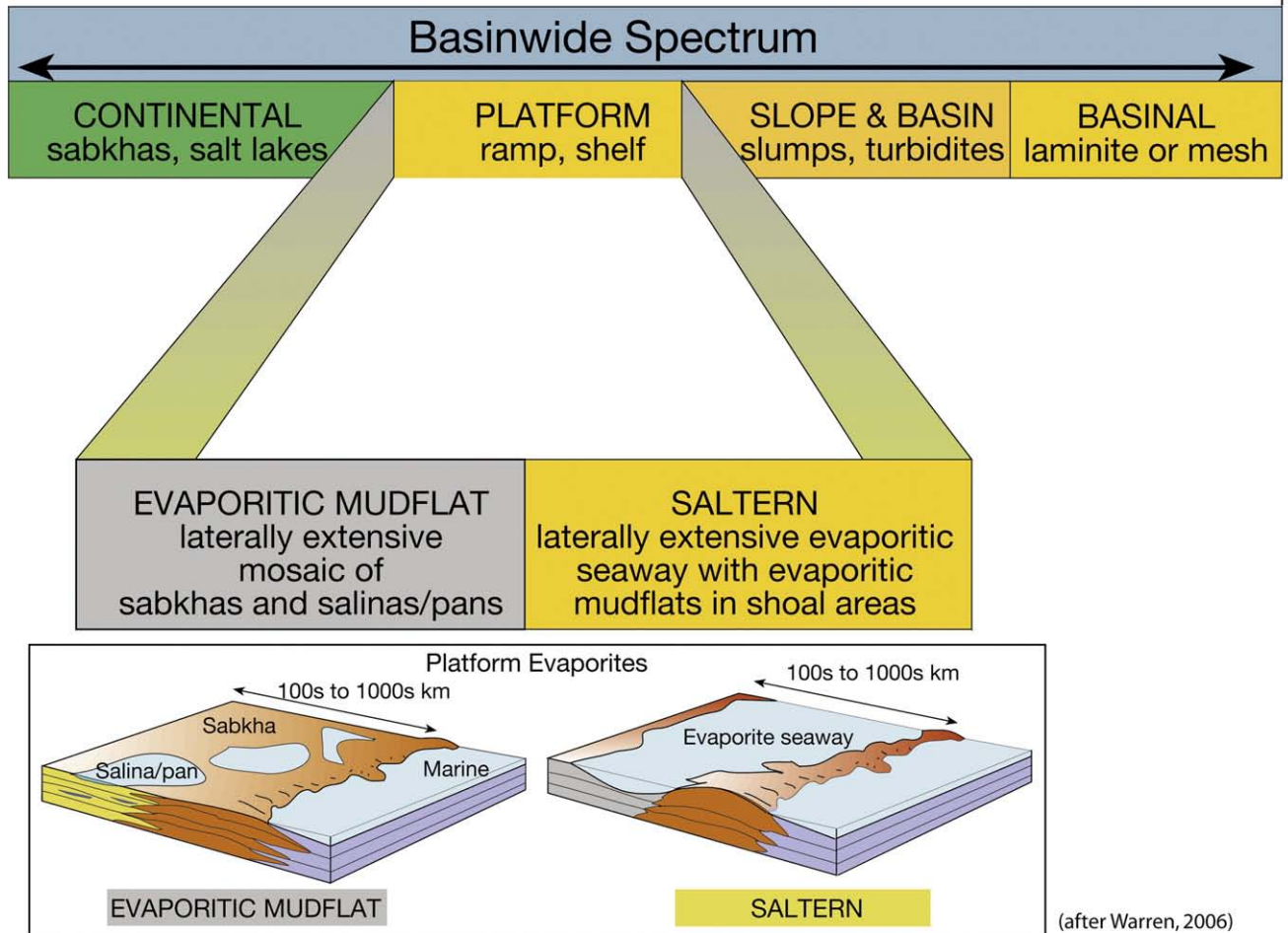


MARINE FEED platform

slope

MARINE FEED basin

Partial textural analogues, no marine Quaternary analogues in scale or tectonic setting (potash, widespread thick halite and anhydrite)



(after Warren, 2006)

Fig. 1. Evaporite depositional settings in the context of time and process (after Warren, 2006). Only continental lacustrine settings have same-scale ancient and Quaternary age counterparts.

Table 1

Uses of evaporite salts, byproducts and brines (after Warren, 2006). Magnesia, Br, I₂ and NH₄ salts are not further discussed in this paper.

Type	Mineralogy	Source	Uses
Rock-salt (halite)	NaCl	Halite, brine processing	Chloralkali industry for manufacture of chlorine, sodium hydroxide and other related industrial chemicals and industrial products, road de-icing, food processing, water softening, swimming pool additive, stockfeed additive
Gypsum	CaSO ₄	Gypsum, including secondary after anhydrite	Construction industry, mostly in wallboard and plaster products, cement retardant, agricultural soil enhancer, high purity forms used in wide range of industrial processes including glass manufacture and smelting
Potash (mostly sylvite)	KCl, KNO ₃ , K ₂ SO ₄	Sylvite, sylvinitic, brine processing	Fertiliser (main usage), use as feedstock to chemical industry to manufacture KCl, KOH, K ₂ CO ₃ , several forms of potassium phosphate, many other potassic chemicals, drilling muds, also used in recycling alumina, electroplating, etc
Borates	B ₂ O ₃	Borax (tincal), boracite, colemanite, hydroboracite, kernite, ulexite	Glass, ceramics, fibreglass, textile manufacture, agricultural chemicals, pharmaceuticals, flux cleansing agent, detergents, water softener, preservative and fire retardant
Sodium carbonate (soda-ash)	Na ₂ CO ₃	Trona, solvay process, brine processing	Glass manufacture, chemicals, soap and detergents, pulp and paper manufacture, water treatment, and flue gas desulfurization
Sodium sulfate (salt-cake)	Na ₂ SO ₄	Mirabilite, thenardite, glauberite, brine processing	Filler in soap and detergent powder, textile and glass manufacture, pulp and paper industry, carpet fresheners
Lithium	Li	Brine Processing, hectorite in some saline clays	Production of ceramics, glass, and primary aluminium, battery technology, pharmaceutical
Calcium Chloride	CaCl ₂	Brine processing	Deicing, dust control, road stabilization, concrete curing, oil well drilling, tire ballasting
Magnesium carbonate, Magnesium oxide, Magnesium sulfate	MgCO ₃ , MgO, MgSO ₄	Brine Processing, magnesite, electrolytic processing	Majority used for refractories. A constituent in aluminium-base alloys, used for packaging, transportation, and other applications. Remainder is consumed in agricultural, chemical, construction, environmental, and industrial applications
Bromine (sodium bromide)	Br ₂ , NaBr	Brine Processing	Additive
Iodine	I ₂	Brine Processing	Animal feed supplements, catalysts, inks and colorants, pharmaceutical, photographic equipment, sanitary and industrial disinfectant, and stabilisers
Ammonium chloride Ammonium sulfate	NH ₄ Cl, (NH ₄) ₂ SO ₄	Brine Processing	Fertiliser, industrial additive

gypsum–halite lacustrine deposits have “... thicknesses that rival their ancient geological counterparts presumed to be of marine origin” and that “... the only important modern potash evaporites deposited today are nonmarine.”

2. Depositional parity across time and space

Such geochemical work did not address the hydrological need for same-scale geohydrological mechanisms that could supply the huge volumes of brine needed to form ancient mega-halite deposits. Nor did it consider the fact that today's marine evaporite settings form within the confines of Quaternary icehouse climate and eustasy: they are not the depositional counterparts to ancient marine evaporites. Most Phanerozoic platform evaporites accumulated under greenhouse climate regimes with inherently different eustatic frequencies and amplitudes and within very different epeiric to pericontinental marine-margin settings. Nor do Quaternary evaporite depositional spectra, which today range across a number of separate continental suprasedalevel landmasses (Fig. 1), give appropriate same-scale matches, especially in terms of tectonic setting, to evaporite depositional spectra in and around the edges of ancient supercontinents (e.g. Pangaea in the mid Phanerozoic and Rodinia in the Neoproterozoic). Many of the larger halite-dominated ancient marine evaporite deposits accumulated in tectonically-induced subsealevel depressions that were associated with past times of widespread world-scale continent–continent proximity, especially in times

marked by the accretion and disaggregation stages of supercontinents (Warren, 2006, 2008).

Worldwide true-scale deposit distribution maps imply that current meteoric water-fed Quaternary lacustrine settings do not explain the scale of depositional settings for ancient saline giants (Fig. 2). Undeniably, as noted by Hardie, 1991, there are a number of Quaternary lacustrine basins containing interbedded halite–mudstone sediment successions up to 900 m thick and up to 10,000 km² in area. These deposits, which are our largest and thickest accumulations of Quaternary bedded halite, occur in local zones of groundwater ponding in regions of endorheic drainage within zones of intermontane lacustrine subsidence (see Chapters¹ 3 and 4 in Warren, 2006 for deposit details). The largest known Quaternary halite deposits in the world are Salar de Uyuni (9654 km² and >120 m thick) and Salar de Atacama (3064 km² and >900 m thick), both deposits are in endorheic depressions located in or near the Andean Altiplano and are more than 2000 m above sealevel.

The Dead Sea depression (1023 km²) is another impressive example of Quaternary endorheic continental salt deposition; not so much in terms of area but in that cm-scale crystalline meshworks of inclusion-free halite are accumulating across the basin floor in water depths down to 370 m (Fig. 1). This deepwater halite has been accumulating since 1979 when the brine column became holomictic, after a meromictic phase lasting some 400 years. The meromictic phase was associated with the deposition of pelagic carbonate laminites on the deep lake bottom. With its current brine surface around 415 m below sealevel, the Dead Sea region is the world's deepest continental landsurface.

In lateral scale and deposit thickness the two South American continental lacustrine deposits dwarf all Quaternary marine-fed sea-edge evaporite deposits including Lake Macleod in Western Australia (Fig. 2). This is the largest of the world's Holocene subaqueous marine

Table 2

World production of evaporite salts, all values are in thousand metric tons (as published by US Geological Survey (USGS) and available from <<http://minerals.usgs.gov/minerals/pubs/commodity>>).

Year	2002	2003	2004	2005	2006
Salt (halite)	214,000	221,000	233,000	246,000	251,000
Gypsum	111,000	114,000	120,000	122,000	125,000
Soda-ash	37,200	38,400	40,600	42,000	42,400
Potash (K ₂ O eqv.)	27,100	28,600	31,100	32,500	29,100
Boron minerals	4580	4720	5070	5090	4260
Salt-cake	No reliable published data; annual production is around 4 million metric tons				

¹ Throughout this review paper I will make reference to various chapters in my last book (Warren, 2006). This is not done as a form of self aggrandizement, but points the interested reader to a discussion and listing of the comprehensive literature base related to the mentioned general topic. For example, the discussion of specific worldwide Quaternary salina, mudflat and playa basins with endorheic hydrologies ties to a literature base of more than 600 references in the two mentioned chapters and listed in the book's reference section.

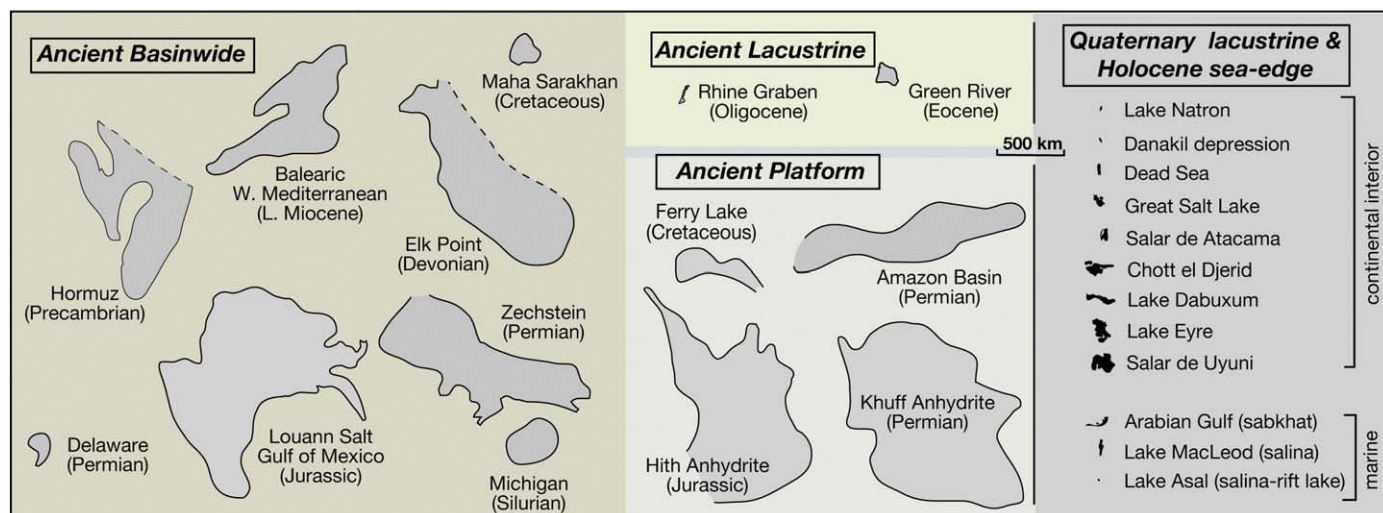


Fig. 2. Evaporite extent past and present. All areas are compiled at the same scale, see 500 km scale bar.

evaporite deposits with an area of 2066 km² and a maximum evaporite thickness (halite + gypsum) of some 12 m. They also outdo, in size and volume, the CaSO₄-dominant Abu Dhabi coastal sabkha system (area of 1654 km² and evaporite thickness less than a metre), which constitutes much of the southeast coastal region of the present-day Arabian (Persian) Gulf and is our largest well-studied example of a modern coastal sabkha.

But the volumes and area of salts in salars Uyuni and Atacama pale to insignificance when compared to ancient marine-fed halite-dominant systems such as the Aptian salt basins of the southern Atlantic (area of 741,000 km², depositional thickness up to 1 km) or the various Messinian sub-basins of the Mediterranean (1,148,000 km², depositional thickness up to 1 km). Similarly there is an obvious scale discrepancy between sulfate extent in modern sabkhas of the Abu Dhabi region and ancient marine-fed sulfate platform evaporites, such as the Middle Anhydrite Marker (aka Nab and Khuff-D members) of the Permian Khuff Fm (1,207,000 km² and 40–50 m thick) or the anhydrites in the Triassic Hith Formation (1,107,000 km² and ≈100 m thick) of the Middle East. Both these ancient Ca-sulfate beds are more than 4 orders of magnitude larger than any modern coastal sabkha or salina.

The same scale discrepancies are obvious when we compare the areal extent of the world's largest Quaternary continental potash deposits with the largest ancient single bed potash examples. The Late Quaternary potash bed forming in Dabuxum Lake, China, as alluded to by Hardie (1991; see earlier quote), has an area of 310 km² and a thickness that is less than a few metres, whereas potash in the Devonian Prairie Evaporite of Canada has an area of 192,000 km² in stacked potash successions where individual ore bed thicknesses range up to 3–4 m. All these scale discrepancies underline the axiom that suitable volumes of NaCl, CaSO₄ or KCl brines were not supplied by arid meteoric water hydrologies to large ancient saline depressions, otherwise we should see the same scales of evaporite deposition in the Quaternary that we see in the past.

Although solar evaporation is the dominant evaporite-forming mechanism in the arid “horse latitude” climate belts of today's world, local aridity is not always tied to higher temperatures. For example, evaporite salts form in some cold arid settings where water or brine freezes and the ionic content increases in the remaining liquid (Marion et al., 1999). Salts, such as halite, calcite, mirabilite, thenardite and hydrohalite and even antarcticite, can accumulate as efflorescences and lake floor deposits in such cryogenic regimes. The mother brine to cryogenic salts can be marine or nonmarine, as in the modern polar desert valleys of Antarctica where saline water is sourced in interstitial cavities and inclusions in small volumes of snow

or ice. These salts are derived by a combination of relict seawater, the reworking of marine aerosols carried inland from the coast, and variable volumes of deeply circulated groundwater (Takamatsu et al., 1998). In the dry desert valleys of Antarctica periodic down-valley katabatic winds, with speeds up to 200 km/h, remove free moisture from the landscape and so precipitate cryogenic salts atop the cold valley floors.

Evaporite minerals, especially gypsum and anhydrite, can also accumulate in heated volcanic terrains via subsurface temperature changes imposed on seawater or hydrothermal brines. For example, in the Naica Silver mine (Chihuahua, Mexico) there are several natural caves containing giant, faceted and transparent single crystals of gypsum that are up to 11 m long (García-Ruiz et al., 2007). They grew from cooling hydrothermal solutions created by dissolution of disseminated anhydrite, previously precipitated during late hydrothermal mineralization of the volcanogenic matrix.

Elsewhere, many active hydrothermal mounds are situated along submarine oceanic ridges and contain high levels of hydrothermal anhydrite that precipitated via heating of seawater during the escape of hot hydrothermal waters. Due to anhydrite's retrograde solubility (refer to Fig. 9B), the heating of adjacent seawater precipitates the anhydrite as “white smokers.” Hydrothermal anhydrite frequently occurs in close proximity to metal sulfide precipitates within “black smokers” of the oceanic ridges or in bedded metalliferous deposits on the floor of the Atlantis II Deep in the Red Sea. Drilling into the metalliferous Tag Mound on the Mid Atlantic Ridge intersected anhydritic breccias that contained more than 25% hydrothermal anhydrite (Humphris et al., 1995). This anhydrite dissolves once active hydrothermal circulation ceases, so that ancient VHMS deposits lack direct evidence of the former presence of substantial amounts of hydrothermal anhydrite and only deposit-specific breccias remain (see Warren, 1999, Chapters 8 and 9 for more detailed discussion).

Volumetrically, hydrothermal and cryogenic salts on Planet Earth are probably less significant than salts derived via solar evaporation (although in terms of hydrothermal halite this statement is contested by Hovland et al., 2006). Extra-terrestrially, the influence of cryogenesis and hydrothermal alteration can be more pronounced, as on the surface of some of the moons of Jupiter and in saline sediment beds among the Martian polar dunes (McCord et al., 1998; Fishbaugh et al., 2007; Osterloo et al., 2008).

On Earth, evaporite deposition and diagenesis is more climate and pore-fluid chemistry dependent than the equivalent processes in either terrestrial siliciclastic or carbonate sediments. Evaporite salts show a propensity to dissolve with brine freshening and/or subaerial exposure. They maintain a high degree of ongoing reactivity both

syndepositionally, via backreactions with the evolving parent brine, or later via diagenetic changes in pore fluid chemistry and the formation of burial salts. It is this ongoing propensity for subsurface alteration and dissolution that drives many base metal associations within evaporite terrains (Warren, 2000a). Alteration, replacement and reprecipitation continue deep into the subsurface until the salt mass is completely dissolved or transformed to meta-evaporite phases, such as sodian scapolite or dravite–uvite tourmaline.

Similarly, a portion of the world's gemstones in metamorphic terrains form because of unusual ionic proportions that occur locally in mineralising fluids tied to metamorphosing evaporites. For example, many marble-hosted rubies in the Tertiary-age Himalayan collision belt of SE Asia can be tied to local closed-system alteration of meta-evaporites. This form of gem ruby precipitated via thermal reduction of evaporites along with organic matter, at pressures of 3 kbar in a temperature range of 620–670 °C. It crystallised during high temperature-medium pressure metamorphism of evaporitic platform carbonates that were caught up in the India–Asia collision (Garnier et al., 2008). Likewise, Columbian emeralds form via thermochemical sulfate-reduction in an organic-rich, meta-evaporite association (Giuliani et al., 2000). Lapis lazuli is another meta-evaporite mineral (Faryad, 2002).

But these deposits emphasise the unusual, let us now return to the main dichotomy that characterizes modern and ancient evaporites, namely the geological and hydrogeochemical character of marine and nonmarine evaporites. To clarify the distinction and to develop a set of observations relevant to world-scale exploration and development models for various evaporite salts, we will place much of the following discussion into a tectonic and time-based framework using GIS-scaled comparisons. Base data for this compilation are extracted from a GIS database collated by JK Resources Pty Ltd.

3. Nonmarine evaporites

Continental waters with a strong meteoric influence have sourced most of the world's currently exploited soda-ash, salt-cake and borate deposits (Table 2). Typically they were deposited in the low areas of saline lacustrine landscapes in intermontane depressions, with basin floor elevations that were well above sea level at the time the salts were accumulating. Most commercially exploited nonmarine evaporite deposits are Tertiary, especially Neogene, in age and, even when buried, still lie at subsurface elevations that are mostly above sealevel (Warren, 1999, 2006).

3.1. Nonmarine hydrogeochemistry

Unlike marine-derived brines, evaporating continental waters do not draw on the near isochemical high-volume reservoir of the global ocean. Compared to marine evaporite mineral assemblages, ionic proportions in nonmarine assemblages are more diverse and less predictable. They precipitate within various suprasedimental, continental depressions and include large accumulations of borates, soda-ash and salt-cake. Such deposits formed from mother brines that could not have had marine-like ionic proportions.

In a closed hydrological system the composition of concentrated lake brines largely depends on labile lithologies that are leached and altered by inflow waters in the drainage basin surrounding a salt lake (Hardie and Eugster, 1970; Eugster 1980). Flow across and through limestone aquifers produces inflow waters rich in Ca and HCO_3 , dolomite dissolution generates Mg-rich waters, igneous and metamorphic matrices tend to yield silica-rich Ca–Na– HCO_3 waters. Pyritic shales and other sulfur-rich sediments, such as tuffaceous ashfalls, will contribute inflows rich in sulfate, whereas basic and ultrabasic rocks tend to produce alkaline Mg– HCO_3 waters.

In all, Hardie and Eugster (1970) distinguished five major water types in what they termed “hydrologically closed”² continental evaporite basins (Fig. 3A):

1. Ca–Mg–Na–(K)–Cl
2. Na–(Ca)– SO_4 –Cl
3. Mg–Na–(Ca)– SO_4 –Cl
4. Na– CO_3 –Cl
5. Na– CO_3 – SO_4 –Cl waters.

As any one of these waters concentrates within a particular evaporite basin, it deposits a characteristic suite of evaporite minerals, that as well as halite and variable levels of gypsum, can include exploitable deposits of borate, soda-ash (Na-carbonates) and salt-cake (Na-sulfates). First precipitates in all groups are alkaline earth carbonates: low-magnesian calcite, high-magnesian calcite, aragonite, and dolomite, with mineralogy of this initial precipitate depending on the Mg/Ca ratio of the parent brine. Proportions of sodium, calcium, magnesium, and bicarbonate ions in the brackish inflow waters determine the subsequent evaporation pathway of “closed basin” brines (Fig. 3B).

If lake waters are enriched in HCO_3 compared to Mg and Ca (i.e. $\text{HCO}_3 \gg \text{Ca} + \text{Mg}$), then the brine follows path I (Fig. 3B). Calcium and magnesium are depleted during the initial precipitation of alkaline earth carbonates, leaving excess HCO_3 in the brine. As HCO_3 is the next most abundant ion in these waters, it combines with Na in the next stage of concentration. Sodium carbonate minerals such as trona, natron, thermonatrite and nahcolite precipitate, typically associated with shortite and dawsonite. It is this nonmarine (lacustrine) path I brine chemistry that controls the formation of the world's exploited soda-ash (trona) deposits, exemplified by the Wilkins Peak Member of the Eocene Green River Formation in the Green River Basin, USA, the Eocene Wulidui Fm. in the Wucheng Basin of China and the Miocene Hirka Fm. in the Beypazari Basin of Turkey. Little or no gypsum forms in pathway-I brines as all the Ca is consumed during the preceding alkaline earth carbonate stage.

Hence, it is chemically impossible to form sodium carbonate minerals by evaporation of brine with the ionic proportions of modern seawater. In seawater, all the HCO_3 , not the Ca, is depleted in the initial alkaline earth precipitates during the evaporation of modern seawater (mostly as aragonite and Mg-calcite). The remaining Ca then combines with SO_4 to form gypsum, which has been a widespread marine evaporite salt since the Mesoproterozoic. Micro-inclusion analyses of Phanerozoic chevron halite shows that calcium has always been present in seawater at concentrations that were well in excess of bicarbonate (Lowenstein et al., 2001). Thus the presence trona and other sodic carbonates, such as nahcolite or shortite (or their pseudomorphs), in bedded evaporites deposited over last 600–800 m.y. indicates a nonmarine brine source.

However, nahcolite and trona were marine evaporite salts in the early Archaean (Sugitani et al., 2003). This was a time when the world's oceans were much warmer, the atmosphere was much richer in CO_2 , and the oceans had a Na– HCO_3 –Cl chemistry, not the Na–Cl dominated water of Phanerozoic seas.

If initial inflow waters have $(\text{Ca} + \text{Mg}) \gg \text{HCO}_3$ then, after the initial evaporitic carbonate precipitates, the brines become enriched in the alkaline earths, but depleted in HCO_3 and CO_3 . If the relative volume of HCO_3 is low, little carbonate can precipitate with further concentration. Brine evolution follows path II, whereby excess alkaline earths (Ca and Mg) left after depletion of carbonate combine with sulfate ions to precipitate large volumes of sulfates (gypsum and/or epsomite). Some Path II waters can precipitate a suite of continental salts dominated by gypsum and halite, with mineral

² In my opinion the term “hydrographically closed” better describes the hydrological situation. Surface inflow is endorheic but many such basins tend to gain or lose subsurface waters and so are not truly “closed” in terms of basin hydrology.

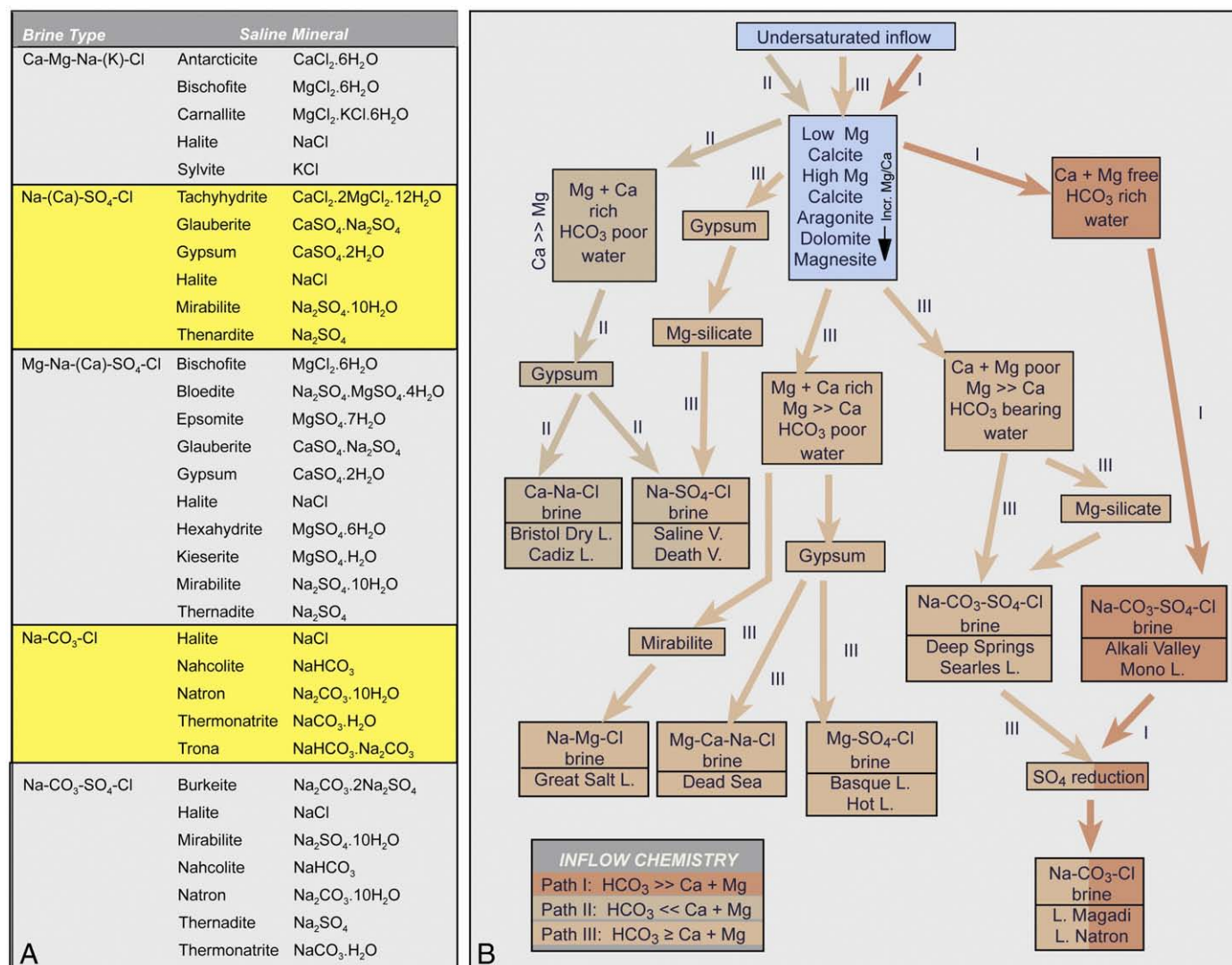


Fig. 3. Nonmarine brine evolution (after [Hardie and Eugster, 1970](#)). A) Five principal brine types and associated minerals in “closed” hydrological settings. B) Evolution of concentrating brines showing dependence on ionic proportions in the inflow waters (Paths I–III).

proportions similar to that derived from modern seawater. Path II continental waters are commonplace in arid saline settings in the modern arid interiors of the cratonic regions of Australia and southern Africa (see [Warren, 2006](#), Chapter 2 for detail).

If the ratio of $(\text{Ca} + \text{Mg})/\text{HCO}_3$ is near unity (path III), then carbonate precipitation can be extensive and voluminous. As Ca is progressively removed from a concentrating brine there is a progressive increase in the Mg/Ca ratio of the residual brine until large volumes of high-Mg lacustrine calcite, dolomite and even magnesite precipitate, as in numerous lakes in the Holocene coastal plain of the Coorong region in Australia and Salda Lake in Turkey.

If path III inflow waters are enriched in SO_4 compared to Ca and Mg then the sodium sulfate (salt-cake) minerals, mirabilite, thenardite and glauberite are typical precipitates. Sulfate-enriched inflows occur in lacustrine settings where the runoff and groundwater passes through lithologies with a high proportion of the appropriate labiles. Mother beds for these brines include active volcanic (andesitic) areas, pyritic labile-rich glacial outwash plains, and source brines derived by the active groundwater recycling of older uplifted marine evaporites in nearby mountain belts ([Risacher and Alonso, 2001](#); [Pueyo et al., 2001](#); [Last and Ginn, 2005](#); [Salvany et al., 2007](#)).

Where such sulfate-rich brines pond in lacustrine depressions in cooler arid climates, the cooling of such waters, on either a diurnal or a

seasonal basis drives the precipitation of mirabilite, as occurs in the seasonally exploited salt-cake lakes of the Great Plains of Canada, some high altitude lakes in the Andes and in the Kara-Bogaz embayment of the Caspian Sea. When sulfate-rich waters concentrate in warmer climates then thenardite and glauberite are typical evaporite salts, as is the case in the exploited Oligo-Miocene deposits of northern Spain ([Salvany et al., 2007](#)) and Turkey ([Orti et al., 2002](#)). In regions where mirabilite is the primary precipitate, it is typically a metastable phase that alters to thenardite/glauberite with burial or with at surface seasonal increases in temperature.

Clearly, it is not just the occurrence of an evaporite mineral that is important as a pointer to a marine or nonmarine source. With the possible exception of the sodian carbonates, no single evaporite mineral or local hydrogeochemistry is an exclusive pointer to a marine or nonmarine setting. However, thick bedded deposits dominated by high levels of salt-cake or soda-ash minerals required a brine source that did not have a marine-like ionic composition, likewise for economic accumulations of evaporitic borates and lithium carbonates.

3.2. Climatic framework

Many geologists working with evaporites have an expectation that bedded salts form mostly in hot arid deserts within world-scale

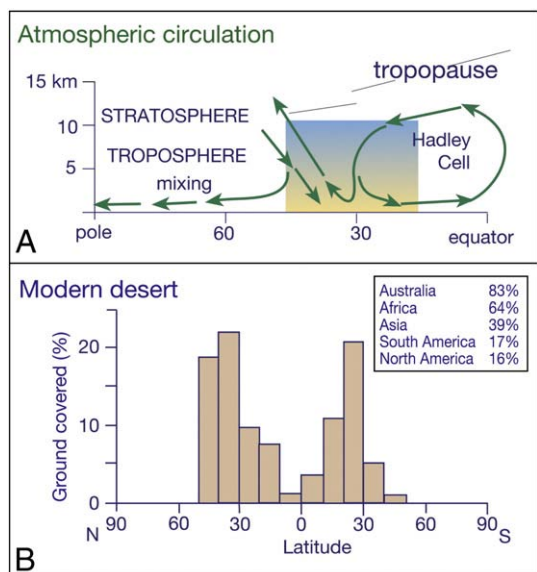


Fig. 4. Modern climatic belts. A) Longitudinal cross section through the earth's atmosphere showing major circulation cells. Belts of cool dry descending air (shaded) around 15–45°N and S of the equator create the main arid zones of the world also known as the "horse latitudes". B) Latitudinal distribution of the area of landsurface covered by world's modern deserts, inset gives percentage of each continental area that is classified as arid or semiarid.

climatic regions known as the *horse latitudes*. The term *horse latitudes* encompasses the regions beneath the north and south Subtropical High atmospheric pressure belts (Oliver, 2005, p. 462). Marked by dry sinking air masses, the Subtropical High atmospheric pressure belts form part of the world's Hadley cells and today are centred around 35° N and 30° S, extending approximately 25° to 40°, respectively, N and S (Fig. 4A). They shift seasonally, to the north in the northern summer and to the south in the southern summer. The two belts correspond approximately to world-scale areas of maximal potential evaporation. Over the oceans the horse latitudes correspond approximately to the areas of maximal evaporation, while over land the air is exceptionally dry and sits atop many of the world's deserts (Fig. 4B).

Fig. 5A illustrates modern Koeppen climatic zones, with hot arid deserts indicated by BWh (after Kottek et al., 2006). Figs. 5B and 6 plot a number of exploited or exploitable nonmarine Quaternary salt deposits against latitude, local Koeppen climate setting and elevation of the basin floor. While some of the listed deposits lie in the horse latitudes, many occur outside this range, with the largest Quaternary halite deposits (Salar de Uyuni and Salar de Atacama) forming in and around the alpine tundra belt of the High Andes.

It seems that many nonmarine evaporite deposits such as Wadi Natrun and Laguna del Rey, which do occur in BWh zones, do not occur in the centres of the encompassing desert plains. Rather, they tend to define the edges of the interior desert in zones of local topography where sufficient volumes of surface and nearsurface water can pond for sufficient time to allow thick salt beds to accumulate. Other Quaternary evaporite deposits, such as Lake Chad and Lake Giuletti, which are situated in hot arid desert (BWh) settings and lie outside the horse latitudes, are a response to high continentality or local adiabatic conditions (see Warren, 2006; Chapter 2 for a detailed discussion of controls on world deserts). Local orographic desert conditions (rain-shadow deserts) in the East African rift valley have created trona

deposits situated a few degrees from the equator (Aw) and have facilitated the accumulation of Quaternary potash in the Dallol salt pan of in the rift valley of Ethiopia at a latitude of 14°N (BWh).

Outside of BWh zones, many Quaternary continental deposits are situated in water-stressed climatic belts typified by cooler temperatures (BWk and BSk), higher altitude arid steppes (BSh and Csa) or snowy arid sometimes mountainous conditions (Dfb and Dwc). Some such small but numerous deposits, dominated by temperature-dependent mirabilite precipitates, dot the cold interior glacial plains of Canada (Dfb) and the alpine tundra (ET) of the High Andes. Salar de Uyuni and Salar de Atacama lie in a BWk zone along the edge of the alpine tundra zone of the Andes. Bedded salts in these various cooler arid settings are a response to lower evaporation rates and associated longer time frames for ponding of surface brines. Accordingly, compared to the less extensive and/or thinner salt deposits of the BWh zone, larger areas and thicker beds of bedded nonmarine Quaternary salts tend to accumulate in these cooler arid settings where hypersaline meteoric surface waters can pond across longer time frames.

Immediately beneath the halite and sulfate beds in many lakes and playas currently situated in arid continental settings, especially in desert (BWh and BWk) margins and arid steppes, there are earlier Holocene and Late Pleistocene sediment records of climatic oscillations. For example, many halite beds in the salars of the Andes and the playas of the Basin and Range contain subaqueous mudstones intercalated with beds of saline pan and subaerial halite (Lowenstein et al., 1999, 2003). These mudstones were deposited in past humid or pluvial climatic episodes, perhaps related to Pleistocene times when the polar icesheets had expanded compared with today. Likewise, there are late Pleistocene pluvial lacustrine deposits beneath modern chott sediments in the marginward portions of the Saharan erg (Swezey et al., 1999). But not all intervals characterised by more humid intervals within saline lacustrine successions are driven by glacial–interglacial oscillations, some climatic effects are driven by tectonics, with episodes of uplift or subsidence changing local drainage basin configurations (Talbot and Allen, 1996).

Although volumetrically minor, more unusual in terms of climatic setting are polar deposits of mirabilite and CaCl_2 brines/minerals, which are forming in the dry desert valleys and icesheets of Antarctica. Cryogenic mirabilite cements the tills of the Hobbs glacier and forms microbially coated salt beds atop the ice sheets of the Ross Ice Shelf in McMurdo Sound (Brady and Batts, 1981). Calcium-chloride bottom brines accumulate today in the small ice-free heliothermic Don Juan pond. This pond is highly unusual in that the calcium chloride mineral antarctite precipitates and remains as an at-surface salt, along with tachyhydrite, in the high- CaCl_2 low- MgCl_2 lake brine. The only other known occurrence of substantial volumes of near-surface low- MgCl_2 , high- CaCl_2 brines and antarctite is found in the pans and trenches of Bristol Dry Lake, California (BWk).

4. Nonmarine salts across time and tectonics

Two points immediately arise from a geographic and time-based GIS analysis of modern and ancient nonmarine evaporites. First, the bulk of exploitable nonmarine bedded evaporites (soda-ash, salt-cake and borates) are Eocene or younger. Otherwise, metamorphic focusing and alteration seem to be required so that a nonmarine evaporite deposit retains sufficiently pure ore grades to remain exploitable. This contrasts with the larger exploited marine evaporite deposits of halite, gypsum and potash (saline giants) that, as we shall see later in this paper, form huge deposits extending in time from the Miocene back throughout the Phanerozoic, but possess poor Quaternary counterparts in terms of deposit size and same-scale inflow hydrologies. Second, when major exploited deposits of borates, sodium carbonate (soda-ash) and sodium sulfate (salt-cake) are plotted on a world-scale topographic and climatic base, it is apparent

³ The various Koeppen climate designations, tied to specific deposits and utilized throughout this paper whenever Quaternary deposits are listed in tables or mentioned in the text (e.g., BWh and BWk), are derived by the over-layering of the specific deposit location (latitude and longitude of centroid) onto a GIS Koeppen climate base published by Kottek et al., 2006.

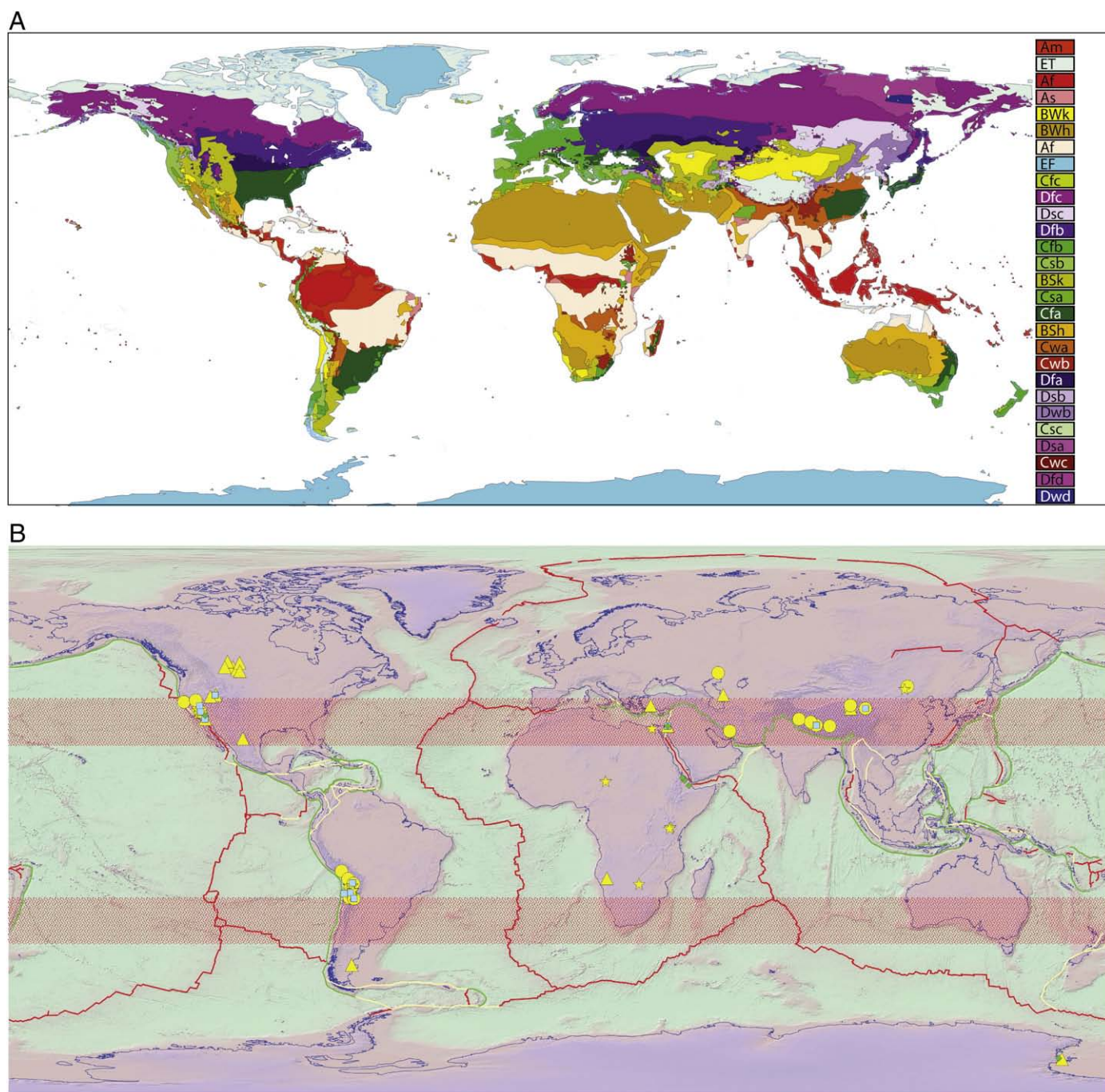


Fig. 5. Quaternary evaporites and climate. A) Koeppen climate zones of today's world (after Kotttek et al., 2006). *Main Climates:* A; equatorial, B; arid, C; warm temperate, D; snow, E; polar. *Precipitation:* W; desert, S; steppe, f; fully humid, s; summer dry, w; winter dry, m; monsoonal. *Temperature:* h; hot arid, k; cold arid, a; hot summer, b; warm summer, c; cool summer, d; extremely continental, F; polar frost, T; polar tundra. This climate base is used as the Quaternary climate reference base for all overlays in this paper. B) Distribution of nonmarine Quaternary salt and brine deposits that are currently exploited or could be in the future. (Stars = Soda-ash; Triangles = salt-cake; Circles = borates; Blue squares = Lithium brines; Green diamonds = CaCl₂ brines; Red stipple indicates latitude belts lying 25°–40° north and south of equator).

that topographic relief or elevation contrast, and not just basin aridity, is typical of most deposits.

Topographic contrast in the landscape facilitates hydrographic closure in the drainage basin, while variations in nonmarine salt mineralogies are largely controlled by chemical responses of inflow waters flowing through and across the various labile lithologies in the drainage basin. Conditions of substantial continental topographic relief about a locally-subsiding lacustrine depression within an endorheic basin are created and maintained by active tectonism. In addition, a nonmarine evaporite basin must be located in a

hydrological and climatic setting where the deposits are not subsequently flushed by substantial volumes of freshened runoff or subsurface waters, otherwise the salts will dissolve.

Older buried salt masses, especially if halokinetic and located at or just beneath the landsurface, can contribute solutes to continental drainage inflows in endorheic depressions. This is the case in the halite-entraining salars of South America, the Holocene potash deposits of the Qaidam Basin in China and the Dallol salt pan of Ethiopia, and was probably the case when the potash-entraining Miocene Upper Red Formation salts were deposited in the Qom region of the Zagros foreland (Warren, 2008).

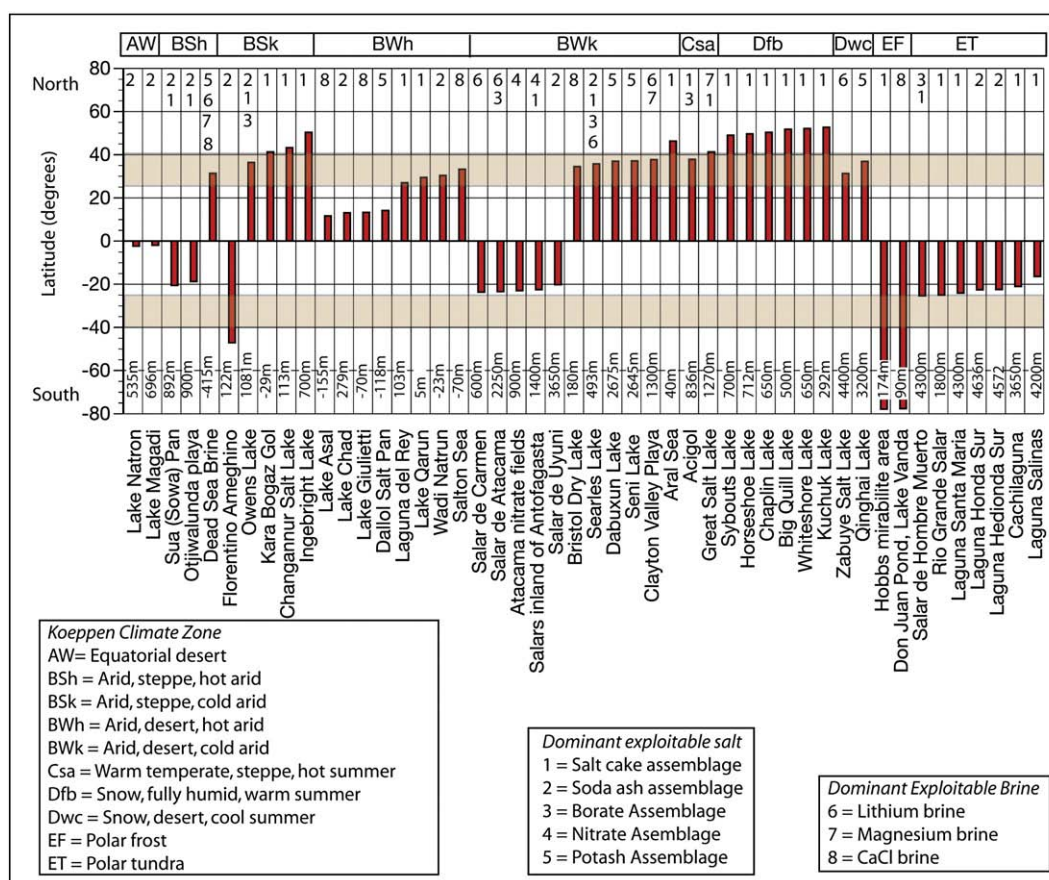


Fig. 6. Quaternary continental lacustrine saline deposits plotted against their latitude and Koeppen climate zone (see Fig. 5A). The brown shade indicates “horse latitude” belts situated some 25–40° north and south of the equator. Exploited or exploitable commodities listed as a set of numeric keys for each deposit, in some lakes the exploited deposits underlie or form about the margins of the current lake/playa and indicate earlier (Pleistocene) or marginward increases in salinity.

4.1. Borate evaporites

Boron in its various forms occurs in trace amounts in every ecosystem in the world, but mechanisms and regions that concentrate its occurrence to levels where it is commercially exploitable are less pedestrian (Table 3). Major exploited borate accumulations occur in the Mojave Desert in the southwestern United States, in the intermontane high altitude basins of the South American Andes and in south central Asia, especially Turkey. Nearly 40% of the world's known borate reserves are located in Turkey, some 20% in North America and the remainder in South America, Russia and China (Katsioularis, 2008).

A world-scale borate deposit map underlines a lacustrine evaporite association with aridity and high-relief topography in the surrounding drainage basin (Fig. 7; Table 3). All borate deposits that are currently exploited or have been exploited, with the exception of three (Inder, Liaoning and Dal'negorsk), are situated in saline intermontane lacustrine depressions in active or formerly active volcanic terrains. All are bedded deposits with the ore mineral assemblages typically dominated by saline sodian borate minerals; ulexite, borax and kernite or the calcian borate mineral colemanite (Appendix A). None of the exploited Quaternary borate deposits accumulated in hot arid deserts, and none have formed at or below sealevel. Rather, economic borates tend to accumulate in cooler arid conditions, generally in high-elevation intermontane fault-bound depressions.

All large bedded borate deposits first precipitated from concentrating waters in one or more of three salinity ranges (dilute, concentrated and highly concentrated; Garrett, 1998). The precipitation site was lacustrine and in one or more of the following depo-

sitional settings; a) subaerial efflorescences or crusts, b) subaqueous pavements or beds beneath a density/salinity-stratified water column, or c) intrasediment displacive nodules and cements (Fig. 8A; Warren, 2006).

Because the colemanite and inderite groups of minerals are so insoluble, they may be assumed to have formed from more dilute waters (Garrett, 1998). In bedded lacustrine borates this lower salinity interpretation is supported by the remains of freshwater organisms in interlayers and bounding beds to the colemanite/inderite horizons. Evaporation ratios (precipitation salinity/inflow salinity) for a geothermal brine borate source are typically 0 to 10 (Garrett, 1998). For colemanite to crystallize, the boron concentration in the mother brine is typically 40–280 ppm and calcium is present at concentrations that are >15–110 ppm. That is, colemanite typically requires salinities similar to those for lacustrine calcite deposition, and occurs well before gypsum saturation.

For ulexite to crystallize, the boron concentration must be 460–630 ppm B, with >30 ppm Ca (Garrett, 1998). In modern playas and salters where ulexite precipitates, the sodium concentration in the brine typically ranges upwards from 10% and halite is a commonplace associated mineral within the ore horizon (e.g. Salar de Atacama; Table 3). For borax deposits, the boron concentration is higher, >2100 ppm B, while Ca is low, with borax brines typically containing <20 ppm Ca. The NaCl and equivalent Na₂CO₃ concentrations are high (based on observations in recent borax deposits) and seasonally are near or at their saturation points so that halite and soda-ash minerals are frequent co-precipitates with the borate minerals (e.g. Searles Lake). Salinity fluctuations in the parent brine perhaps explains why in the Kirka and Loma Blanca deposits the borax layers occur between

Table 3

Borate deposits, listed by country, areas and Koeppen climate for Quaternary playas/salars. See Fig. 7 for locations (reserves in mt (million metric tons) of B₂O₃ after Garrett, 1998; for overviews see Carpenter and Kistler (2006), Warren (2006) and references within).

Location (area)	Age	Elev. (m)	Koeppen	Mineralogy/setting/ comments
Location (area)	Age	Elev. (m)	Koeppen	Mineralogy/setting/ comments/key references
Loma Blanca, Argentina	Miocene (7 Ma)	3970	–	Borax, lesser inyoite and ulexite, some kernite, minor colemanite in Sijes Fm (2.7 mt). 30 m of borate is interlayered with green–grey tuffites and clays and overlain by volcanics. Active open pit. (Alonso et al., 1988; Helvaci and Alonso, 2000)
Salar de Hombre Muerto, Argentina (565 km ²)	Quat.	4300	ET	Ulexite on playa surface and shallow subsurface, also large brine reserves (second largest playa after Arizaro in Argentine Puna region). Borate recovered as byproduct during lithium recovery (3 mt). Typical lake brine contains 230 ppm B and 540 ppm Li. Low Mg/Li. (Garrett, 1998; Vinante and Alonso, 2006)
Sijes district (Monte Amarillo, Monte Verde, Esperanza, and Santa Rosa deposits), Argentina	Mioc. 5.7–6.8 Ma	4050	–	Bedded colemanite [Monte Verde, Esperanza (upper beds)], inyoite [Monte Verde (middle beds)], and hydroboracite [Monte Amarillo (lower beds)] within the Sijes Formation (4 mt). Deposited in more than ten 1–4 km ² sub-basins as a chain of lakes, fed via thermal springs probably opened by emplacement of the Quevar volcanic complex. Deposits change laterally from borates to gypsum (or anhydrite) to clastics or pyroclastics and are folded and dip to the east. Open pit mining. (Garrett, 1998; Orti and Alonso, 2000)
Tincalayu, Argentina	Mioc. 5.86 Ma	3938	–	Borax (4.8 mt) in Sijes Fm, occurs as limited zones of kernite in lower part of ore bed, or veins, ulexite nodules in clays occur above ore. Irregular borate member (folded) lies atop a halite unit (that is less than 100 m thick) and is covered by 25 m-thick pelitic member. (Erickson, 1993; Helvaci and Alonso, 2000)
Lagunas Pastos Grandes, Bolivia (100 km ²)	Quat.	4430	ET	Brine, ulexite. Lithium and potassium recovery from lake brine is possible. This salar is slightly southwest of Uyuni, in Bolivia. There is also a Pastos Grandes in Argentina. Typical lake brine contains 230 ppm B and 540 ppm Li. (Jones and Renaut, 1994; Muessig, 1958, 1966; vanderVoort, 1997)
Salar de Uyuni, Bolivia (9654 km ²)	Quat.	3650	BWk	Ulexite (10 mt). Surface salt crust in the southern area is being mined for its ulexite content (in 1996 at a rate of 5000 tons/mo), and salt has been mined from the central area since the 1500s. Typical lake brine contains 320 ppm B and 187 ppm Li. (Garret, 1998, 2004; Risacher and Fritz, 2000)
Aguas Calientes Sur, Chile (76 km ²)	Quat.	3770	ET	Ulexite. Previously mined. Lake brines have elevated levels of both boron (474 ppm) and lithium (152 ppm). Possible future lithium resource. (Garrett, 1998; Chong et al., 2000)
Salar de Ascotan, Chile (232 km ²)	Quat.	3960	ET	Ulexite. It was first Puna salar to be mined (1852), but there was no significant production until the 1880s, by 1900 it was among the world's largest producers, reaching a peak in 1913 and almost totally stopped from 1967 to 1978. Harvesting resumed in late 1990s. (Garrett, 1998; Chong et al., 2000)
Salar de Atacama, Chile (3065 km ²)	Quat.	2300	BWk	Natural ulexite nodules on or near parts of salar surface. Borate as byproduct during potash and lithium production via brine processing (10 mt). Previously mined for borates in early part of last century. Lake brine contains up to 440 ppm B and 1570 ppm Li. (Bobst et al., 2001; Boschetti et al., 2007)
Salar de Surire, Chile (141 km ²)	Quat.	4250	ET	Ulexite (5 mt). Perennial lake with hot springs below, still producing ulexite via open pit method. Sporadically mined since 1880s. Lake brine contains up to 1820 ppm B and 340 ppm Li. (Garrett, 1998; Chong et al., 2000)
Liaoning Borate region, China	Paleoproterozoic	500	–	Szaibelyite (ascharite) and szaibelyite–ludwigite, with some suanite. Metasediments and metavolcanics in Liaoning and Jilin provinces. 55 underground and open pit mines in 112 separate borate deposits (12 contained 98% of the reserves) in the Liaoning area (40 mt). (Peng and Palmer, 2002)
Numerous lakes and flats, Tibet Plateau, China (>50–100 km ²)	Quat. (<40 ka)	3200	Dwc	Numerous (>60) low carbonate–borate lakes on Qaidam–Ziqang flats (e.g. lakes Koko and Qinghai) with B potential via brine processing. Lake waters up to 2000 ppm B and 310 ppm Li. See Xiao Chaidam and Dujali Lake for representative deposits) Borate nodules in Qaidam saltflats are more extensive than in water-covered lake beds. (Vengosh et al., 1995; Li et al., 2001; Zheng and Liu, 2009)
Xiao Chaidam (Qaidam Lake), Chaidamu Basin, China (Tibet) (51 km ²)	Quat.	3154	BWk	Pinnoite, ulexite, halite, minor mirabilite in perennial lake beds on edge of Quidam Basin. Upper 2.5–3.5 m are porous with gypsum and mirabilite beds, next 1–2 m contain ulexite with gypsum and lentiform mirabilite, below is 1–2 m of gray-to-black mud with gypsum. Lake brines contain up to 3600 ppm B and 280 ppm Li. (Garrett, 1998; Zheng, 1997)
Dujiali Lake (Guojialin), China, (Tibet) (480 km ²)	Quat.	4632	ET	Borax, tincalconite. Section made up of thin beds of borax interlayered with mirabilite and trona. Lake was a major borate supplier to Medieval Europe (gold flux), salt crusts are still periodically harvested. Lake brine contains 1540 ppm B. (Garrett, 1998; Zheng, 1997)
Nei (Inner) Mongol Plateau Lakes, China (up to 990 km ²)	Quat.	998	BSk	Borax/Boric acid (byproduct of soda-ash production at lakes Chaganor (aka Qagan Nur) and Ordus lakes). Numerous borate springs in region. Lake beds typically composed of two alternating layers, one of natron, mirabilite, halite and trona, which is interbedded with black mud containing illite, some gaylussite, dolomite and calcite. (Garrett, 1998; Zheng, 1997; Zheng et al., 1993; Zheng and Liu, 2009)
Zabuye Salt Lake, China (Tibet) (251 km ²)	Quat.	4426	Dwc	Borax. High concentrations of the alkali metals (K, Li, Rb, and Cs) as well as borax, sodium, chloride, sulfate, and carbonate. Similar to Seale Lake. Lake brine contains 1760 ppm B. Lithium plant. (Wang et al., 2004; Zheng, 1997; Zheng et al., 1993; Zheng and Liu, 2009)
Zhacang Salt Lakes (Zhacang Caka), China (Tibet) (26 km ²)	Quat.	4962	ET	Mirabilite in uppermost sediments, as well as kurnakovite, pinnoite, inderite, ulexite. A large playa basin in interior of the Tibetan Plateau. There are three salt lakes (Lakes I, II and III) in playa, with areas between 23 km ² and 58 km ² , and salt depths of 30 cm to 2 m. (Xiyu, 1984; Zheng et al., 1993)
Puga Valley, Kashmir, India	Quat.	4400	ET	Kernite crusts periodically removed since 1860s. Hot springs with kernite crusts, is part of the extensive Ladakh borax spring zone. (Garrett, 1998)
Deh-e-Shotoran playa, Iran	Quat.	1806	BSk	Ulexite. Minor occurrences of ulexite precipitated in halite-rich saline depressions in a region draining tourmaline-rich granites. (Garrett, 1998)

(continued on next page)

Table 3 (continued)

Location (area)	Age	Elev. (m)	Koeppen	Mineralogy/setting/ comments
Location (area)	Age	Elev. (m)	Koeppen	Mineralogy/setting/ comments/key references
Inder Lake, Kazakhstan (106 km ²)	Quat.	−25	BSk	Hydroboracite is main ore mineral, also borax, colemanite, inyoite, sylvite, ulexite. Receives drainage from the borate-containing Inder salt dome and has formed a porous, 36-m deep brine-filled lake atop salt mass (1 mt) with borate veins in salt dome caprock. (Garrett, 1998)
Magdalena, Mexico	Mid-Tert. (Mioc?)	850	–	Howlite veins in Tertiary lacustrine sediments, minor meyerhoffite and priceite. Colemanite in subsurface (high arsenic levels make processing difficult). 50% of veins are 10–30 cm thick in pale red–green tuffaceous shales, 40% are 1- to 20-cm beds in fine-grained silty sandstone, 10% are 1- to 80-cm beds in zeolitic or lithic tuffs. (Lefond and Barker, 1979)
Laguna Salinas, Peru (110 km ²)	Quat.	4400	ET	Inyoite, ulexite. It becomes partly flooded (50 cm deep) after the winter rains (December–March) and dries rapidly to form surface crusts containing ulexite, halite, glauber salt and thenardite. Beneath the surface are irregular 10- to 100-cm beds or lenses of ulexite (3 tons). (Muessig, 1958)
Bor (Dalnegorsk), Russia	Trias?	270	–	Datolite and danburite. Rhythmically banded pyroxene–wollastonite skarn (3 stage) in Triassic limestone and siltstone; 2 km long, <500 m wide, >1000 m deep. Mined as open pit (54 mt). (Obolenskiy et al., 2007)
Bigadic region, Turkey	Miocene 17 Ma	444	–	Ulexite and colemanite, minor but locally significant probertite and hydroboracite. Borate beds (0.2 to 0.5 m thick) alternate with marl, tuff, claystone mudstone. Ulexite sits atop colemanite (330 mt) (Helvacı, 1995)
Emet region, Turkey	Mid Olig.	1028	–	Colemanite with minor ulexite, hydroboracite, intercalated claystones. Borate zones mostly discontinuous, nodular in beds 2–20 m thick (200 mt). (Helvacı and Alonso, 2000)
Kestelek region, Turkey	Mioc. 17.4 Ma	748	–	Colemanite, ulexite, and probertite predominate, with coarse hydroboracite. Nodular colemanite in 5 m thick zone intercalated with volcanoclastic claystones (3 mt). (Helvacı, 1994)
Kirka region, Turkey	Mioc. 17 Ma	1000	–	Main borate minerals is borax, with lesser ulexite and colemanite (140 mt). Borate lacustrine interval is up to 145 m thick and hosts the only sodium borate orebody in Turkey, with a B ₂ O ₃ content of 20–25%. (Helvacı and Orti, 2004)
Sultancıyir region, Turkey	Mioc. 20.01 Ma	210	–	Priceite in gypsum-clay matrix, minor howlite. District with first (1865) borate mine (underground mine) in Turkey, region is now depleted. (Helvacı, 1994)
Borax Lake, California, USA (1.2 km ²)	Quat.	500	–	Layered borax grits some 0.6–1 m below lake floor clays. Small (100 ha) shallow perennial lake, adjacent to active hot spring in recently active volcanic area. First commercially exploited deposit in US (1860 s). (Garrett, 1998)
Death Valley region, California, USA (54 km ²)	Quat.	−24	BWk	Ulexite is common on the modern halite playa, along with halite, thenardite, and trona. (Crowley, 1993)
Death Valley Borate deposits, California, USA	Mioc. 6–7 Ma	950	–	Colemanite with ulexite and probertite in central core. 23 deposits in area. Borates interbedded with lacustrine clays, tuffaceous mudstones, mainly in Black Mountain tectonic block (8 mt; deposits include; Biddy–McCarthy; Billie; Boraxco; Corkscrew–DeBely; Gertsley; Grand View Mine). (Tanner, 2002)
Hector (Fort Cady area) Ca, USA	Mioc.–Plioc?	900	–	Colemanite intersected in a 58-m drillhole interval at 410 m depth as stacked <60 cm thick beds of spherulitic crystals in a tuffaceous clay or anhydrite rock host. Some secondary veins of clear colemanite or anhydrite and minor howlite (potential 7 mt) (Garrett, 1998)
Kramer, Boron, California, USA	Mioc. (19 Ma)	800	–	Borax, colemanite, kernite, tinalconite. Lacustrine deposit underlain and overlain by arkoses with Saddleback Basalt as base to deposit (46 mt)
Little Borax (Hachinham) Lake, California, USA (0.1 km ²)	Quat.	400	Csb	Borax from solar evaporators on edge of small shallow (>1 m deep) perennial saline lake in volcanic crater. Operational only from 1869–1872, could not compete with playa ulexite deposits (Garrett, 1998)
Owens Lake, California, USA (278 km ²)	Quat.	1081	BSk	Trona is the dominant salt, also borax, some burkeite, mirabilite, natron, and thermonatrite. In winter considerable natron, glauber salt, and borax crystallize, but melt in summer. From 1915–1953 soda-ash from brine evaporators with borax byproduct. Salts derived from leaching of nearby active geothermal springs (3 mt) (Alderman, 1985; Garrett, 1998)
Searles Lake, California, USA (132 km ²)	Quat.	493	BWk	Trona is the dominant salt, also borax, some burkeite, mirabilite, natron, and thermonatrite. In winter considerable natron, glauber salt, and borax crystallize, but melt in summer. Mother brine via dissolution of buried glauberite (43 mt) (Garrett, 1998; Smith, 1979)
Soda Lakes, Nevada, USA (0.16 km ²)	Quat.	1000	BWk	Borax as minor byproduct of soda-ash brine operations in 1860s. Is a small playa adjacent to Big Soda Lake. (Garrett, 1998)

ulexite beds, with colemanite (and sometimes inyoite) beds occurring beneath or above the ulexite. Models of ore genesis typically use either groundwater flushing or surface brine concentration changes to explain the distribution of salinity-dependent suites of borate salts (Fig. 8B).

Boron is not a major element in the earth's crust and waters, in the upper continental crust it averages only 3–20 ppm and is a minor component in seawater (Garrett, 1998). But, being both mobile and volatile, boron (like lithium) tends to accumulate in the last precipitative and extrusive phases in magmatic chambers and/or eruptions. In tectonically active regions, boron is readily leached by hydrothermal waters circulating through such lithologies, creating by far the most common economically exploited boron association, namely, bedded borate salts formed by the evaporation of surface and nearsurface waters in volcanic terrains characterized by active geothermal springs (Warren, 2006; Fig. 8A). Most of the world's larger borate deposits are invariably interlayered with, or sit within, a matrix of tuff, basalts and

volcanoclastic muds and are routinely associated with elevated lithium levels in host sediments.

Most mined borate-rich mineral assemblages accumulated within arid suprasealevel intermontane depressions in active volcanic terrains (Figs. 7A and 8A). At the world-scale these regions are best developed in continent–continent collision belts and/or continent/ocean plate subduction zones and, with the exception of Lake Inder, are not located within or atop ancient marine mega-evaporite basins (Fig. 7A, B).

In an earlier paper Ozol (1977) noted that there was an association of borate deposits with subduction zones. The plot in Fig. 7A would argue that the association is more directly with volcanogenically-influenced plate margins that are experiencing varying combinations of continental plate fracture and uplift rather than solely with subduction. In this way the borate association then also includes the numerous bedded borate deposits of the Basin and Range region of the USA.

Fig. 7 illustrates three exceptions to this general exploration paradigm that exploited borate deposits occur in Tertiary-age

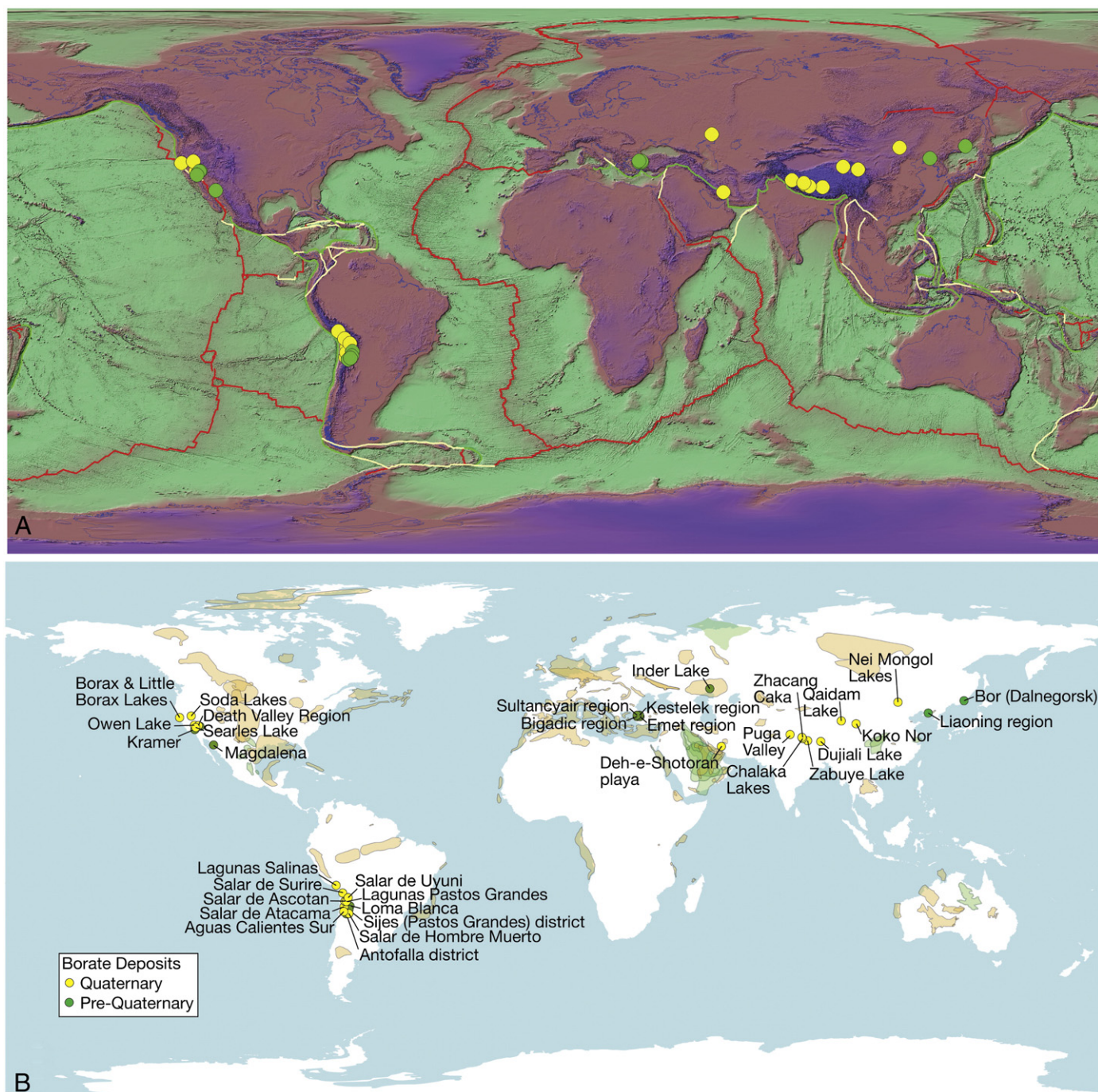


Fig. 7. Borate deposits. A) Deposits plotted on a world topographic/tectonic base. Quaternary deposits are indicated by yellow circles, Pre-Quaternary deposits by green circles. For plate tectonic boundaries Red lines indicate active spreading ridges, green lines indicate subduction zones and yellow lines indicate active transforms (GIS data for plate tectonic boundaries courtesy of the Institute of Geophysics <<http://www.ig.utexas.edu/research/projects/plates/index.htm>>). B) Deposits plotted on a marine evaporite basin base where brown shading indicates halite-dominant and green indicates megasulfate. See Table 3 for borate deposit details and Fig. 18 for marine evaporite basin detail. Plot shows that all borate deposits (except Inder) do not occur within marine-fed mega-evaporite basins.

nonmarine, endorheic intermontane depressions in active or formerly active volcanogenic terrains. They are Inder, Liaoning and Dal'négorsk. These three deposits were not derived directly from the solar evaporation of a nonmarine brine, their ore mineral assemblages are not dominated by sodian or calcian borate mineral suites, and their ages extend well back into the Proterozoic (Table 3).

No longer actively mined, the Inder ore deposit was previously a major supplier of borate minerals to the former USSR. Inder ore was extracted from a diapiric Permian marine evaporite and the dominant ore mineral was hydroboracite (but ascharite may well have been the

parent mineral). Priceite, colemanite, inyoite, ulexite, inderite, and boracite also were also present in the ore beds, and all but the last two had commercial value (Garrett, 1998). This is the only borate deposit to sit atop an ancient (Permian) marine-fed mega-halite basin (Fig. 7B).

Liaoning is a 1.9 Ga Proterozoic meta-evaporite in northeast China with its borate mineral assemblage dominated by the borosilicates; suanite, szaibelyite and ludwigite. Most of the ore occurs as veins filled with borates, magnesite, and magnetite in fractured magnesian marble. Originally, borates were deposited in the Paleoproterozoic in a nonmarine saline lacustrine volcanogenic province then metamorphically altered to

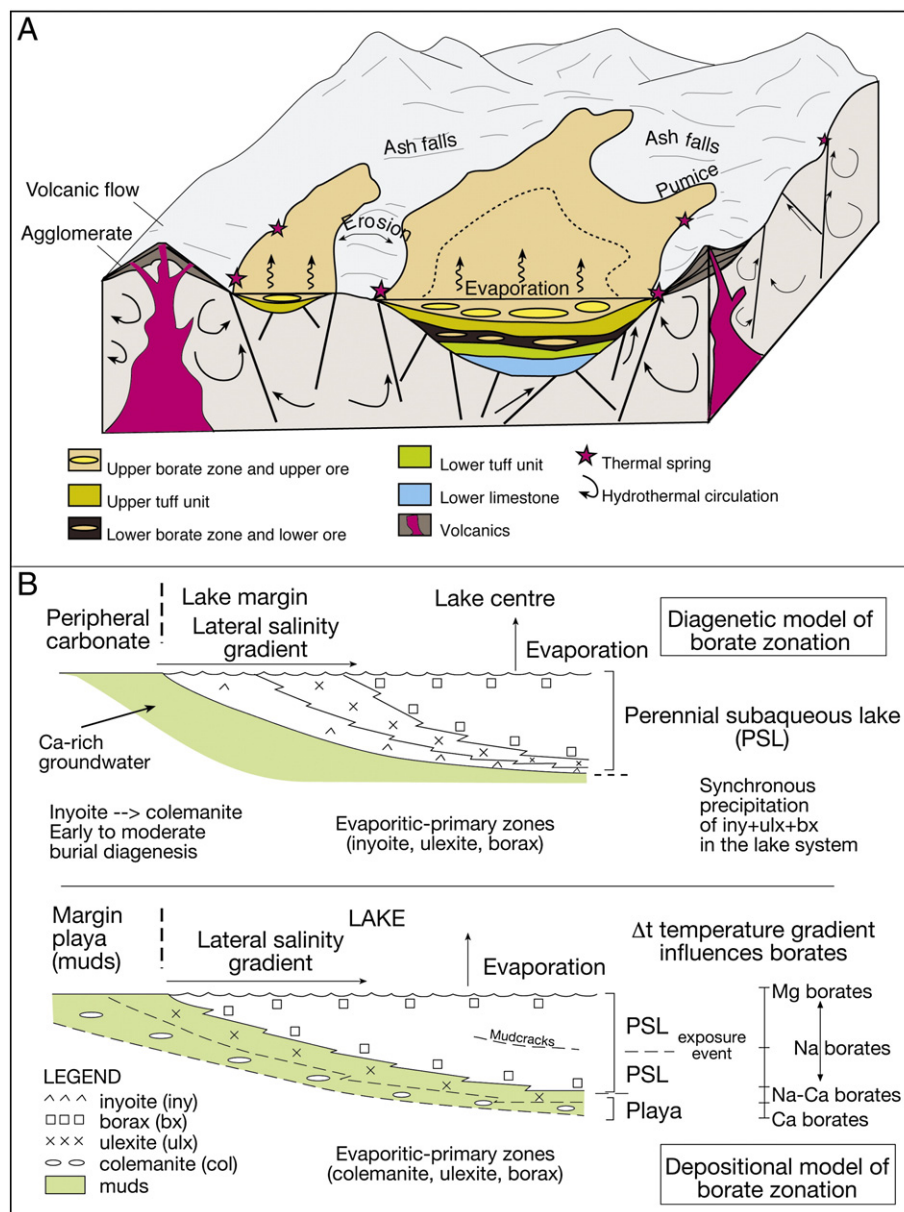


Fig. 8. Borate depositional setting and genesis based on Turkish borate deposits. A) Model of Bigadic region showing strong influence of volcanogenesis on lake sediments and waters (after Helvacı, 1995). B) Two models used to explain mineral paragenesis: one uses diagenetic flushing by subsurface waters (after İnan et al., 1973), the other explains mineralogies as reflections of temperature and salinity changes in lake waters (after Helvacı and Orti, 2004).

the current borosilicate vein assemblage as the region was caught up in a Precambrian orogenic belt (Peng and Palmer, 2002).

Dal'negorsk is a skarn with the ore mineral assemblage dominated by the borosilicates datolite and danburite within a garnet–hedenbergite–wollastonite skarn. This B-rich skarn formed during successive metasomatic replacements of limestone by wollastonite, grossularite, radite, hedenbergite, and by danburite, datolite, axinite, quartz, and calcite (Obolenskiy et al., 2007). Boron isotopic data from the deposit suggest that the source of the boron solutions was a deep-seated granitoid intrusion. The crystallisation succession consists of the early formation of grossular–wollastonite skarn, with datolite, in a Triassic limestone host some 50–60 Ma. This was followed by formation of thin-banded wollastonite aggregates with danburite after datolite that probably occurred simultaneously with a later eruption some 32–50 Ma of a postaccretionary ignimbrite sequence that overlies an accretionary wedge complex. Danburite was altered to axinite ($(\text{Ca}, \text{Mn}, \text{Fe})_6\text{Al}_4\text{Si}_8\text{B}_2\text{O}_{31} \cdot \text{H}_2\text{O}$) at the edges of the skarn.

4.2. Sodium sulfate evaporites (salt-cake)

After sodium chloride (halite), the sodium sulfate salts are the most common of the naturally occurring saline sodium salts (Tables 2 and 4). Sodium sulfate salts typical of ore mineral assemblages include: thenardite, mirabilite (also called glauber's salt), glauberite, astrakanite (also called bloedite) and burkeite (see Appendix A). Sodium sulfate mineral assemblages show interesting stability relationships to salinity and temperature, with corresponding effects on crystallization assemblages in natural and processed brines (Fig. 9A and B).

Sodium sulfate solubility in water changes as a nonlinear function of temperature (Fig. 9A). Ice and mirabilite tend to precipitate from freezing seawater below 1.2 °C. As the temperature increases above 0 °C, increasing amounts of hydrous sodium sulfate (as the decahydrate mirabilite) become soluble, while the hydrous form (thenardite) is the precipitative phase in brines saturated with respect to the sodium sulfate salts. At 32.4 °C in pure water, a transition point on the solubility curve is reached, whereby mirabilite melts in its own water

Table 4

NaSO₄ deposits, listed by country. Reserves in million metric tons (mt) of NaSO₄ after Garrett, 2001, for overviews see Austin and Humphrey (2006), Warren (2006) and references within).

Location	Age	Elev. (m)	Koeppen	Mineralogy/setting/comments/key references
Hobbs mirabilite area, Antarctica	Quat.	174	EF	Pure bedded mirabilite to mirabilite-cemented till of Hobbs Glacier in region between glacial nose and coastline. Mainly sourced by freezing of seawater-influenced aerosols. Not exploited (4 mt) (Bowser et al., 1970)
Cerro Blanco, Argentina	Pliocene	3926	–	Thenardite, small deposit (1.2 mt) in Upper Member of Rodeo Fm. Hosted in clay, shale, gypsum and volcanic ash. (Garrett, 2001)
Florentino Ameghino, Argentina (13 km ²)	Quat.	122	BSk	Mirabilite, halite. Four “mineralized levels” (beds) containing multiple lenses (several metres long and up to 10 cm thick) associated with similar sized lenses gypsum after anhydrite. Numerous springs. (Garrett, 2001)
Rio Grande Salar, Argentina (67 km ²)	Quat.	3630	ET	Mirabilite/thenardite, bedded salar salts, occasional extraction (≈6000 tons/yr) via trenching in Salta Province. (Garrett, 2001)
Sua (Sowa) Pan, Botswana (3306 km ²)	Quat.	892	BSh	Brine processing active in Makgadikgadi playa. Salt-cake is possible future byproduct from brine carbonation in existing soda-ash facility. Estimated there is ≈110 mt of NaSO ₄ in brine stored in pan aquifer. (Low et al., 2000)
Weldon, New Brunswick, Canada	Lower Carb.	4	–	Glauberite (25 mt) at 344 m depth in upper part of lacustrine Albert Formation. Overlies at least 60% of halite extent and grades into, a 13 km ² halite deposit in the small nonmarine Weldon–Gautreau Basin. Not exploited, ≈ 25 mt. (Garrett, 2001; Webb, 1977)
Canadian saline lakes on the Great Plains Canada	Quat.	650–712	BSk	Mirabilite/thenardite. Supratill depressions, some lakes with permanent mirabilite beds, others with ephemeral mirabilite (winter) recovery by various combinations of dredging and brine processing. Ingebright Lake (2.8 km ² , BSk) had largest reserves of the Canadian lakes (11.7 mt). Other exploited and now depleted lakes (in BSk and Dfb climate) include Big Quill Lake (7 mt), Chaplin Lake (3 mt), Dead Moose (1.6 mt), Freefight Lake (1.3 mt), Horseshoe Lake (3.7 mt), Sybouts Lake (3.3 mt), Whiteshore Lake (6.5 mt). (Last, 2002)
Salars inland of Antofagasta (>100 salars), Northern Chile (<10 km ²)	Quat.	1400	BWk	Mirabilite/thenardite in small playas of Atacama and Central Valley. Bedded salar salts, occasional extraction via trenching, association with pedogenic nitrate (1200 mt). (Garrett, 2001)
Chaganor Salt Lake, China (Inner Mongolia) (21 km ²)	Quat.	968	BSk	Brine processing. Nine porous brine-filled beds of salts with 11.3 mt of sodium carbonate, and 4.5 mt of sodium sulfate. Beds of natron, mirabilite, halite, burkeite and trona interbedded with black mud containing illite, some gaylussite, dolomite and calcite. (Zheng, 1997)
Beida Lake (Wadi Natrun), Egypt (1.2 km ²)	Quat.	–23	BWh	Massive 1–4 m thick thenardite below 0.5 m halite bed. Lowest lake in Wadi Natrun chain, which are spring-fed depressions sourced in Nile. No brine-based salt-cake production, historically mined (1.1 mt). (Nahkla and Saleh, 1985; Shortland, 2004)
Lake Qarun, Egypt (226 km ²)	Quat.	5	BWh	Thenardite via brine processing in El Faiyum depression, possibly not implementable as lake brine is very dilute (4 mt). (Rasmy and Estefan, 1983)
N. Aral Sea, Kazak. and Uzbek. (400 km ²)	Quat.	40	BWk	Mirabilite/thenardite in shallow bed up to 60–70 cm thick beneath 1.5–2 m gypsiferous silt in Lesser Northern Sea, processing required. Seasonal mirabilite precipitation (≈200 mt). (Créteaux et al., 2009)
Tien Shan region, Kyrgyzstan	Tert. Late?	1500 to 2200		Halite with glauberite (after thenardite as it sits atop glauberite). Lenses up to 5 m thick that aggregate to a several hundred metre thick saline section hosted in more than 2000 m of Miocene sediment. Found in various intermontane sub-basins in Kochkorka, Kegen Dzhambol, Frunze and Naryn regions (≈4000 mt). (Garrett, 2001; Wünnemann et al., 2007)
Bacadehuachi Valley, Sonora (includes Oro Blanco Pit), Mexico	Oligo–Mioc.	700	–	Thenardite, lesser mirabilite, hosted in fine-grained, vitreous lacustrine tuff beds, beneath dissected alluvial fan conglomerate. Lenticular beds 20 m thick, outcrops in Baucarit Group, ore zone that is 4 km wide, area 13 km ² , in block-faulted basin in Occidental Sierra Madre Mountains (100 mt). (Austin and Humphrey, 2006)

of crystallization and thenardite crystallizes. The presence of other dissolved salts changes the transition temperature and solubility characteristics of sodium sulfate due to the double salt effect. Fig. 9B

plots solubility versus temperature in terms of NaSO₄ and CaSO₄ in various NaCl solutions. It clearly shows the retrograde solubility of both salts and in part explains why glauberite is a common low

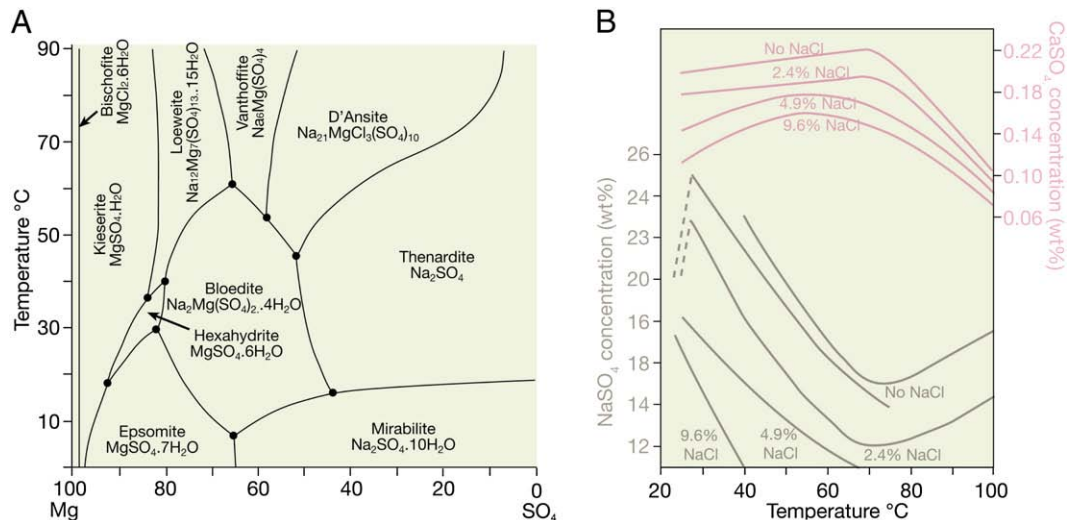


Fig. 9. Sodium sulfate chemistry. A) Temperature dependency of Na₂SO₄ minerals in a NaCl saturated NaCl–Na₂SO₄–MgCl₂–H₂O system (after Braitsch, 1964). B) Solubility of sodium sulfate and calcium sulfate (different scales) when glauberite and gypsum/anhydrite are both present at 20–100 °C, and with 0–9.6% NaCl, wt.% (after Garrett, 2001).

temperature replacement of gypsum/anhydrite in many salt-cake beds.

Natural temperature drops in sodium-saturated brines during the autumn transition to winter, and even during cooling on summer nights in higher altitudes are sufficient to precipitate mirabilite in saline lakes of the Canadian plains (Fig. 10), the Russian steppes and the high Andes (Table 4). In many places, mirabilite crystals redissolve into the lake brine with the next passage to warmer temperatures, this can be on the next day or with the passage of winter into spring.

Historically, temperature-dependent brine processing and seasonal precipitation has been important in precipitating mirabilite in numerous Quaternary saline lakes of the Central Plains of Canada (Last and Ginn, 2005). The mirabilite crystallises in numerous small perennial saline lakes via winter cooling of lake waters (Fig. 10A). Since commercial mirabilite production peaked in the 1970s, extraction of mirabilite/thenardite from these deposits has been declining and most operations are no longer active. Most of the richer bedded salt-cake has been mined and the remaining operations are mostly small scale brine processors (Fig. 10B). The largest problem for the Canadian operators was maintaining a high purity economic product that was comparable to the cheaper but higher purity product from dry playa leachate operations at Laguna Del Rey.

Worldwide, the largest and purest of exploited bedded deposits of NaSO_4 occur in two saline Quaternary playas/lakes located in arid deserts, namely; Kara Bogaz Gol in Turkmenistan (Bwk) and Laguna del Rey in Mexico (Bwh; Fig. 11). In both the prime target beds are dominated by glauberite/halite with lesser astrakanite (bloedite). Searles Lake in California (Bwk) constitutes a third Quaternary saline lacustrine system where NaSO_4 is recovered via brine extraction and solar processing from a Late Pleistocene trona/halite bed that contains significant thenardite, but soda-ash, not salt-cake is the primary product. Today, all three of these deposits are in an extraction phase where brine pumping and processing rather than mining of the solid salt drives the economics (Figs. 12 and 13).

Karabogazgol, along with the adjacent Caspian Sea, is a lacustrine foreland remnant of the former Tethyan seaway. Kara Bogaz lies in the cool arid steppes of Kazakstan at the edge of the Caspian Sea with a brine surface some 29 m below sea level (Fig. 12). The speculated total resource beneath the lake/playa is some 2–4 billion tons of salt-cake (Garrett, 2001). The waters of Karabogazgol are derived from the

Caspian Sea via a narrow inlet that gives the Gulf its name (Karabogazgol means Lake of the Black Throat). In the past 100 years water levels in Karabogazgol have been a metre or so less than the adjacent Caspian surface, which has fluctuated between 25 and 29 m below sea level (See Warren, 2006, Chapter 11 for a detailed discussion of bay hydrology).

NaSO_4 salts occur in 4 main beds (Salt members 1–4), dominated by glauberite/astrakanite, with alteration textures suggesting a mirabilite precursor. Depending on the water salinity in Kara Bogaz, the following succession of various salts precipitates in response to increasing salinity: carbonates–gypsum–mirabilite–glauberite–halite (in the summertime) and mirabilite (in the winter)–epsomite–astrakanite. Today mirabilite precipitates each winter across the Gulf, but much of it is redissolved with the passage into warmer weather and drying of much of the Gulf floor. Hence, across the central parts of the Gulf, mirabilite is not currently contributing large volumes of precipitates to the at-surface gypsum bed (Fig. 12).

Each of the 4 glauberite beds is a likely remnant from cooler climatic periods over the last 10,000 years (Karpychev, 2007). Then large amounts of mirabilite formed each winter, much like today, but unlike today the cooler more humid climate meant the bay was not as subject to summer desiccation, so that dense residual bottom brines were perennially ponded and so preserved a sealing bed of summer-halite. This allowed the underlying mirabilite/epsomite winter precipitates to be preserved across the lake floor. During the following winter the process was repeated as mirabilite/epsomite/halite beds/crusts stacked one atop the other to create a possible ore horizon. Today, a portion of the air-brine mirabilite winter precipitates do not sink but remain as crystal rafts that are blown by prevailing winds to the lake shore. Early last century the resulting mirabilite/epsomite cumulates were harvested along the bay strandzone by the local peasantry.

In time, the combination of groundwater and exposure, especially nearer the Gulf's strandzones, converted most of the mirabilite along with epsomite to astrakanite, and then both phases to glauberite. This, and the windblown piling of mirabilite rafts along the lake strandzone, explains the association of the richer thicker glauberite zones with the lake edges (Fig. 12; Strakhov, 1970). Water of crystallisation created by the mirabilite conversion, then slightly diluted any strong residual brine, so facilitating precipitation of a high sodium-sulfate mineral and a sulfate-brine composition across the bay (Kurilenko et al., 1988).

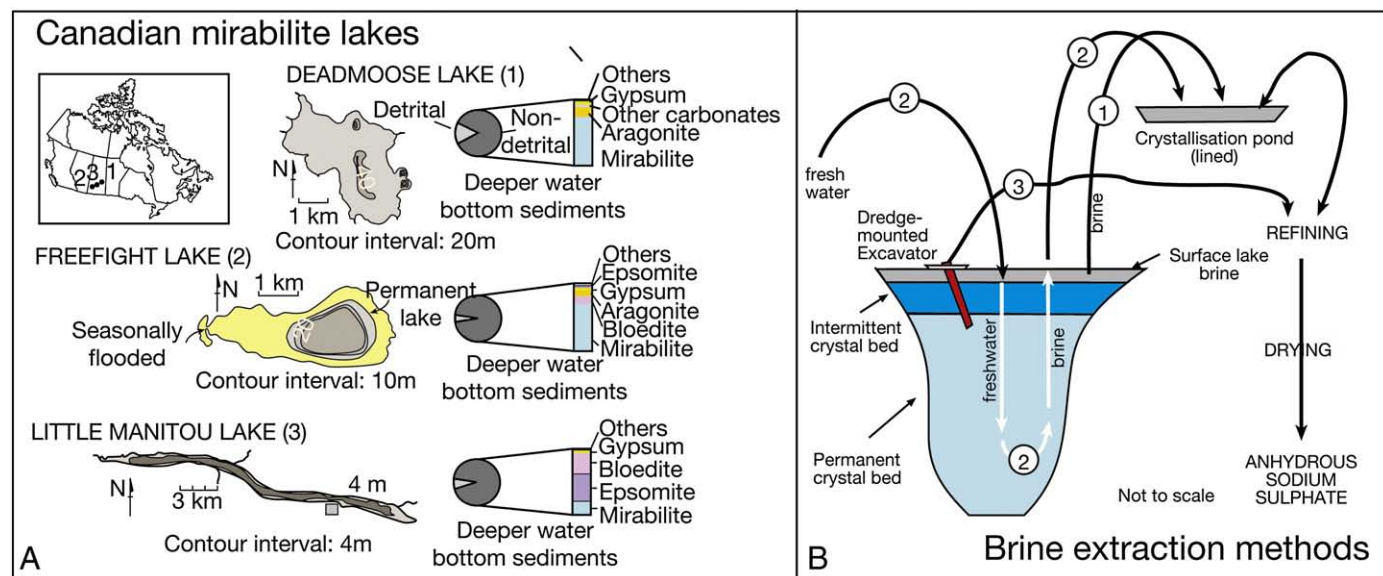


Fig. 10. Sodium sulfate lakes, Canada. A) Selected mirabilite lakes in the plains of Canada, showing bathymetry and bottom sediment composition in deeper subaqueous parts of lake floor (after Last, 1994). B) Extraction methods in various Saskatchewan sodium sulfate deposits (after Garrett, 2001); 1) Evaporative concentration of lake brine in crystallization pond, followed by precipitation of crystals of Glauber's salt (mirabilite) as the brine cools in autumn; 2) Solution mining of thick crystal beds. The return brine is treated as in 1; and 3) Dredging of lake bottom crystal beds.

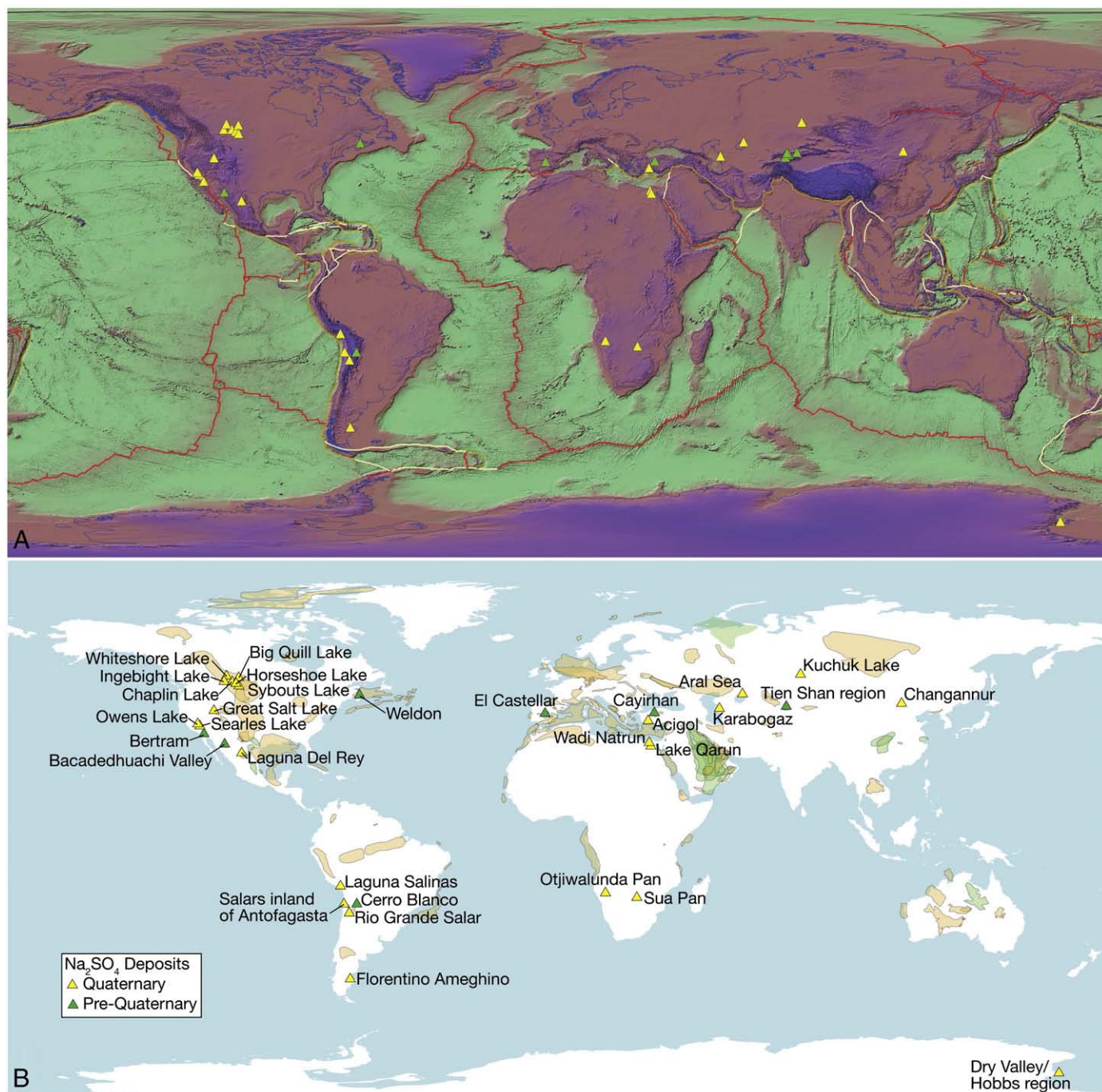


Fig. 11. Sodium sulfate deposits. A) Deposits plotted on a world topographic/tectonic base. Quaternary deposits are indicated by yellow triangles, Pre-Quaternary deposits by green triangles. For plate tectonic boundaries the red lines indicate active spreading ridges, green lines indicate subduction zones and yellow lines indicate active transforms (GIS data for plate tectonic boundaries courtesy of the Institute of Geophysics <<http://www.ig.utexas.edu/research/projects/plates/index.htm>>). B) Deposits plotted on a marine evaporite basin base where brown shading indicates halite-dominant and green indicates megasulfate. See Table 4 for deposit details and Fig. 18 for marine evaporite basin detail. Plot shows that most salt-cake deposits (except Canadian Lakes) do not occur atop marine-fed mega evaporite basins.

The Laguna Del Rey deposit, like Kara Bogaz, is dominated by a nearsurface bedded glauberite/astrakanite (bloedite) assemblage, with lesser halite and epsomite (Fig. 13A). It retains minor mirabilite, mostly as a pore-filling cement between glauberite crystals. But unlike the BSk climates of Kara Bogaz and Searles Lake, the Laguna Del Rey today lies in a hot arid desert valley setting (BWh). Only for a few days in the winter can temperatures be as low as -15°C , while typical summer temperatures are in excess of 30°C and as high as 45°C . Del Rey is the only large economic Quaternary salt-cake deposit in a BWh climatic zone, although Neogene depositional counterparts are found

in Spain and Turkey. The targeted salt-cake bed is up to 35 m thick in the lake centre, with a porosity around 25%, and is exploited by a grid of more than 120 brine wells (Fig. 13A; Sanchez-Mejorada, 1986). The target bed lies some 1–2 m beneath modern gypsiferous playa sediments and it began to form by evaporation of cooler perennial surface brines toward the end of the last interglacial with the onset glacially induced climate changes some 100,000 years ago.

The ultimate source of its sodium sulfate is via inflow waters leaching gypsum (after exhumed anhydrite) in adjacent uplifted Mesozoic evaporites that constitute much of the substrate in the

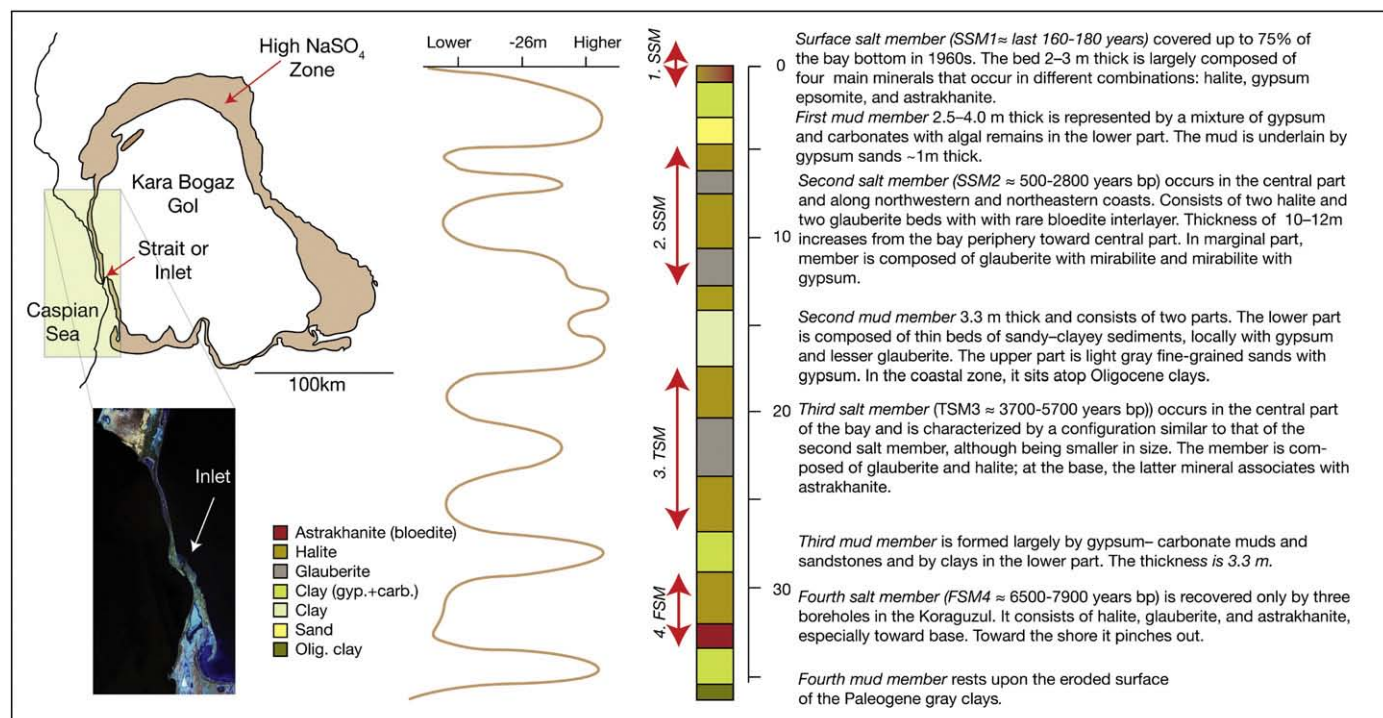


Fig. 12. Kara Bogaz Gol, Kazakhstan, on plan view shows distribution of second salt member zones with higher NaSO₄, they tend to occur about bay margin (after Strakhov, 1970). Landsat image courtesy NASA <<https://zulu.ssc.nasa.gov/mrsid>> shows detail of the narrow inlet allowing surface entry of Caspian Seawater into bay. Typical lake stratigraphy showing thickness, relative water levels and Holocene ages of the four salt members that define the saline successions in the bay (after Karpychev, 2007).

drainage basin. Further enrichment of sodium by ion exchange of calcium for sodium took place in groundwaters moving into the depression through a rim of reactive lake clays. Oxidation of sulfides in the large silver–lead region of Sierra Mojada in the drainage to the north possibly contributed acidic inflow waters capable of leaching Mesozoic dolomites and so forming precursors to the high-magnesium pore brines stored in the exploited salt beds (Sanchez-Mejorada, 1986).

Searles Lake, California, is a desert playa located in the lower central portion of a small block-faulted desert valley with a drainage area of 1600 km² (Fig. 13B). It is a BWk playa and the Pleistocene counterpart to the lacustrine evaporites that entrain the exploited Neogene borax deposits of Boron and Death Valley. The central pan, some 103 km² in extent, overlies a crystalline mush of mixed salts dominated by sodium carbonates, but also with borax, clays, and hypersaline interstitial brines. The brine recovery operation is a multicomponent chemical system and borax is only one of the products recovered; others include sodium sulfate, lithium compounds, potash, bromine and other salts.

There are two main solution-mined salt horizons beneath the central pan: the “upper salt,” some 9 to 27 m thick (averaging 15 m), with a brine content averaging 1.0% B₂O₃; and the “lower salt,” some 8 to 14 m thick, (averaging 12 m), with a brine content averaging 1.2% B₂O₃. The upper salt is overlain by a recent surficial mud and salt crust some 7 to 9 m thick and is separated from the lower salt by 3 to 6 m (average 4 m), of relatively impervious clays called the “parting muds” (Fig. 13B). The upper two salt beds accumulated in the period 3.5–40 ka in a setting that was somewhat more humid than the last 4000 years. There is also a much deeper salt bed with a mineralogy dominated by trona–nahcolite–halite with lesser amounts of burkeite–thenardite. Historically, until 1979, the upper salt was the solution mining target, since then the lower salt was exploited as a trona target and processed using a combination of solution mining and carbonation.

Until mining operations ceased or slowed in the last few years, the largest solid-salt sodium sulfate extraction operations were the glauberite–thenardite mines of Spain. These large Spanish deposits

formed as mudflat and subaqueous precipitates in three nonmarine Tertiary-age playa basins (Madrid, Ebro, Catalayud) with parent brine evolution tied to evaporation of sulfate-rich groundwater outflows driven by the uplift of the Pyrenees and the groundwater reworking of Triassic evaporites (Fig. 14, Table 4; Salvany et al., 2007; Orti and Rosell, 2000). A combined reserve of 3 Gt of Na₂SO₄ is held in these three basins (Garrett, 2001). The FMC-Fort mine extracted ore from a 4–8 m thick bed of thenardite and a thin underlying glauberite bed. The nearby Sulquisa plant extracted salt-cake via “in-situ” leaching of a 25–45 m thick high-grade (40–42% Na₂SO₄) glauberite bed.

Sodium sulfate salts are also extracted from the Upper Miocene Kirmir Formation at Cayirhan Mine, Turkey (Orti et al., 2002). Unlike most of the Spanish ores, thenardite (after mirabilite) is a significant depositional component in the bedded evaporite portion of this lacustrine ore association. However, none of the mirabilite remains as it converted to thenardite with moderate burial. The Evaporite Member of the Kirmir Formation, which is composed of secondary gypsum at outcrop, can be subdivided into a bedded lower unit and a massive upper unit, much like the Spanish deposits (Fig. 14A). Most of the current outcropping and subcropping gypsum of the bedded lower unit was transformed during exhumation from its glauberite/thenardite parent.

Glauberite layers (“clear glauberite”) still remain at depth, as in the Cayirhan mine, where textures suggest it was deposited as a primary, subaqueous, cumulate precipitate on the saline lake floor. But more typically, the glauberite textures are nodular, suggesting it was an early (syndepositional to precompaction) interstitial precipitate, indicating crystal growth occurred just below the sediment surface as passive and displacive crystals within a poorly lithified clayey magnesian matrix (Fig. 14B). Thenardite layers in the glauberite beds in the Cayirhan mine, show disruption structures created by syndepositionary dissolution and infill. These structures, together with their pseudomorphic textures, suggest mirabilite, not glauberite, was the original sodium sulfate lake floor precipitate.

Compared to other low temperature salt-cake occurrences, deposits in depressions on the Great Plains of Canada are unusual in

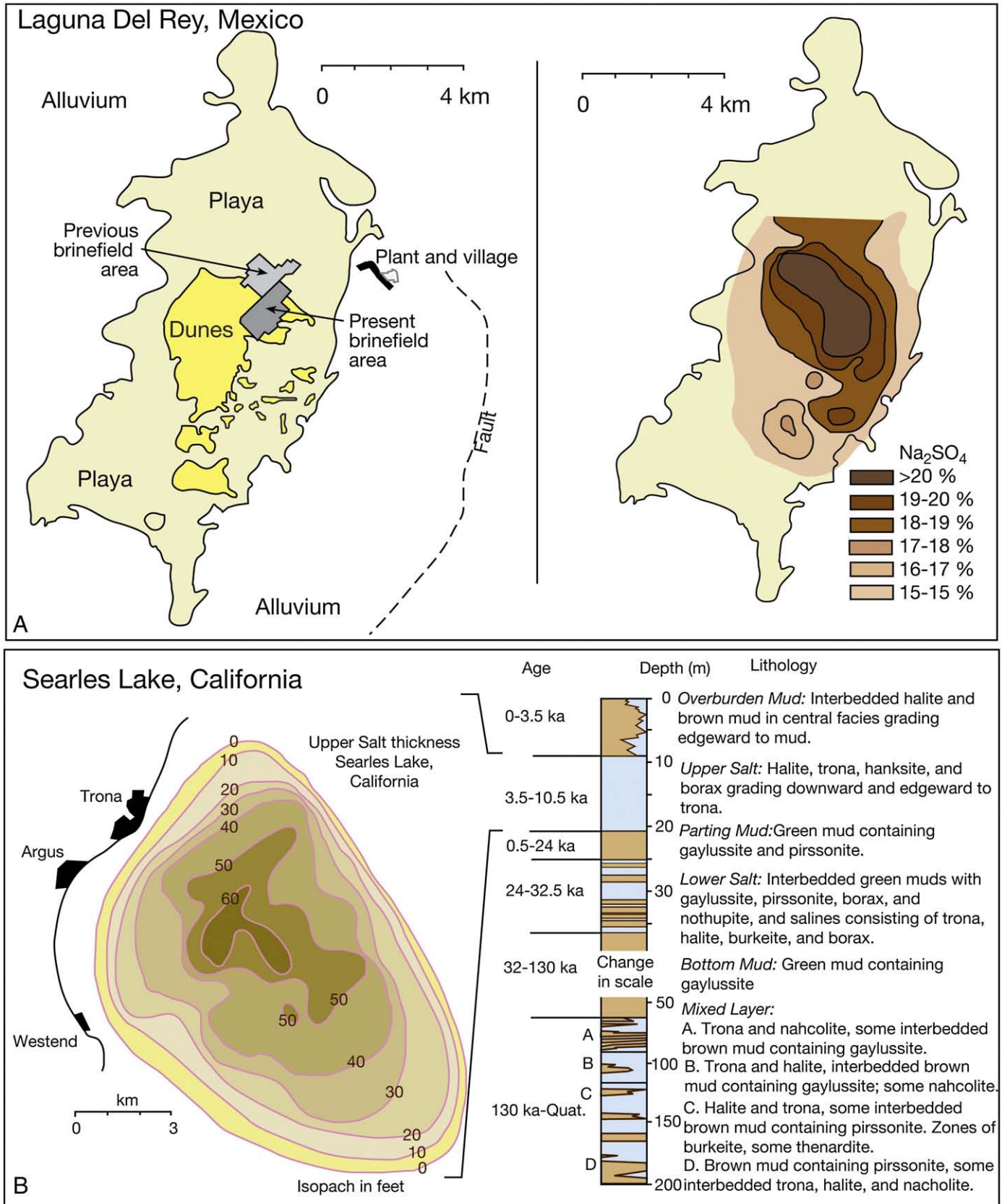


Fig. 13. Quaternary NaSO₄ playas. A) Laguna del Rey, Mexico showing distribution of surface features and the distribution of Na₂SO₄ in brines in the exploited shallow subsurface salt bed (after Garrett, 2001). B) Searles Lake, California showing isopach of the "Upper Salt" in feet and the stratigraphy of the three salt layers and intervening clays (after Smith, 1979).

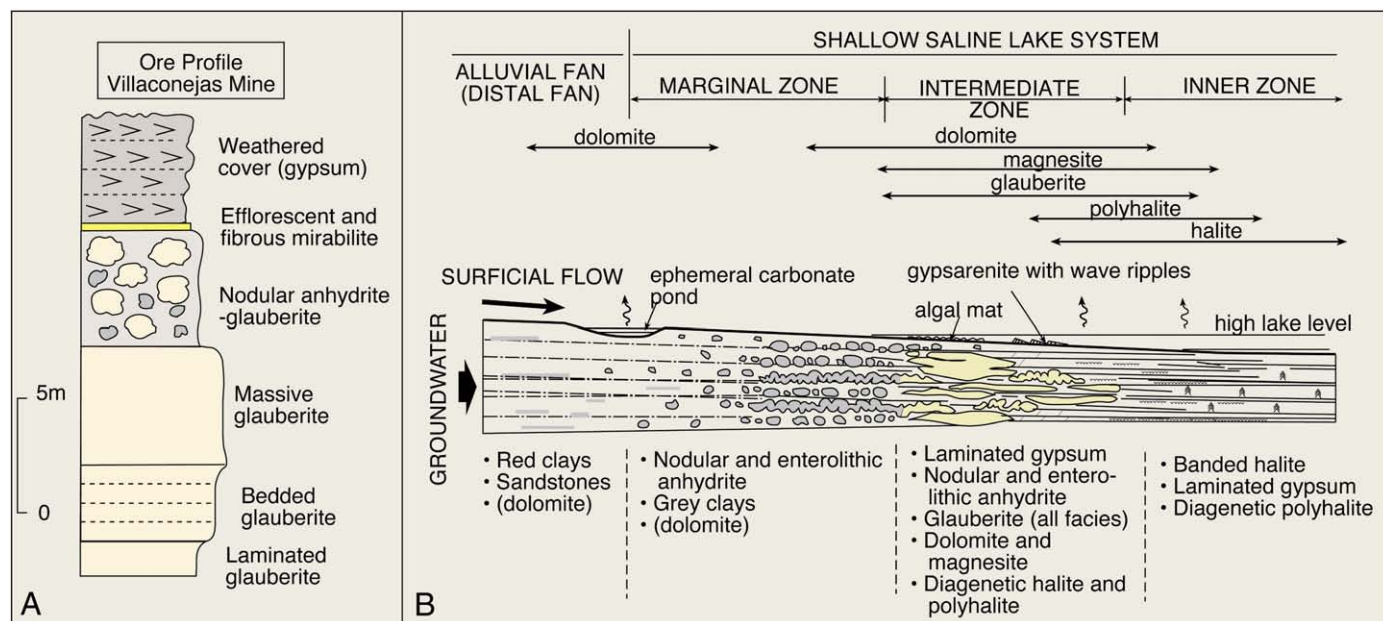


Fig. 14. Miocene glauberite in Spain. A) Profile of the ore zone in the Villaconejas Mine, Spain. B) Sedimentological model for deposition of Spanish glauberite deposits (after Salvany and Orti, 1994).

that they occur atop partially dissolved megahalite beds of the Devonian Prairie Evaporite Fm (Fig. 11B). Some earlier workers concluded that the fractional dissolution of this underlying evaporite acted as the brine source for the salt-cake (Grossman, 1968). Subsequent work has found that dissolution-reworking of these ancient marine salts is probably a less important brine source in the various Canadian lakes. Oxidation of pyrite and other labile sulfur sources within the widespread Pleistocene tills and outwash sediments that underlie the lakes is the dominant source, much like the acid sulfate sources in other salinized soil profiles worldwide (Hendry et al., 1990; Salama et al., 1999).

All the world's exploited sodium sulfate deposits accumulated in saline lacustrine settings with sulfate-rich nonmarine brine feeds (Fig. 11; Table 4). A Quaternary-age association with high-relief high-elevation topography is not as well developed as for borate deposits (compare elevations in Tables 3 and 4). This is because the precipitative mechanism for the sodium sulfate salts can be driven one of two saline hydrological mechanisms. 1) Solar concentration of surface brines with associated increasing temperature in endorheic continental playa depressions, as in the Quaternary playas of the USA and Mexico. Arid desert playa settings also characterised the Miocene continental playa deposits of northeast Spain. 2) The winter onset of saline brine cooling, as in Kara Bogaz Gol in Turkmenistan, the Great Plains of Canada, Acigol in Turkey, Lake Kuchuk in Russia, the buried mirabilite beds in Great Salt Lake, Utah, and the desert valleys of Antarctica).

Where cooling temperatures and brine freezing are the dominant precipitative mechanism, then closed-basin high-relief topography is a less significant influence on brine ponding and salt-cake precipitation. Deposits due to brine cooling occur in many arid cold steppe depressions, typically with lesser relief in the surrounding drainage basins compared to closed basin playas accumulating salt-cake. Mirabilite is the dominant precipitate, although it typically converts to thenardite and/or glauberite with passage to warmer temperatures via change of seasons, burial or groundwater flushing. This temperature control to mineral precipitation is also why, unlike Quaternary borate and soda-ash lakes, Quaternary salt-cake deposits are found well beyond the horse latitudes (Fig. 11).

Also notable in the worldwide distribution of large sodium sulfate deposits is that all the currently exploited sodium sulfate deposits

have Eocene or younger ages (Table 4). As for the majority of the world's exploited borates and sodium carbonates, a relatively young age reflects a combination of high solubility and a need for a formative inflow hydrology that has nonmarine ionic proportions. The need for such waters means the resultant deposits have relatively small volumes and areas compared to marine evaporites. Most intermontane nonmarine lacustrine salt deposits are transient features that are lost or recycled with ongoing uplift and ultimate weathering and erosion of the mountains (Warren, 2006; Chapters 4, 5, and 11). Even if the intermontane salt deposits are preserved into subsequent deeper burial, once the burial hydrology moves the salt beds into deeper diagenetic settings they pass into pore-fluid hydrologies where cross-flushing basinal waters tend to dissolve these relatively small volumes of salts.

4.3. Sodium carbonate (soda-ash)

The bulk of the world's soda-ash supply is produced industrially (Solvay Process) and natural soda production accounts for around 26% of world annual total production of 43 mt (47 million st.; Kostick and Demirkilic, 2008). Sodium carbonate end usage is mostly in glass manufacture followed by chemicals, soap and detergents, pulp and paper manufacture, water treatment, and flue gas desulfurization (Table 1). Current world production of natural sodium carbonate is dominated by room-and-pillar mining of Eocene lacustrine trona beds hosted in Wilkins Peak Member of the Green River Formation in Wyoming where soda-ash reserves are estimated at 70 billion tons of trona and 40 billion tons of nahcolite (Table 5; Bradley and Eugster, 1969). Other exploited ancient trona deposits are in Turkey and China, while the best known modern examples come from Lake Magadi and Lake Natron in the African Rift valley (Fig. 15).

The Eocene Green River Formation consists of a variety of lacustrine sedimentary rocks, including sandstone, claystone, shale, dolomitic marlstone, oil shale, and numerous, generally thin beds of volcanic/dacitic tuff mostly deposited in and around two large lakes in the Green River and Uinta basins (Fig. 16A; Dyni, 1996). Green River Formation sediments grade from fine-grained sandstone, mudstone, claystone, and shale in shoreward areas of the lakes into carbonate- and trona-bearing sediments enriched in organic matter toward basin centre (Dyny, 1996).

Table 5

Sodium carbonate deposits, listed by country, reserves listed in million (mt) or billion (Gt) metric tons of sodium carbonate equivalent (for overviews see Garrett, 2001; Santini et al., 2006; Warren, 2006 and references therein).

Location	Age	Elev. (m)	Koeppen	Mineralogy/setting/comments/key references
Laguna Santa Maria, Argentina	Quat.	4300	ET	Thin trona beds in a moderately small (19 km ²) alpine deposit some 5 km from border with Chile.
Cachilaguna (Laguna Cachi), Bolivia	Quat.	3650	ET	Trona, small (1.5 km ²) alkaline brine lake, brine depth ≈ 17 cm. Salts precipitated when lake brine freezes in winter to form a 6–10 cm thick crust of trona and thermonatrite (Ahlfeld and Muñoz Reyes, 1955)
Laguna Hedionda Sur, Bolivia	Quat.	4572	ET	Trona, small (2.8 km ²) alkaline brine lake (pH 10.46) covering, average brine depth 75 cm. (Ahlfeld and Muñoz Reyes, 1955)
Laguna Honda Sur, Bolivia	Quat.	4636	ET	Trona, small alkaline brine lake (pH 9.88) covering 30 ha (0.3 km ²), average brine depth only 10 cm. (Ahlfeld and Muñoz Reyes, 1955)
Sua (Sowa) Pan, Makgadikgadi Basin, Botswana (3307 km ²)	Quat.	892	BSH	Trona, brine processing plant commenced operations in 1991. Salt-cake as possible byproduct. Produces 300 kty of soda-ash and 600 kty of halite for South African market. (360mt) (Low et al., 2000)
Lake Chad, Chad (22,351 km ²)	Quat.	264	BWh	Natron mixed with halite, small anthropogenic crystalliser pans in interdunal depressions (<5 km ²), NE Lake Chad. Low quality product for local consumption. (Eugster and Maglione, 1979)
Anpeng Basin Trona Mine, China	Eoc.	1266	–	Nacholite, trona, mirabilite, gypsum. Solution-mined, 17 nacholite beds (0.6–3.6 m thick) mixed with sulfate- and carbonate-bearing layer in a depth of around 1310–2520 m. Located near Anpeng, about 35 km NW of Tongbai. (Wang, 1987)
Wucheng Basin Trona Mine, Henan Province China	Neogene	142	–	Trona, halite, lesser nacholite (minor northupite and shortite), 36 trona beds (693–974 m deep), 1 over 15 beds are 0.5–1.5 m thick, thickest 2.38 m; upper 21 beds are 1–3 m thick, maximum 4.56 m) hosted and underlain by dolomitic oil shales of Wulidui Fm. (Zhang Youxun, 1985)
Chaganor Salt Lake (Qagan Nur), China (Nei Mongol) (21 km ²)	Quat.	968	BSk	Trona in nine porous brine-filled saline beds containing 11.3 mt of sodium carbonate, and 4.5 mt of sodium sulfate. Beds <10,000 years. Current lake area of 21 km ² consisting of smaller northeastern sub-basin (East Chagannur) and a larger southwestern sub-basin (West Chagannur) joined by a narrow channel. (Zheng, 1997; Yu et al., 2001)
Wadi Natrun, Egypt (500 km ²)	Quat.	–23	BWh	Natron beds with burkeite, gaylussite, trona, halite, northupite, pirsonite, thenardite in various lakes in the depression. Exploited by ancient Egyptians. (Shortland, 2004)
Lake Magadi, Kenya (110 km ²)	Quat.	696	Aw	Trona, nacholite, burkeite, magadiite, kenyaite. Contains up to 30 billion tons of trona in Holocene unit 74 km ² area and 15–40 m thick. Current production ≈ 350 kty (via dredging) with ≈ 200 kty renewed. (Jones et al., 1977)
Lake Natron, Tanzania (561 km ²)	Quat.	538	Aw	Trona/nacholite/burkeite. A 2100 km ² area of northern part lake is covered by a 1.5 m thick trona bed (≈150 mt resource). (Manega and Bieda, 1987)
Sasykkul Lake, Tajikistan (Pamir)	Quat.			Small, heliothermal lake with local halite and trona precipitation. Similar alpine association to Bolivian trona lakes (Volkova, 1998)
Beypazari region, Turkey	Mioc. 21.5 Ma	738	–	Trona, halite, minor nacholite (in lake margin). Some 33 trona beds in two fault-bound lensoid bodies in and atop oil shales of Lower Hirka Fm (16 in lower, 17 in upper). NaSO ₄ in overlying Kimir Fm (Helvacı, 1998; Suner et al., 2003)
Green River Fm., WY, USA	Eoc.	1900	–	Trona, halite, shortite, dolomitic oil shale of Wilkins Peak Member of Green River Fm over some 31,000 km ² made up of 42 layers of crystalline trona in basin, 25 of which exceed 1 metre thickness. World's largest exploited natural deposit (127 Gt of trona). Nearby in the Piceance Creek basin (18,700 km ²) is the world's second largest known NaCO ₃ occurrence, some 27 Gt of nacholite and 17 Gt of dawsonite in the lower part of the Piceance River Formation (see text)
Owens Lake, CA, USA (278 km ²)	Quat.	1081	BSk	Trona/burkeite/thermonatrite/halite. Small playa valley in block-faulted Basin and Range region (anthropogenic salinity). (≈52 mt of sodium carbonate equivalent). (Alderman, 1985)
Searles Lake, CA, USA (132 km ²)	Quat.	493	BWk	Trona–nacholite–halite. Two saline beds with trona–nacholite dominant in lower salt bed. Soda-ash via brine extraction and processing, salt-cake as byproduct. Playa in block-faulted Basin and Range valley (1.06 Gt of sodium carbonate equivalent) (Smith, 1979)

The more abundant sodium carbonate salts in the Green River Formation and its equivalents include trona, nahcolite, shortite, dawsonite, and less commonly eitelite and wegscheiderite (Appendix A). The most important lake desiccation event occurred in the Eocene during Wilkins Peak and Parachute Creek time when vast deposits of trona and nahcolite were precipitated across the Green River and Piceance Creek Basins, respectively. More than 42 beds of crystalline trona were deposited in the Wilkins Peak member, 25 of which are more than a metre thick (Fig. 16B). The lake systems were tied to an 8 my period of peak activity in the Absaroka and/or Challis volcanic fields (Smith et al., 2008). Evaporative terminal sinks were initially located in the Greater Green River and Piceance Creek Basins (51.3–48.9 Ma), then gradually migrated southward to the Uinta Basin (47.1–45.2 Ma).

The trona carbonate lakes in the Green River region were hydrographically closed terminal lake systems (endorheic, no surface outlets). The underlying and overlying siliciclastic successions define times when the same lake depressions were hydrographically open. The lateral transition from coarse-grained siliciclastic margin (with abundant dacitic ash) through carbonate mudflats to carbonate salts in the drawdown lake centre is reflected in vertical sequences in the Green River Formation and its equivalents in the Green River, Piceance Creek, and Uinta Basins (Fig. 16A).

Increasing salinity of the alkaline lake waters seeping into the lake depression meant divalent cations of calcium and magnesium, supplied

by runoff and seepage through siliciclastic/dacitic aquifers, were first precipitated as varying combinations of calcite, Mg-calcite, and dolomite in lake-fringing mudflats. Increasingly saline groundwaters continued to seep across these dolomitic mudflats toward the more central drawdown lake depressions. Levels of dissolved sodium, bicarbonate, and chloride continued to build in the pore waters until final precipitation as pan trona and other carbonate salts in shallow lakes and pans, either as bottom nucleates in shallow brine sheets or as displacive intrasediment nodules in mudflats. Halite was a common co-precipitate with the carbonate salts, especially from the more saline brines. The calcium sulfate minerals, gypsum and anhydrite, are notable by their absence in all the world's trona deposits (Fig. 3).

Elsewhere in the world, significant volumes of trona are dredged from Holocene Lake Magadi in the East African Rift valley where total resource is estimated to be 30 Gt (Laznicka, 2006). The trona resource in Lake Magadi is pure and readily extracted. At current rates of dredging it there is substantial proportion of renewable resource in the Magadi depression (Table 5). There are also trona brine plants in Quaternary salt pans of southern Africa, these deposits are situated within hydrographically-closed depressions on the low relief craton and lie well outside the rift valley. Some 40,000 years ago trona, along with various salt-cake salts, accumulated within the hydrographically-closed saline playa of the Searles Lake depression, which lies in the tectonically active Basin and Range region of California (Fig. 13B).

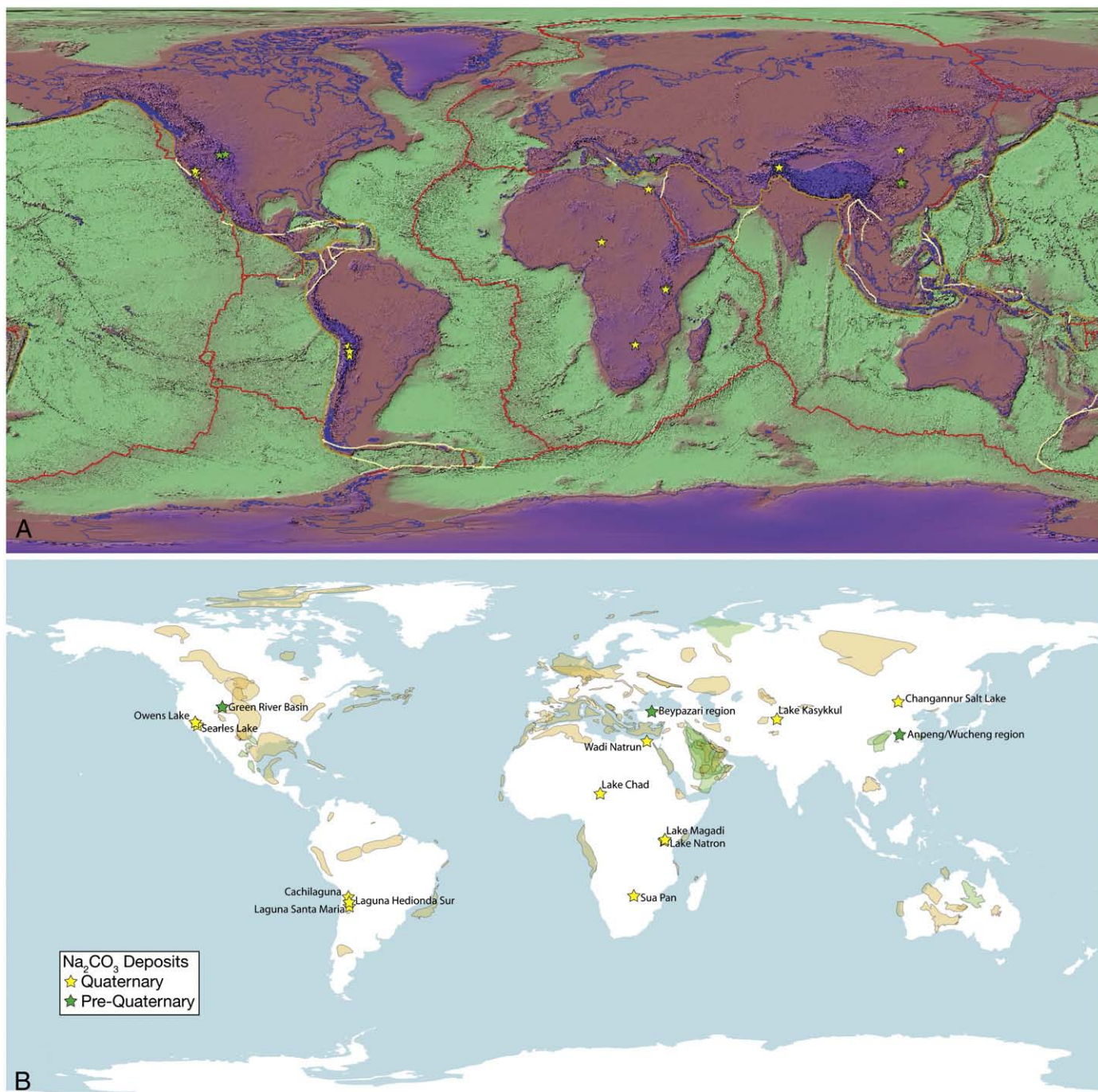


Fig. 15. Sodium carbonate deposits. A) Deposits plotted on a world topographic/tectonic base. Quaternary deposits are indicated by yellow stars, Pre-Quaternary deposits by green stars. For plate tectonic boundaries the red lines indicate active spreading ridges, green lines indicate subduction zones and yellow lines indicate active transforms (GIS data for plate tectonic boundaries courtesy of the Institute of Geophysics <<http://www.ig.utexas.edu/research/projects/plates/index.htm>>). B) Deposits plotted on a marine evaporite basin base where brown shading indicates halite-dominant and green indicates megasulfate. See Table 5 for deposit details and Fig. 18 for marine evaporite basin detail. Plot shows that soda-ash deposits do not occur atop or within marine-fed mega-evaporite basins.

Solution mining is a less frequent supplier of natural soda-ash feedstock than room and pillar extraction. Eocene nahcolite beds are solution mined in China and nahcolite beds were the target a few years ago in the Piceance Creek Basin, USA. Some seventeen 0–6 to 3.5 m-thick nahcolite beds occur at 1310–2520 m depth in the Anpeng Basin, China (Lu, 1998; Zhang Youxun, 1985). Likewise, in the now-mothballed solution-mining operation in Colorado nahcolite was the target in the Eocene Parachute Creek Member of the Piceance Creek Basin (Fig. 16A; Table 5). Solution mining is the principal soda-ash brine extraction method in Searles Lake, California (Fig. 13B; Table 5). Solution mining operations are planned in the Beyazari valley of Turkey where Miocene

trona volumes could approach those of some of the East African rift lakes. Other sodian carbonate minerals that may have future economic potential include dawsonite, eitelite, and shortite.

Although current natural sodium-carbonate operations target a variety of bedded saline lacustrine salts, there is a misconception among some geologists that the presence of thick-bedded ancient trona indicates a carbonatite-rift association, as exemplified by trona deposits currently accumulating in the African rift lakes. The plot of the world's Quaternary trona deposits shows this is not the case (Fig. 15). Certainly there are geologically scenic Holocene trona deposits in the African rift valley in lakes Magadi and Natron and these

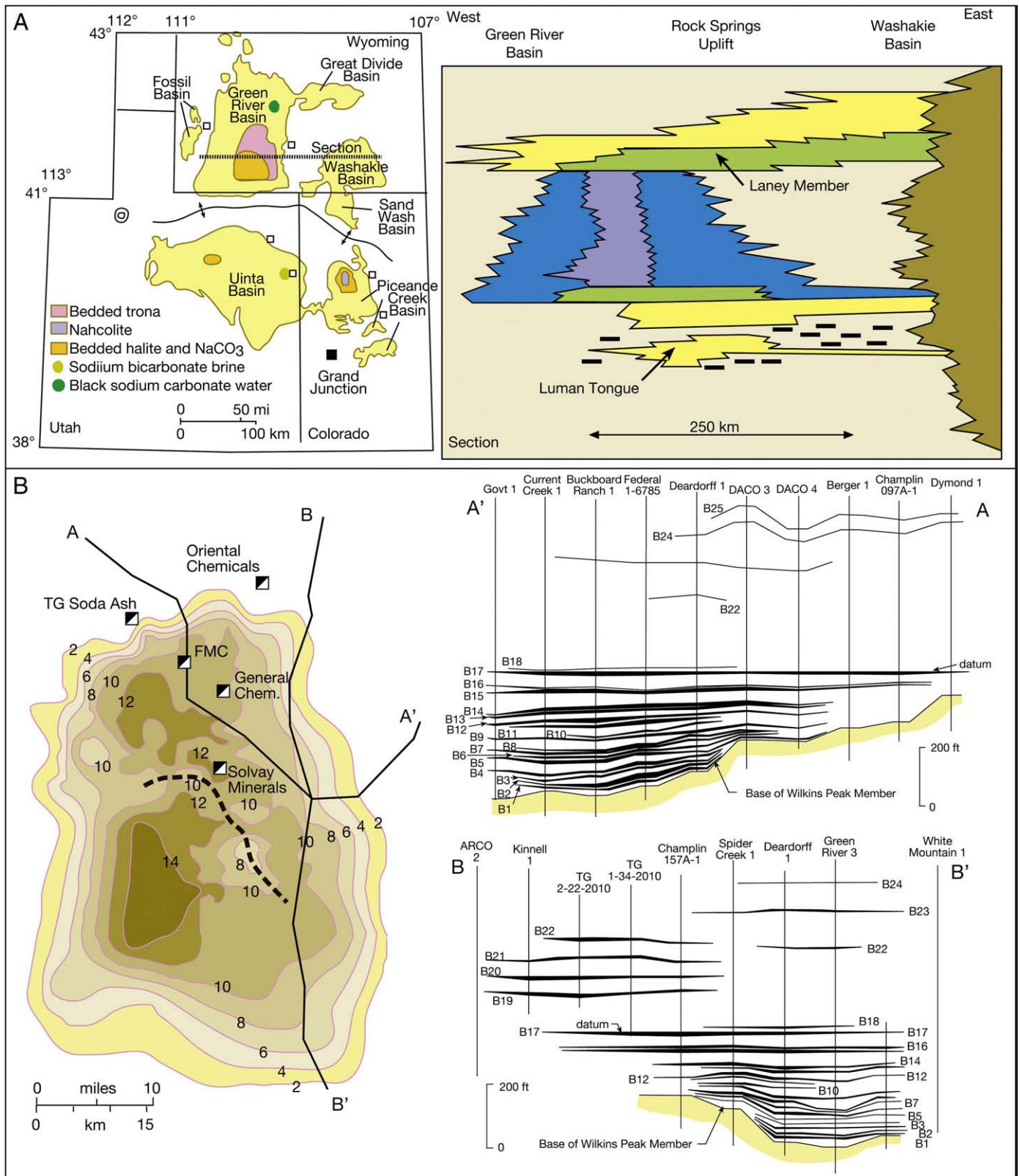


Fig. 16. Trona distribution in the Wilkins Peak Member of the Eocene Green River Formation in Wyoming. A) Areal distribution of the Green River Formation in the various lacustrine basins, showing the locations of sodium carbonate deposits in Utah, Colorado, and Wyoming, along with a schematic E–W cross section. B) Isopach of Bed 17 and is in feet. Heavy dashed brown line indicates approximate northern extent of halitic facies. The two cross sections use Bed 17 as a datum; halitic facies are not shown and the wells are equally spaced in the cross sections (after Dyni, 1996 and Wiig et al., 1995).

lakes are surrounded by high-relief rift volcanoes spewing natro-carbonatites. But, without exception, all the world's larger ancient exploited trona deposits and resources formed in continental foreland

and transpressional depressions, as exemplified by the saline Eocene lakes of Wyoming and China and the Miocene lakes of Turkey and not in active carbonatitic rift valleys (Table 5).

Trona is a commonplace mineral in numerous nonmarine saline lacustrine sediments located in suitably alkaline groundwater terrains that are relatively depleted in sulfate and chloride. The absence of sulfate and relative depletion in chloride proportions permits the evolving brine to become relatively enriched in Na and CO_3 and so move toward the appropriate “closed basin” type-1 concentration (Fig. 3). Upon evaporation, many continental ground waters in metamorphic, volcanic, or igneous terrains will produce suitable alkaline waters, but it is impossible for Phanerozoic seawater to ever precipitate trona (Fig. 3; Hardie and Eugster, 1970).

But, when concentrated by solar evaporation, not all continental alkaline waters can precipitate trona (Jones et al., 1977). Additional conditions are needed to precipitate trona from Phanerozoic Path I brines. They are: (1) an underfilled suprasealevel tectonic basin where the rate of downwarping exceeds the rate of sedimentation, (2) a closed hydrographic basin in which evaporation exceeds outflow, (3) evolution of solutes in the lake waters that lead to high $\text{Na}/(\text{Ca} + \text{Mg})$ and $(\text{HCO}_3 + \text{CO}_3)/(\text{SO}_4 + \text{Cl})$ ratios, that is alkaline brines, (4) a more-or-less permanent body of nutrient-rich water, (5) a warm climate favouring high primary productivity by microbes and algae, (6) a high rate of bacterial sulfate reduction and 7) an excess of CO_2 in the feed brine.

Earman et al. (2005) argue that much of this excess CO_2 comes from magmatic CO_2 , others argue it is due to planktonic blooms and is co-indicated by high levels of organic matter (oil shales) in the lake sediments. Given the presence of these requisite conditions, varying intensities of photosynthesis and temperature, along with changes in the volume of degassing thermal/spring waters, control the CO_2 content of the brines and hence the mineralogy of the sodium bicarbonate precipitates (Fig. 17). The presence of widespread depositional nahcolite in the Anpeng and Green River Basins is used to infer higher CO_2 levels and higher temperatures in the Eocene greenhouse atmosphere (Lowenstein and Demicco, 2006); variable estimates of 100–3500 ppm of atmospheric CO_2 are given in the literature, the modern atmosphere contains around 380 ppm CO_2 .

In a time framework the volume of trona/nahcolite that accumulated throughout the Phanerozoic, when soda-ash was a continental Path 1 brine deposit, is insignificant if compared to the volumes of nahcolite/trona precipitating in evaporitic seaways of the early Archaean. Then the ocean waters were sodian chloro-bicarbonated systems and not the sodium chloride waters of today (Maisonneuve, 1982). There was so much CO_2 in the hot Archaean atmosphere that

nahcolite/trona was a primary marine evaporite salt (Sugitani et al., 2003). Inherently high levels of sulfate reduction probably also characterised the early Archaean oceans. However like all evaporite salts, the inherently high solubility of Archaean carbonate salts means that these large volumes of saline sediments now no longer exist as bedded salt layers. They have been recycled into and through the earth's crust via multiple cycles of subduction and orogenesis so that all that remains as evidence for widespread soda-ash marine evaporites of 3–4 Ga are occasional pseudomorphs and perhaps locally elevated volumes of sodic anorthosite in some Archaean terranes (e.g. Gresens, 1978).

At any time in earth history an abundant supply of CO_2 is needed to form trona. Post the CO_2 /methane-rich atmosphere of the Archaean, such a supply of excess CO_2 in a saline lacustrine setting is typically produced by a combination of intense photosynthesis and periodic dieback and decomposition of mesohaline lacustrine planktonic organisms. Remains of such a biota are associated with oil shales, as in both the Green River and Wucheng deposits and the Late Pleistocene diatomaceous muds of Lake Magadi. Likewise the Miocene Beypazari trona deposit in Turkey is accompanied by bituminous shale (Helvacı, 1998). Along with elevated CO_2 , a lack of sulfate is a consistent observation in all the various trona pan and lakes worldwide, and perhaps reflects bacteriogenic sulfate reduction in the various lake brines, as is occurring in modern trona lakes in the African rift valley.

For sodium carbonate salts to accumulate, sodium must be present in abundant quantities along with elevated levels of CO_2 . Hydrolysis of detrital silicate minerals and glassy volcanic ash (zeolites) contributes additional amounts of dissolved sodium and other ions to pore waters in the inflow aquifers. Tuffaceous/dacitic debris amounts to roughly 5% of the total sediments in the Green River Formation, while labile volcanic/dacitic ash was commonplace in the Eocene Green River Fm watershed and granitic/rhyolitic metamorphic and igneous rocks surround the Wucheng deposit (Zhang Youxun, 1985). Silicate hydrolysis of these minerals produced a high ratio of Na to other cations in the ambient water inflows to both deposits (Fig. 3B).

At the worldscale, exploited trona deposits group into 2 major and three minor subdivisions (Fig. 15, Table 5): 1) Eocene–Miocene lacustrine deposits formed in intermontane depressions within actively subsiding foreland depressions with relatively high relief surrounding drainage terranes, and, 2) Quaternary lacustrine deposits at the termina of hydrographically-closed drainages and further divisible into: a) Intermontane depressions surrounded by relatively high topographic relief in the drainage basin where either i) hot arid conditions allows bedded NaCO_3 to accumulate (Lake Magadi, Lake Natron, Searles Lake) or, ii) high altitude conditions where seasonal brine freezing facilitates the formation of trona crusts (high altitude lakes of South America and the Pamirs and Nei (inner) Mongolia. Cryogenic soda-ash deposits tend to be uneconomic unless the sodium carbonate phase is a byproduct of other brine processing operations. b) Terminal pans in lower-relief hot arid cratonic settings where NaCO_3 resource resides within annually replenished NaCO_3 brines, often in combination with NaSO_4 (Sua Pan, Wadi Natrun, Lake Chad). Elevated CO_2 levels are common to all NaCO_3 settings modern and ancient; nahcolite was a typical bedded co-precipitate with trona during the peak Eocene greenhouse period when atmospheric CO_2 levels more than double that of today.

5. Marine evaporites

Salt mineralogies in all the world's larger ancient evaporite basins (saline giants) are dominated by halite (mega-halite) and/or anhydrite (mega-sulfate), along with varying amounts of evaporitic carbonates and potash salts. Borate, salt-cake and soda-ash volumes are minor to insignificant in these salt masses. The prodigious volumes of evaporite salts in these huge basins required a mother

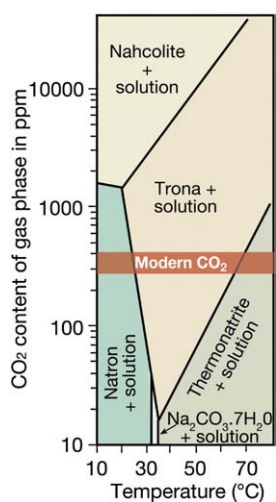


Fig. 17. Sodium carbonate phases in equilibrium with a saturated solution as a function of CO_2 content of the gas phase and temperature (in part after Eugster, 1971). CO_2 content of today's atmosphere (≈ 380 ppm) is plotted as a red band, Eocene estimates range from 100–3500 ppm.

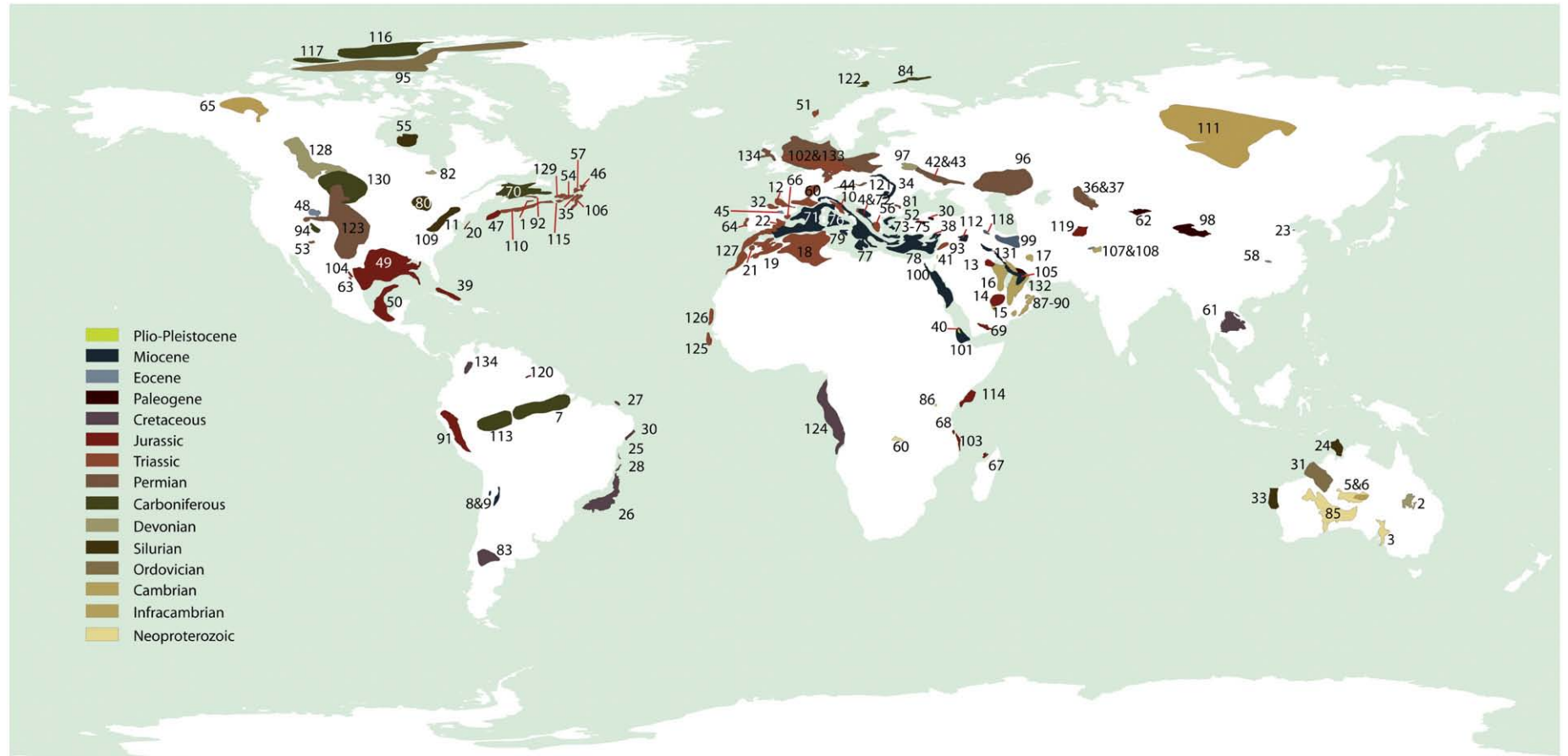


Fig. 18. Distribution of halite-entraining basins across time. To make it readable at this output scale this plot does not illustrate most of the calcium sulfate-dominant systems in the Middle East. Basins: 1. Abenaki (N. Scotian); 2. Adavale; 3. Adelaide fold belt; 4. Adriatic–Albanian foredeep; 5. Amadeus Basin; 6. Amadeus Basin (Chandler); 7. Amazonas; 8. Andean; 9. Andean; 10. Apennine; 11. Appalachian; 12. Aquitaine; 13. Arabian Basin (Gothia Salt Basin); 14. Arabian Basin (Hith Salt Basin); 15. Arabian Basin (Hormuz central Saudi); 16. Arabian Basin (Hormuz Gulf region); 17. Arabian Basin (Hormuz–Kerman region); 18. Atlas (Algerian–Tunisian); 19. Atlas (Moroccan); 20. Baltimore Canyon; 21. Berrechid; 22. Betic–Guadalquivir Basin; 23. Bohai Basin; 24. Bonaparte (Petrel); 25. Brazilian Aptian Basin (Camamu); 26. Brazilian Aptian Basin (Campos–Santos); 27. Brazilian Aptian Basin (Ceara); 28. Brazilian Aptian Basin (Cumuruxatiba); 29. Brazilian Aptian Basin (Sergipe–Alagoas); 30. Cankiri–Corum; 31. Canning Basin; 32. Cantabrian–West Pyrenees; 33. Carnarvon Basin (Yaringa); 34. Carpathian foredeep; 35. Carson Basin (Grand Banks); 36. Chu–Sarysu (Devonian); 37. Chu–Sarysu (Permian); 38. Cilicia–Latakia; 39. Cuban; 40. Danakil; 41. Dead Sea; 42. Dniepr–Donets; 43. Dniepr–Donets; 44. Eastern Alps; 45. Ebro Basin; 46. Flemish Pass Basin (Grand Banks); 47. Georges Bank; 48. Green River Basin; 49. Gulf of Mexico (Northern; Gulf coast); 50. Gulf of Mexico (Southern; Salina–Sigsbee); 51. Haltenbanken; 52. Haymana–Polatli; 53. Holbrook Basin; 54. Horseshoe Basin (Grand Banks); 55. Hudson Bay; 56. Ionian; 57. Jeanne d’Arc Basin (Grand Banks); 58. Jiangnan Basin; 59. Jura/Rhodanian; 60. Katangan; 61. Khorat Basin; 62. Kuqa Foreland (Tarim Basin); 63. La Popa (Monterrey) Basin; 64. Lusitanian; 65. Mackenzie Basin; 66. Maestrat; 67. Majunga Basin; 68. Mandawa Basin; 69. Ma’Rib–Al Jawf/Shabwah (Haramut); 70. Maritimes Basin; 71. Mediterranean–Western; 72. Mediterranean–Adriatic; 73. Mediterranean–Andros Basin; 74. Mediterranean–Cretean Basin; 75. Mediterranean–Samoethraki basin; 76. Mediterranean–Tyrrhenian; 77. Mediterranean–Central; 78. Mediterranean–Eastern; 79. Mediterranean–Sicilian; 80. Michigan Basin; 81. Moesian; 82. Moose River Basin; 83. Neuquen Basin; 84. Nordkapp Basin; 85. Officer Basin; 86. Olduvai depression; 87. Oman (Fahud Salt Basin); 88. Oman (Ghaba Salt Basin); 89. Oman (Ghudun Salt Basin); 90. Oman (South Oman Salt Basin); 91. Oriente–Ucayali (Pucara) Basin; 92. Orpheus Graben; 93. Palmyra; 94. Paradox Basin; 95. Parry Islands Fold Belt; 96. Pricaspian Basin; 97. Pripyat Basin; 98. Qaidam Basin; 99. Qom–Kalut; 100. Red Sea (North); 101. Red Sea (South); 102. Rot Salt Basin; 103. Ruvuma Basin; 104. Sabinas Basin; 105. Sachun Basin; 106. Salar Basin 118 (Grand Banks); 107. Salt Range (Hormuz–Punjab region); 108. Salt Range (Kohat Plateau); 109. Saltville 119 (Appalachian); 110. Scotian Basin; 111. Siberia, East; 112. Sirjan Trough; 113. Solimoes; 114. Somalia/Kenya; 115. South Whale Basin (Grand Banks); 116. 120 Sverdrup Basin (Ellef Ringnes–NW Ellesmere); 117. Sverdrup Basin (Melville Is); 118. Tabriz Salt Basin; 119. Tadjik Basin; 120. Takutu Salt Basin; 121. Transylvanian; 122. Tromso Basin; 123. USA Midcontinent; 124. West Africa (Angola–Gabon); 125. West Africa (Gambia–Guinea Bissau); 126. West Africa (Mauritania–Senegal); 127. West Africa (Morocco–S. Spain); 128. Western Canada (Alberta Basin); 129. Whale Basin (Grand Banks); 130. Williston Basin; 131. Zagros (Mesopotamian Basin); 132. Zagros (Mesopotamian Basin); 133. Zechstein (NW Europe); 134. Zechstein (onshore UK); and 135. Zipaquirá Basin.

brine source that could only have been supplied via connections to a large NaCl-rich reservoir of seawater (see earlier). A plot of the world's marine evaporite basins shows these large basins occur in all the continents of the world (Fig. 18). They range in age from Neoproterozoic to Neogene and, as we shall discuss shortly, indicate particular past plate-tectonic, eustatic and hydrogeochemical associations, all with a reliable seawater seepage source.

The oldest preserved NaCl-dominant saline giants are the various salt basins of central and southern Australia. These 800 my NaCl basins still contain large volumes of salt in the Officer and Amadeus basins, while salt has largely dissolved in the Adelaide fold belt to create what is now a classic *rauhwacke*⁴ succession (Fig. 18; Warren, 2006, Chapter 4 for detailed *rauhwacke* discussion). Similar *rauhwacke* sediments dominate the billion-year-old sediments of the Katangan copper belt in central southern Africa. Other major Neoproterozoic marine megahalite associations define the Eocambrian Ara and Hormuz salt basins of the Middle East. Salt successions in these basins straddle the Cambrian–Precambrian boundary and in the South Oman Salt Basin the succession still retain remnants of potash-grade bitterns and salts (Schröder et al., 2000).

At the other end of the time spectrum, the youngest saline giant or megahalite deposits constitute the various Messinian basins of the Mediterranean region. The oldest mega-sulfate platform deposits are the Cambrian deposits of Siberia and central Australia, while the youngest mega-sulfate platforms are defined by the Eocene anhydrites of the Rus Fm. and its equivalents in the Middle East.

All these megahalite and mega-sulfate successions precipitated via the inflow and evaporation of vast volumes of seawater seeping into hydrographically isolated subsealevel depressions. Evidence from inclusion and isotopic studies, published in the last two decades, has shown that the ionic proportions of seawater, although isochemical at any particular time, has evolved (Lowenstein et al., 2001; Hay et al., 2006). It does so in response to varying rates of seafloor spreading and the intensity of continent–continent collision (Warren 2006, Chapter 2).

5.1. Marine hydrogeochemistry

To interpret brine-related controls on marine evaporite sediments we first use modern seawater as a guide to the sequence of minerals that precipitate as a marine brine concentrates. Throughout the Quaternary, composition and ionic proportions in a seawater-derived brine have been near constant and its ionic composition dominated by Na–Cl with lesser Mg, SO₄, Ca and HCO₃ (Fig. 19A).

Likewise, the salt suite formed by simple single-stage evaporation of Quaternary seawater is predictable and well understood. Almost all of the bicarbonate in concentrating seawater is used during the initial precipitation of mesohaline carbonate, when salinities are some 1.5 to 3 times that of the original seawater (>60‰). Extraction of bicarbonate leaves excess Ca in the concentrating brine, which then combines with sulfate to precipitate gypsum or anhydrite. This begins when the seawater brine reaches 5–6 times its original concentration (150‰; Fig. 19A and B). Ongoing gypsum/anhydrite precipitation removes almost all of the Ca from a seawater brine leaving excess sulfate in the liquor. After halite has precipitated (onset at 10–11 times its original seawater concentration, ≈350‰), the sulfate combines with the magnesium (conservative concentration of Mg to this point) to precipitate a series of MgSO₄ salts along with the KCl bitterns (Fig. 19C). The bitterns begin to precipitate when seawater reaches 60–70 times its original concentration.

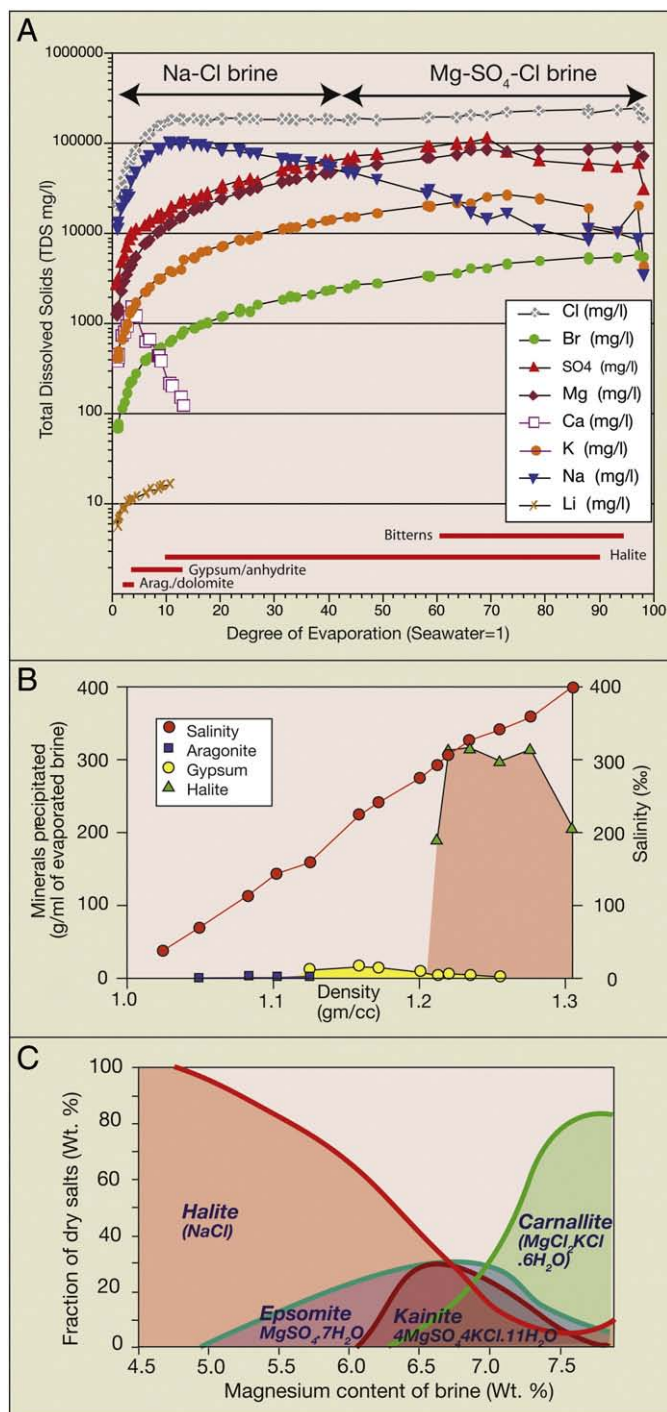


Fig. 19. Marine hydrogeochemistry. A) Changes in ionic proportions due to sequential precipitation of aragonite, gypsum, halite and bittern salts as modern seawater is evaporated to 100 times its original concentration (in part after McCaffrey et al., 1987). B) Pre-bittern (0–400‰) mineral precipitation sequence in a concentrating marine brine (replotted from Table 1 in Briggs 1958). C) Sequential precipitation of potash bitterns from modern seawater plotted against increasing Mg content in bittern (after Garrett, 1970).

The volume of potential halite precipitate held as solute in seawater far exceeds that of any other salt. When seawater brine is evaporated completely, halite by volume makes up more than 90% of the total amount of precipitated salts (Fig. 19B). However, any evaporite basin can attain hydrologic equilibrium (amount of water lost via evaporation equals the amount of solute inflow) at any salinity stage of the evaporation series. If hydrologic equilibrium in a drawdown ancient basin is attained when salinities are appropriate for gypsum

⁴ *Rauhawacke* horizons are a distinct type of evaporite dissolution breccia defined as the weathered and leached remnants of what were once 'weak' salt-entraining layers (Warren, 2006; p 486). Under stress, their evaporitic precursors acted as rheologic inhomogeneities providing surfaces of décollement during orogeny. Halite, or sometimes anhydrite/gypsum, were the main lubricants during the formation of stratiform tectonite or décollement layers.

precipitation (≈ 135 – 270%) then the basin fill will be dominated by gypsum/anhydrite, not halite, and a mega-sulfate basinwide succession forms the majority of the salt mass (e.g. Permian Castile Fm. USA and Permian Werra Anhydrite in the Zechstein Basin, NW Europe).

Complete evaporation of Quaternary seawater produces two sequential types of high density, high viscosity brine: Na–Cl brines and Mg–Cl– SO_4 brines. Na–Cl brines dominate in the salinity range of 35–330‰ (Fig. 19A). Brines at higher salinities become progressively dominated by Mg–Cl– SO_4 , indicating preferential removal of Na by halite precipitation. At first, Mg is the dominant cation in the bittern brines but, as the various MgSO_4 bitterns crystallise, K takes its place and the various KCl bitterns precipitate with carnallite being the dominant potash bittern precipitating from modern seawater (Fig. 19C). Cl remains the dominant anion throughout the evaporation sequence of modern seawater (Fig. 19A).

Unlike the carnallite- and MgSO_4 -dominated bittern salts precipitated from modern seawater (Fig. 19C), the bittern assemblages in many Phanerozoic marine-fed salt basins were dominated by sylvite and carnallite and lacked primary MgSO_4 salts. MgSO_4 -depleted evaporites indicate times in the Phanerozoic when the world oceans were Ca-rich and SO_4 -poor (CaCl_2 seas), compared to Quaternary seawater (Fig. 20A; Lowenstein et al., 2001, 2003). These KCl/ CaCl_2

oceans correspond to what are also known to carbonate sedimentologists as the Phanerozoic calcite oceans, where calcite and Mg–calcite, not aragonite, were the dominant marine carbonate minerals. These KCl/ CaCl_2 seas coincide with periods of rapid seafloor spreading, times of high influxes of mid-ocean-ridge brines rich in CaCl_2 , and elevated sea levels (Hardie, 1996). Thus Phanerozoic oceans have undergone two long-term fluctuations in major-ion composition that are in phase with 100–200 million-year oscillations in sea level, icehouse-greenhouse climates, and global volcanicity (Fig. 20A).

Inclusion studies of chevron halite also show that independent of Phanerozoic fluctuations in Mg, Ca and SO_4 proportions, the ionic composition of seawater has always been dominated by Na and Cl. That is, halite and/or gypsum (now anhydrite in the subsurface) have always been the most volumetrically significant marine evaporite salts throughout the Phanerozoic. Free sulfate levels in the world's oceans first became sufficient to allow gypsum to precipitate as a significant marine evaporite salt in the Mesoproterozoic (Warren, 2006, Chapter 2).

Across the Phanerozoic time frame the salinity of the oceans shows a general decrease (Fig. 20B; Hay et al. 2006). The greatest falls in salinity are related to major extractions of NaCl into young ocean (extensional continent–continent proximity) or foreland (compressional continent–continent proximity) ocean basins (Fig. 21A and B). Phanerozoic seas were at their freshest in the Late Cretaceous some 80 Ma, not today. This is because a substantial part of the Mesozoic salt mass, deposited in the megahalites of the circum-Atlantic and circum-Tethyan basins, has since been recycled back into today's ocean via a combination of dissolution and halokinesis. Periods characterised by marked decreases in salinity (Fig. 20B) define times of mega-evaporite precipitation, while periods of somewhat more gradual increases in salinity define times when portions of this salt were recycled back into the oceans (compare Fig. 20B with Fig. 21A, B).

The last major extractions of salt from the ocean occurred during the late Miocene in the various Mediterranean Messinian basins created by the collision of Eurasia with North Africa. This occurred shortly after the large-scale extraction of water from the ocean to form the ice cap of Antarctica and the deposition of the Middle Miocene Red Sea rift evaporites. Accordingly, salinities the early Miocene were between 37‰ and 39‰ compared to the 35‰ of today (Fig. 20B). The preceding Mesozoic period was a time of generally declining salinity associated with the salt extractions in the opening North Atlantic and Gulf of Mexico (Middle to Late Jurassic) and South Atlantic (Early Cretaceous).

After the deposition of the Hormuz/Ara salt successions at the Cambrian–Precambrian boundary the next major salt extractions of the Phanerozoic occurred during the Carboniferous–Permian and related to the final accretion of the Pangaea supercontinent (compare Fig. 20B with 21B). There were only a few large extractions of halite from seawater during the intervening Palaeozoic. The Hay et al. (2006) model suggests that the Palaeozoic was a time of relatively stable, but slowly increasing, salinity ranging from the upper 40s to the lower 50s (in parts per thousand).

The change in Palaeozoic salinity implies that arid-zone marine-fed evaporites and evaporitic mudflat carbonates perhaps formed more readily from seawater brines in the early Phanerozoic epeiric seas compared to the less saline oceans and narrower steeper icehouse continental shelves of today (less freeboard). It also implies that halite saturation was more easily attained from Palaeozoic ocean waters. Yet the volumes of extracted marine halite were low for most of the Phanerozoic (Fig. 21A, B). Perhaps conditions were less suitable for world-scale salt extractions at that time due to the more dispersed nature of the major continental plates and the associated paucity of locales of continent–continent proximity. Most Paleozoic megahalites accumulated in epeiric intracratonic sags (distal effects of orogeny) rather than as deposits along a cratonic periphery (see later).

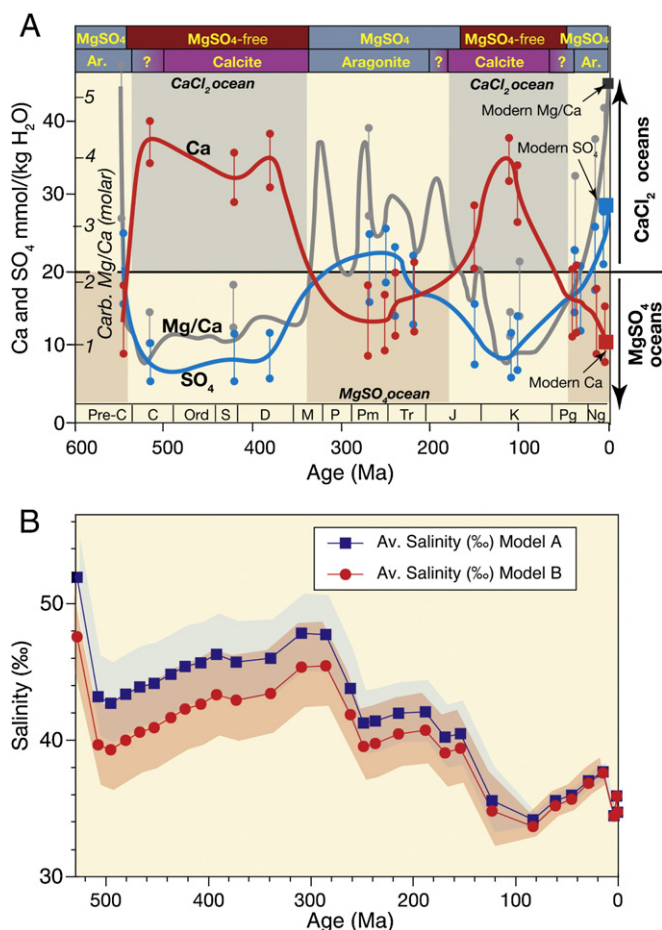


Fig. 20. Seawater chemistry changes across deep time. A) Secular variation in the amounts of Ca and SO_4 in seawater for the last 600 my estimated from fluid inclusions in marine halites (vertical bars), compared to predicted seawater secular variations. The horizontal line around 20 mmol/kg H_2O is the approximate divide between CaCl_2 and MgSO_4 seas. Also plotted are the temporal distributions in the primary mineralogies of Phanerozoic nonskeletal carbonates (calcite and aragonite) and periods of MgSO_4 -free and MgSO_4 bitterns. For Mg/Ca, the grey plot bars are from halite inclusions measurements but the Mg/Ca curve is from marine carbonate data (after Lowenstein et al., 2001, 2003). B) Oceanic salinity changes for the last 500 my (after Hay et al., 2006). Note the time scale (530 Ma) is not the same as Fig. 20A (600 Ma).

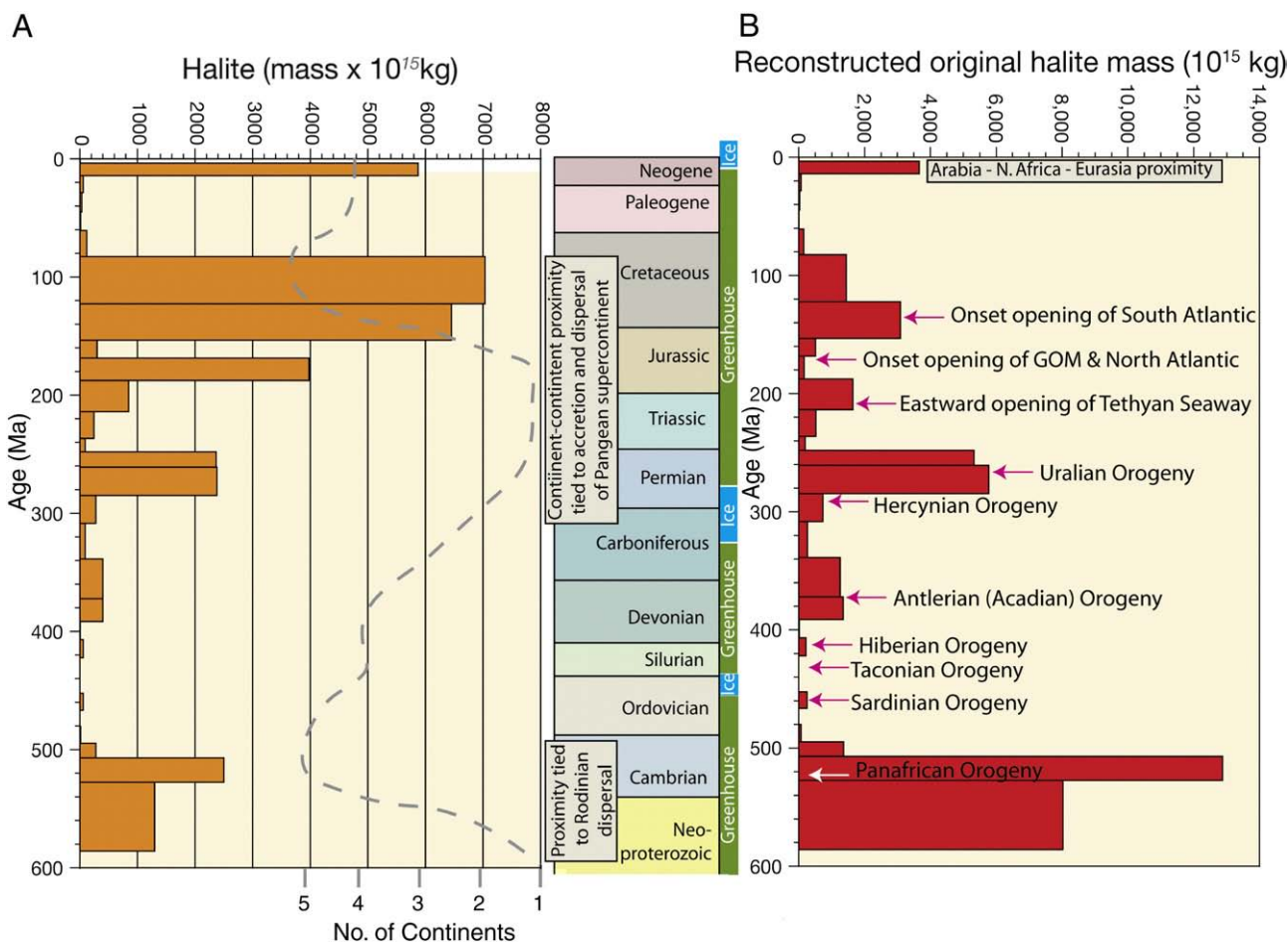


Fig. 21. Phanerozoic evaporites. A) Mass of Phanerozoic halite residing in basin (after Hay et al., 2006; Number of continents curve from Condie 2004). B) Reconstructed mass of recycled Phanerozoic halite lost by combination of erosion and dissolution (after Hay et al., 2006). Time of halite precipitation as influenced by accretion and disintegration (dispersal) of Pangean supercontinent as well as other orogenic and tectonic events is also shown (greenhouse after Fisher, 1981; tectonics after Haq and Van Eysinga, 1998; Haq and Al-Qahtani, 2005).

When estimates of the volume of salt being recycled back into the oceans are added to volumes of actual salt in the various megalite beds of the world an interesting picture emerges of actual precipitated salt volumes at various times of enhanced evaporite deposition. (Fig. 21B; Hay et al., 2006). The greatest volumes of halite still remnant in sedimentary basins are defined by Jurassic and Cretaceous successions. Deposition was largely within the circum-Atlantic salt basins and tied to the early rift to drift transition during the opening of the Neotethys and the northern and the Southern Atlantic. Yet when recycled halite estimates are added, these Mesozoic deposits are lesser volumes compared to the Permian and Neoproterozoic/Cambrian successions, with the greatest volume of salt deposited across the past 600 million years occurring in the various Neoproterozoic–early Cambrian Hormuz and Ara halite deposits of the Middle East (Fig. 21B).

Variations in the world's salt sediment mass across time lead to questions such as: How are large volumes of halite and gypsum extracted from seawater? What are the tectonic and climatic controls? Why are no megalite or mega-sulfate deposits found in Quaternary successions?

5.2. The now and then of marine climates

Hadley cells are the broadest scale climatic influence on the latitudinal position of today's warm arid belts and the associated distribution of desert sediments (Figs. 4 and 5). Hadley cells are a planet-scale atmospheric circulatory response to the varying intensity

of solar irradiation from the equator to the poles and must have played a significant role in the distribution of the world's arid belts throughout time (Table 6). Unfortunately, the climate of the Holocene or the Pleistocene is not well suited to act as a baseline for the extent and distribution of arid Phanerozoic climates. The last 8000–10,000 years is an interglacial and, based on world δO^{18} curves in deep-sea sediments, is a state typical of some 10% of the icehouse climate of the past few million years (Hay et al., 1997; Warren, 2006, Chapter 5). It is a time of relative sea-level stability after a rapid 130-m rise from the lowstand of the last glacial maximum some 18,000 years ago. The last few million years is a period when physical geologic processes are operating at unusual rates and much of the earth's geochemical system is not in a steady state.

During most of the Phanerozoic, except for part of the Permian–Carboniferous, the earth's climate was warmer and more under the influence of greenhouse conditions (Table 7, Fig. 21). In greenhouse times there were no widespread continental or polar ice sheets and the planet's meridional temperature gradient was much less steep than it is at present.

Yet for the past few million years, possibly since the mid Miocene (≈ 12 Ma) and the initiation of permanent grounded Antarctic ice sheets, the distribution and effects of broad-scale atmospheric circulatory belts (including the Hadley cells) have been modified by the waxing and waning of polar ice. During glacial periods the expanded circum-polar ice sheets act as frigid plateaus, forcing a stronger meridional temperature gradient, so altering significant portions of the world's atmospheric circulation, as well as creating

Table 6

World-scale climate processes controlling distribution of evaporites in modern deserts (after Warren, 2006).

Cause and scale	Situation	Quaternary examples
Descending or stagnant air mass (Planet scale)	Subtropical regions. Regions beneath the descending limbs of Hadley cells, centred around 20–30° north and south of the Equator.	Sahara, Namibia, Kalahari (Africa) Chihuahuan and Sonoran (North America) Great Sandy and Simpson deserts (Australia) Arabian, Iranian, Thar deserts (Middle East and India)
Continentality (Plate tectonic scale)	Regions within the continental interior. Locations isolated by distance from moisture sources, principally the oceans.	Saharan (Africa) Turkestan, Talimaklan, Gobi (Asia) Great Basin (North America)
Orographic or Rain shadow (Plate tectonic scale)	Regions located in the lee of topographic barriers, such as mountains and plateaus. Cooling of rising airmass creates rainfall on the windward/ seaward side of a mountain range or barrier. As airmass subsides on the leeward side it warms and dries.	Turkestan, Talimaklan (Asia) Great Basin, Colorado Plateau (North America) Monte, Patagonian (South America) Cool sea surface
Cool sea surface temperatures (Plate tectonic scale)	Continental regions adjacent to cool (upwelling) seawater zones. The amount of moisture evaporated from the ocean surface is less under cooler conditions, so yielding drier coastal air. Cooler sea surface temperatures also stabilize air masses, further reducing convective rainfall.	Western Sahara, Namibia (Africa) Peruvian, Atacama, (South America) Rub'Al Khali (Saudi Arabia)

their own ice-cap associated pressure systems. Whenever ice-caps expand, the Hadley-related circulation belts are pushed and compressed toward the equator. This has occurred numerous times during glacial maxima of the current icehouse climate mode. These ice-sheet forced climatic oscillations have had a marked effect on sediment styles in Quaternary deserts. Many halite-entraining continental playas with sedimentary records extending back a few hundred thousand years entrain water-full versus dry stages (e.g. Baker et al., 2001; Hesse et al., 2004; Yan et al., 1998).

Times of expanded ice sheets, with their more intense ice sheet-induced atmospheric circulation cells, are probably the least representative states for the world's Phanerozoic climate. Interglacial periods within icehouse mode, like the Holocene, are perhaps a little closer to the “average” Phanerozoic climate. But today's climate is still a long way from a climate more representative of the bulk of Phanerozoic time when the polar regions were free of permanent ice and world climate and the eustatic frequencies and amplitudes were in “greenhouse” not “icehouse” mode.

In addition to glaciological intensity, another three factors influencing the broad scale distribution of the world's arid climate belts in time and their associated evaporite sediments. They are continentality, adiabaty and intensity of oceanic upwelling (Table 6). As we shall see, variations in the Phanerozoic scale of development of all three is controlled by the latitudinal position of continental plates and variations in styles of plate–plate interaction (i.e. the Wilson Cycle). When a supercontinent lies in an arid *horse latitude* belt, large portions of its interior will show a high degree of continentality. This was the case during the Carboniferous to Triassic in Central Europe,

which at that time was part of the interior of the Pangaeon supercontinent (Reinhardt and Ricken, 2000; Warren, 2008).

Likewise, orographic deserts are better developed at times when two continental plates collide or a transcontinental rift valley forms (Kendall et al., 2003; Warren, 2006, Chapter 5). A rising mountain range is a barrier to atmospheric circulation, especially if perpendicular to the in-coming circulation. For example, the Late Tertiary uplift of the Kunlun Mountains some 5.3 Ma prevented moisture from the Indian Monsoon reaching this part of the Tibet Plateau. It created the Taklamakan desert, the second largest active sand desert in the world (Sun et al., 2008). The uplift also created a dry easterly jet stream, moving arid cool air across the Tibet Plateau around the northern side of the Himalayas and down the across the Arabian Peninsula toward Somalia where it descends and warms. This stream of cool southward flowing dry air warms as it moves south across the Eastern Mediterranean land areas and so accentuates existing aridity. It helps create an adiabatic desert zone that extends across Arabia and northern Africa almost to the Equator (Fig. 4A). In a similar fashion the sandy deserts of the Rotliegend in the Permian Zechstein Basin region of Europe once lay in the continental interior of the Hercynian foreland and stretched across more than 30° of latitude. Only when and where seawater could enter an intra-continental subsealevel depression behind a 2000-metre high mountain range were the thick Late Permian salts of the overlying Zechstein series deposited (Fluteau et al., 2001).

Orographic deserts and their evaporite sediments form also as continental plates split in arid climate zones. This is the case with the Late Pleistocene MgSO₄ bittern salts that accumulated prior to the

Table 7

Characteristics of icehouse and greenhouse climate modes (after Warren, 2006).

	ICEHOUSE	GREENHOUSE
Age	Late Cenozoic, Late Carboniferous to Early Permian, Ordovician, Late Neoproterozoic	Cambrian to Middle Carboniferous, Middle Permian to Early Cenozoic
Tectonic style	Collision, telescoping	Stretching, rifting
Seafloor spreading	Slow	Rapid
Subduction/ volcanism	Low	High
Marine margin basins	Narrow shelves, limited short-lived interior seaways with small aerial extent	Wide shallow (pericontinental) shelves and large long-lived interior seaways (epeiric seas)
Marine eustasy	High amplitude (≈ 100 m) change on 100,000 year times scale (4th order). World sealevel is low (caught up in long-term polar ice sheets)	Low amplitude (>5 – 10 m) change on 100,000 year times scale (4th order). World sealevel is high (no polar ice sheets)
Ocean Basins	Cold, oxygenated	Warm, often anoxic
High latitude climates	Glaciers, taiga and tundra	Deciduous forest
Mid latitude climate	Deciduous forest, glacial advances and steppe	Tropical wet and stressed forest
Low latitude climate	Rainforest, savanna and desert	Desert
Erosion/ weathering	Fast/mechanical	Slow, chemical
Depositional styles of large evaporite basins	Tectonically induced endoheic continental depressions (terrestrial lacustrine; no marine-seep platform and basinwide evaporites accumulating at present time; but basinwides can form in suitably isolated icehouse conditions, and did so most recently in the Middle and Late Miocene)	Tectonically and eustatically induced endoheic continental and marine margin depressions (terrestrial lacustrine, marine-fed platform and marine-fed basinwide styles can be widespread whenever suitable combinations of tectonics and eustasy occur)

present continental evaporites of the Holocene Danakil desert. This marine seepage depression lay in the rain shadow of the Danakil Mountains. Lake Magadi and Lake Natron also occur in orographic depressions in the deeper parts of the Gregory Rift in the East African rift valley. Similar rain shadow effects influenced the various Mesozoic salt basins of the opening Atlantic (Kendall et al., 2003).

As for collision basins, thick salt beds cannot form in a rift valley unless the arid basin depression can draw on a large oceanic brine reservoir. This was the case, for example, in the Mid-Miocene in the Red Sea area and the Aptian in the various proto-South Atlantic salt basins (Bosworth et al., 2005; Davison, 2007). Both areas were rift-bound hydrographically-isolated sub-sealevel depressions able to draw on the huge reservoir of oceanic waters via seepage drawdown. Throughout the Phanerozoic such extensional sag and compressional plate interactions have helped induce hyper-aridity atop large subsealevel seepage depressions that were capable of accumulating thick halite and gypsum successions (Kendall et al., 2003; Warren 2006, Chapters 2 and 5).

Upwelling-induced deserts are also controlled by the positions of drifting continental plates within arid zones. Today, the western edges of most horse latitude deserts are washed by upwelling-induced cool ocean currents driven by large-scale ocean gyres, which rotate anticlockwise in the Southern Hemisphere and clockwise in the Northern Hemisphere. Throughout much of the Phanerozoic, coastal deserts in ancient horse latitude belts, as indicated by aeolian dunes and evaporites, have been enhanced by upwelling along the western sides of continents drifting into arid latitudinal belts (Hay, 1996; Parrish et al., 1982).

When the latitudes of Holocene evaporite occurrences in modern deserts are plotted (as an equal area plot) against palaeolatitudes of ancient deserts, a bimodal latitude-related is obvious from the Permian to the present (Fig. 22; Ziegler et al., 2003). It indicates the time constancy for the broad distribution of the world's Hadley cells and the resultant horse latitude belt. This latitudinal similarity of evaporites through time is tied to planet-scale circulation in the world's atmosphere. As Fig. 22 is an equal area plot, it does not indicate any time-related changes in the volume of salts accumulating within the world's two arid climatic belts centred some 15–45° north and south of the equator.

As we have seen, the volume of halite and other evaporite sediments does vary substantially with particular time periods (Fig. 21A and B; Hay et al., 2006). Today the volume of marine evaporites is one to two orders of magnitude less than particular times in the past. In addition to the climatic influences just discussed and which influence the distribution of evaporites past and present, there are three additional tectonic/eustatic factors needed to encourage the depositional of mega-sulfates and megahalites. They are; 1) hydro-

graphic isolation, 2) greenhouse eustasy, and 3) continent–continent proximity.

6. Marine evaporites across time and tectonics

At particular times in the earth's past the hydrologies that facilitated deposition of widespread sulfate or halite evaporites across large parts of ancient salt basins are tied to platform or basinwide settings that have no same-scale modern counterparts. When they were active within appropriate arid climatic and hydrological settings then huge volumes of seawater were drawn into the evaporitic depressions. These systems were typical of regions where the evaporation rates of ocean waters were at their maximum, and so were centred on the past latitudinal equivalents of today's *horse latitudes*. But, like today's nonmarine evaporites, the location of marine Phanerozoic evaporites in zones of appropriate adiabatic aridity and continentality extended well into the equatorial belts (Fig. 22).

Because water cannot flow uphill, all systems drawing on large volumes of seawater as the primary source of solutes must by definition be hydrologies with subsealevel brine surfaces or water tables. Oceanic aerosols can supply small volumes of chlorides and sulfates to supra-sealevel evaporite systems, as they do today in the groundwaters of the Great Artesian Basin of Australia, and pedogenic gypsum crusts in the Atacama and Namibian deserts (Zhang et al., 2007; Rech et al., 2006; Eckardt and Spiro, 1999). But marine seepage is the only viable hydrological mechanism to supply the volumes of brine needed to form a mega-evaporite.

Groundwater and hydrological restraints mean the depositional setting for all large ancient evaporite salt masses was a hydrographically isolated, endorheic, drawdown marine evaporite seaways, perhaps with an occasional seawater flood across what was otherwise a subaerial barrier zone that separated the various brine seaways from the open ocean (refer to Warren, 2006; Chapters 2 and 5 for detailed quantification and the relevant references for this argument of hydrographic isolation). At the basin scale seawater-fed evaporite systems are divisible into platform and basinwide settings.

6.1. Platform evaporites

Platform evaporites are defined as ancient bedded marine evaporites formed in subsealevel seepage lagoons. Brine surfaces (tied to potentiometric head) responded to slow low-amplitude 4th-order eustatic rises and falls of greenhouse sealevel and the resultant bedded evaporites were interlayered with normal marine shelf and platform carbonates (Fig. 23). These platform evaporite successions may contain halite, especially in intracratonic basinwide settings, but

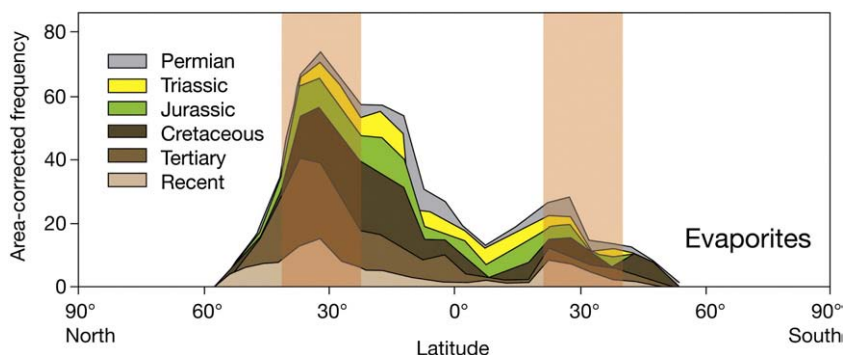


Fig. 22. Latitudinal distribution of evaporites from Permian to present (after Ziegler et al., 2003). Shaded belts indicate *horse latitudes*. Note, this plot is a count of an evaporite occurrence in each one degree latitude–longitude region; unlike Fig. 21A and B, it plots latitude occurrence and is not a plot of evaporite volume. The dominance of northern hemisphere occurrences reflects the dominance of landmasses in the northern hemisphere across the Permian to Recent.

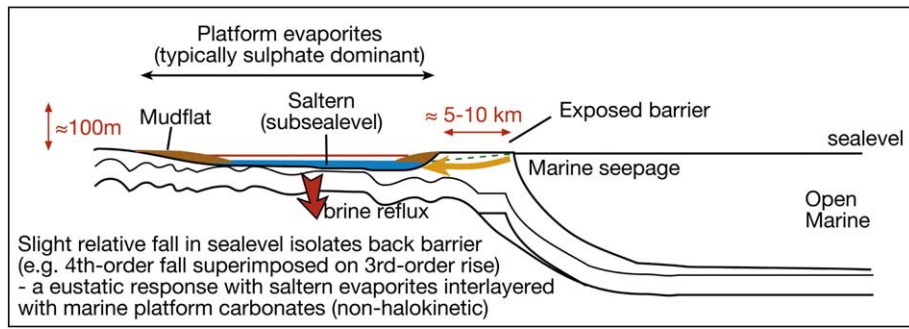


Fig. 23. Schematic cross section of an ancient marine evaporite platform at a time when hydrographic isolation from the ocean has converted the former marine shelf lagoon into a marine-fed saltern with extensive evaporite mudflats in the shoal water parts. At the time the widespread subaqueous evaporites are forming there is no reliable surface connection, only a seepage supply of mother brine.

in periplatform settings are typically dominated by 5–40 m thick Ca-sulfate beds intercalated with normal marine platform carbonates (Figs. 23 and 24; Table 8). The lateral extent of these epeiric platform salts, like the Khuff Anhydrite with an area of 1,206,668 km², constitute some of the most aerially extensive evaporite beds ever deposited (Fig. 2).

Platform-wide megasulfate beds of Eocene age in the Middle East, centred on Iraq, Kuwait and Saudi Arabia (Rus Fm. and equivalents) are our most recent example of a time when an epeiric carbonate platform succession was covered and interlayered with a widespread combination of saltern and evaporitic mudflat gypsum and anhydrite (Table 8). A similar set of bedded platform-carbonate saltern-sulfate interlayers characterises the depositional cycles of Jurassic Arab Fm sediments (especially the Hith Anhydrite) of the Middle East, the Middle Anhydrite Marker (and equivalents) in the Permian Khuff Fm of Saudi Arabia, Qatar and the Emirates (Fig. 2). There are numerous other large-scale Ca-sulfate saltern/mudflat examples including the anhydrite portion of depositional cycles in the Cretaceous limestone

platforms and atolls of the circum Gulf of Mexico (e.g. Ferry Lake Anhydrite), the Permian back-shoal lagoons of West Texas and New Mexico (e.g. San Andres Fm. and equivalents) and the Cambrian carbonates of the Georgina Basin in Australia (e.g. Red Heart Dolomite and equivalents).

In many cases, especially in older examples such as the Red Heart Dolomite and Cambrian Cool Creek Fm of Oklahoma, the anhydrite has dissolved and all that remains as evidence of a former widespread anhydrite bed is a dissolution breccia, or dispersed nodules and burial salt cements. In some cases these breccias are mineralised MVT deposits, as with the San Vicente Mine, Peru and the ore zones in the Cadjebut mine region of the Canning Basin Platform. In the latter case the ore zones pass laterally into saltern anhydrite beds (Warren and Kempton, 1997).

Rather than the icehouse climate mode of today, periplatform evaporite systems required greenhouse eustasy in order to establish the required seepage hydrology (Warren, 2006, Chapter 5). Times of greenhouse climate were times when 4th order (100,000 year)

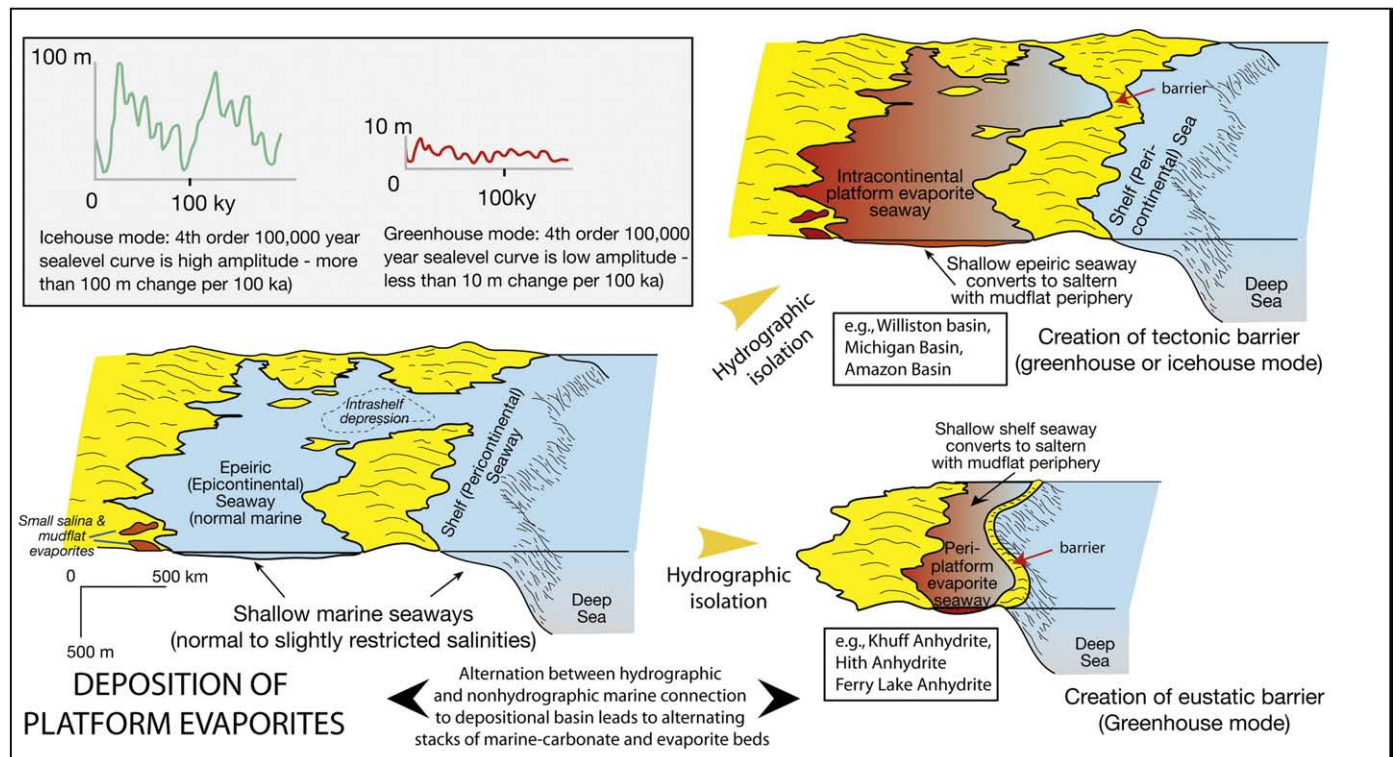


Fig. 24. Platform evaporites tend to form across isolated epeiric seaways during times of hydrographic isolation when seawater seeps in to the subsealevel depression through a subaerial barrier. Inset illustrates the very different 4th order eustatic character between icehouse and greenhouse climate modes in earth history.

Table 8

Selected platform evaporites (dominantly megasulfate systems).

Periplatform evaporite successions	Age	Comments/key references
Rus Fm., Arabian Basin, Qatar, Saudi Arabia	Eoc., Lower	Has a total thickness of about 100 m, composed of limestones and dolomitic limestones (often argillaceous) passing upward into massive 10 m thick saltern anhydrite. (Al-Saad, 2003; Whittle and Alsharhan, 1994; Ziegler, 2001)
Ferry Lake Anhydrite, NE Gulf coast, USA	Cret. Lower	Divided in 9 individual saltern anhydrites that are traceable from southern Mississippi to southern Florida and intercalated with normal marine bioclastic limestones. (Pittman, 1985; Petty, 1995)
Smackover/Buckner Fm., N Gulf Coast, USA	Cret. Lower	Buckner Anhydrite made up of intercalated 2–6 m thick saltern anhydrites and marine limestones. It extends from Florida Panhandle to South Texas (Mann, 1988)
Hith Anhydrite, Arabian Basin, Middle East	Jur., Upp.	Hith anhydrite is a regional seal that extends across much of the Arabian Peninsula and locally reaches 170 m in thickness. It is composed of bluish-gray to alternating bands of blue and white anhydrite with two internal carbonates and separates marine carbonates of underlying Arab Fm from overlying Yamama (unconformable base). (Alsharhan and Kendall, 1994; Ziegler, 2001)
Middle Anhydrite Marker, Khuff Fm., Middle East	Perm., Upp.	Middle Anhydrite can be traced from eastern Saudi Arabia to offshore UAE, and reaches the onshore Fars Province of Iran. This anhydrite is some 12–17 m (20–39 ft) thick and consists of massive saltern anhydrite with minor thin interbeds of dolomite. (Alsharhan, 2006)
San Andres Fm., Northern Delaware Basin margin, USA	Perm., Upp	Anhydrite occurs as widespread saltern units composed of massive nodular mosaic anhydrite beds up to 5 m thick capping cyclic shoaling variably-dolomitised platform carbonates. Individual anhydrite beds (P1–P5) that can be traced from Palo Duro basin into shelf edge of the Slaughter-Level and trend (Elliott and Warren, 1989)
Cadjebut Fm., Canning Basin margin, Australia	Dev. Mid.	Saltern anhydrites up to 5 m thick extend across a Devonian platform embayment pass and pass laterally into the sulfide mineralised ore horizons of the Cadjebut Mine region. Saltern sulfates capped shoaling oncologic and bioclastic muds that overlie normal marine grainstones and wackstones. (Cathro et al., 1992)
Cool Creek Fm., Arbuckle platform, USA	Ord. Low.	At least three 1–2 m thick breccias, interpreted to be of solution collapse origin, are present in the Cool Creek and define the presence of former widespread saltern anhydrite units that capped restricted marine stromatolitic carbonate platform sediments. (St. John and Eby, 1978)
Red Heart Dolomite, Georgina Basin, Australia	Camb. Low.-Mid.	Red Heart Dolomite which extends across much of Central Australia is a completely dolomitized 100 m-thick platform carbonate deposited in an evaporitic shallow-water epeiric seaway It is characterized by at least four shallowing-upwards saltern anhydrite-capped cycles. Many of the surface and near-surface anhydrites caps are now leached and represented by collapse breccias. (Nicolaidis, 1995)
Intracratonic Platform evaporite successions	Neopr. to Eoc.	North Sahara Basin, Africa; Canning Basin, Australia; Muschelkalk and Paris Basins, SW Germany and Spain; Amazonas Basin, South America; West Siberian Basin, Russia; Michigan Basin and Williston Basin, USA (Warren, 2006)

sealevel changes were an order of magnitude less than the 100 m sealevel cycles that typify 4th order eustatic cycles in the icehouse-driven world of the last 10–12 million years (inset in Fig. 24). There was another Phanerozoic episode of icehouse-dominated eustasy some 300 Ma in the Permo-Carboniferous and another somewhat shorter possible episode some 440 Ma in the Ordovician (Fig. 21A and B; Fischer, 1981).

During icehouse times the oceanic eustatic response to rapidly waxing and waning polar icesheets is excessively high amplitude and time-wise too short to allow periplatform-margin biogenic buildups to grow into continuous platform-edge barriers (more than 100 m of sealevel oscillation every 100,000 years). It is the long-term elevated sealevels of greenhouse times, along with their lower fourth order amplitudes (less than 5–10 m of sealevel change every 100,000 years), that allow continuous platform-edge reefs and shoals to form (see inset in Fig. 24). With a subsequent slight fall in sealevel, these continuous platform-edge barriers became subaerial barriers to any hydrographic connection of the back-barrier lagoon to the open ocean. This facilitated the creation of marine-seepage fed lagoons (salterns) in their hinterland (Warren, 2006; Chapter 5).

Periplatform evaporites tend to be megasulfate rather than megalite systems and act as regional seals to many of the world's oil and gas fields (e.g. Hith Anhydrite, Middle Anhydrite marker of the Khuff Fm and the Ferry Lake Anhydrite; see Warren, 2006, Chapter 10 for details on various evaporite-sealed oil and gas fields). But there are also some intracratonic basinwide systems where widespread sulfate and halite beds are interlayered with units of normal marine platform carbonate. Nonhalokinetic bedded halite tend to tends to be part of the depositional succession in this type of platform evaporite and these type of platform evaporite successions tend to occur in intracratonic sags, as in the Amazonas and Michigan basins

(Table 8). Rather than being eustatically driven, intracratonic platform evaporite depressions tend to be a response to tectonically-induced hydrographic isolation and routinely are the result of the distal effects of orogeny (Figs. 21 and 24). Intracratonic evaporites can be considered a transitional subset of basinwide evaporite successions related to gentler topographic expression and slower relative subsidence typical of intracratonic sag basins compared to saline giants deposited in rift and collision basins.

6.2. Basinwide evaporites

In contrast to platform evaporites, basinwide evaporites are defined as marine evaporite successions that have filled large-scale tectonically and hydrographically isolated subsealevel sedimentary basins to their hydrological equilibrium level (Fig. 25). Basinwide successions are typically dominated by thick massive salt beds, which typically are made up of thick stacked halite beds (more than 100 m thick), but can also contain substantial volumes of thick-bedded Ca-sulfate and evaporitic carbonate, as in the Delaware and Otto Fiord Basins (Fig. 18). Basinwide systems also entrain the larger accumulations of the world's potash salts, even though our only Quaternary examples of economic potash are continental systems (see later). Many halite-dominant basinwide beds are also remobilised into various halokinetic geometries.

Basinwide evaporite deposits are the result of a combination of tectonic and hydrological circumstances that are not currently active on the world's surface. They were last active in the Miocene in association with soft-suture collision basins tied to the Alpine–Himalaya orogenic belt and to rift basins developed in the early stages of the Red Sea. They will be active again in the future at sites and times of appropriate plate–plate interaction when two continental plates

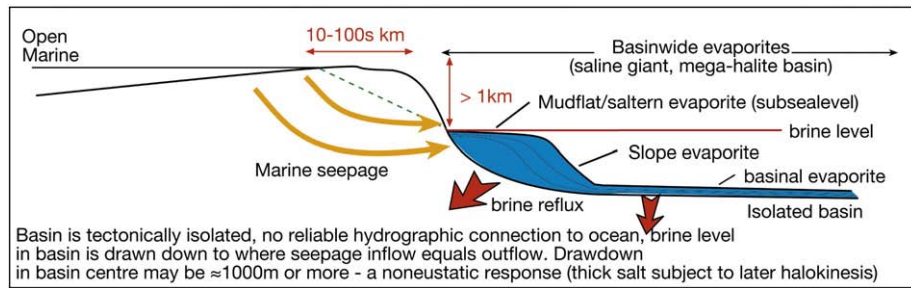


Fig. 25. Schematic cross section of an ancient marine basinwide setting at a time when hydrographic isolation from the ocean has converted the former marine basin into a marine-fed drawdown basin. This drawdown setting shows a range of evaporite depositional settings extending from the continental about the basin strandzone through to saltern with extensive evaporite mudflats in the shoal water parts to deepwater evaporites in the basin centre (see Fig. 1). At the time the widespread subaqueous evaporites are forming there is no reliable surface connection, only a seepage supply of mother brine. The salinity in the basin, and hence the dominant salt mineralogy, is controlled by the salinity attained when the basin reaches hydrological equilibrium (inflow = outflow).

are in close proximity and the intervening floor at or near a plate-edge rift or suture is both subsealevel and hydrographically isolated.

6.3. Tectonic settings for marine-fed basinwide evaporites

Placing basinwide evaporite occurrences into a plate tectonic framework simplifies the discussion of where suitable world-scale subsealevel marine seepage evaporite depressions can occur. At the plate tectonic scale the world's lithosphere is divisible into a number of major and minor plates, which because their interiors are relatively cool and rigid are mostly tectonically stable. Plate edges, also known as plate margins, are zones where moving plates interact one with another and tend to be tectonically unstable, these are the zones where the largest and thickest basinwide evaporites tend to form.

Plates are composed of variable amounts of continental and attached oceanic lithosphere. They float atop the asthenosphere are carried about on the upper part of its convective cells. In places where the lithosphere in a plate is largely composed of continental siliceous material (sial) it is less dense and tends to float above the geoid (and above sealevel) so constituting the suprasedalevel portions of the larger continents. Where the plates are dominated by less dense basaltic material (sima), the surface of the plate tends to lie below the geoid and sealevel, constituting much of plates beneath the deep ocean floor (Fig. 26A).

Most of the larger continental blocks have elevations within a few hundred metres of sealevel, while most of the ocean floor lies some 5 km below the seafloor (Fig. 26A). The difference in elevation between the continental surfaces and the ocean floors is the result of a number of factors that include; thickness and density contrasts between continental and oceanic crusts, tectonic activity, erosion, sealevel and the ultimate strength of continental rocks, which determines their ability to maintain an unsupported slope above oceanic crust.

There is an overall positive correlation between areas of continents and microcontinents and their average elevation relative to sea level (Fig. 26B; Cogley, 1984; Condie, 2004). Small continental fragments, such as Agulhas and Seychelles, lie 2 km or more below sea level. Arabia and India are higher than predicted by the area–height relationship, a feature probably related to their collisional tectonic histories. The height of a continental block relative to sea level depends on the uplift rate and the rates of erosion and subsidence. Collision between continents resulting in lithosphere thickening is probably the leading cause of continental uplift in response to isostasy. The anomalous heights of India and Arabia undoubtedly reflect the Neogene collision of these microcontinents (Fig. 21B).

The six large continental blocks have undergone numerous collisions in the last 2 Ga, each thickening of the lithosphere in collisional zones leads to a greater average continent elevation both in the lead up to and after the collision. Hotspot activity can also elevate continental interiors and portions of the seafloor, it explains the

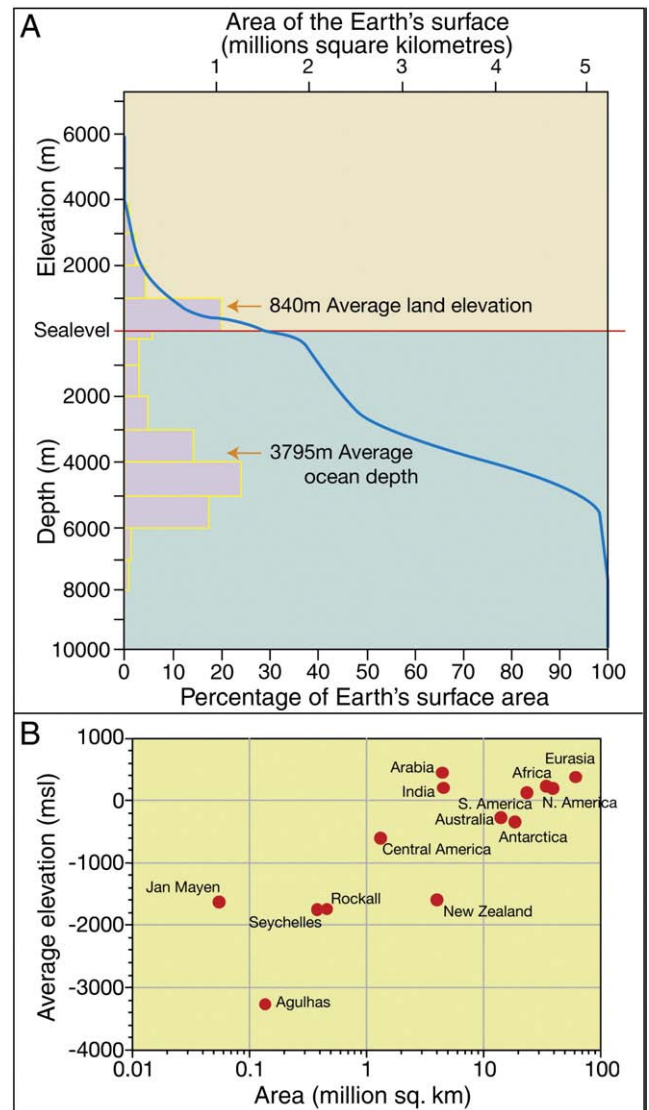


Fig. 26. Isostasy. A) Distribution of earth surface elevations. Histogram shows percentage/area of the earth's surface within elevation intervals of 1 km. Cumulative curve (blue) shows the percentage of the earth's surface that is above a particular elevation. B) Mean continental heights as a function of areas of continental lithosphere in selected continental and micro-continental blocks (replotted from data in Cogley, 1984).

relatively high elevation of the basaltic Jan Mayen Island mass. In both uplift situations any supracrustal depositional system has the potential to pass from submarine to continental. Likewise, in a newly formed continental rift atop an upwelling mantle plume, the depositional system will pass from continental to submarine as the rift widens and underlying crust thins and cools.

It goes beyond the needs of this review paper to delve more deeply into the causes and outcomes of hypsometric analysis, other than to note one self-evident truism and then make a set of simple deductions that must characterise basinwide and platform evaporites. First the truism: Sediments deposited within a continent tend to accumulate above sealevel. This may seem to be a trite statement, but it has substantial implications in terms of hydrological controls on ancient evaporites. We have seen how the volumes of solute needed to explain the huge volumes of halite in ancient evaporites must come from seawater (or dissolution-related reworking of older marine evaporites into the landscape drainage). We know that water cannot flow uphill and so such marine-derived evaporite systems must by definition be accumulating in subsealevel depressions. Yet, we also know that evaporites cannot form when a restricted basin has a surface connection to the ocean. Evaporite basins require hydrographic isolation and a surrounding barrier that facilitates marine seepage. Thus, substantial volumes of evaporites can never accumulate in open marine situations (characterised by large distances between continental masses), nor in highly elevated continental situations where there is no huge isochemical solute reservoir to draw upon (seawater cannot flow uphill). We saw earlier how endorheic drainages at suprasedalevel elevations in continental settings so allow relatively small evaporite deposits to form. These are the borates, salt-cake and soda-ash salts discussed earlier, which have precipitated from the requisite nonmarine mother brines.

The need for a large volume of seawater in order to accumulate huge volumes of halite or calcium sulfate in a sedimentary basin, means it can only happen in an arid, subsealevel, hydrographically isolated marine-fed seepage depression. That is, the evaporite basin is isolated from a hydrographic connection to the ocean, yet still remains in a subsealevel position so as to allow seawater seepage. The basin is desiccated and its hypsometric position is passing either from the continental into the marine realm or immediately prior to the passage from the marine to the continental realm. This happens when two or more continental plates are in close proximity, either as; 1) an opening continental rift causes the floor of a rift valley to pass below sealevel or, 2) in a situation of continental–continental closure as the rising floor of the closing basin is still subsealevel as the hydrographic connection is lost (Fig. 27, Table 9). The former situation characterised the formation of Miocene halite in the Red Sea, the latter characterised the precipitation of Messinian halite across the floor of the Mediterranean.

Timing and styles of plate–plate interaction are summarised by the Wilson Cycle, which breaks down a plate tectonic cycle into a time of divergence passing to convergence via stages A through H (as shown in inset in Fig. 27). Named in honour of J. Tuzo Wilson, the Wilson Cycle encapsulates the notion that as new ocean basins open, via the formation of new seafloor, others must close driven by the process of subduction and ultimately by continent–continent collision (Wilson, 1966).

Compilations of the time-related distribution of ancient marine evaporites shows there are four plate tectonic situations where thick evaporite beds have accumulated at particular times in the past (Table 9). They are (Fig. 27): 1) Areas of rifting where continental plates are beginning to move apart (divergent plates in “rift to drift” transition in Wilson cycle stages B to early C); 2) Areas where continental plates are coming close to one another (convergent or colliding plates in Wilson cycle stage F); 3) areas of intracontinental or intraplate sagging (intracratonic basins), which are often the result of farfield plate stress induced by continental orogeny acting on zones

of pre-existing crustal weakness such as an old rift belt (aulocogen) or farfield sags tied to the formation of foreland depressions (intracratonic basins in Wilson cycle stage A); and 4) Thick (km-scale) halite sequences in local regions of rapidly subsiding continental crust in transform or strike-slip settings where the plates are sliding horizontally past one-another (conservative or neutral plate margin).

Only in Wilson stages F (continent–continent collision) through the onset of Stage C (intracratonic through rift through incipient ocean) can continental plates be in sufficient proximity to create the hydrographic isolation needed to facilitate marine seepage to a desiccated subsealevel basin floor and so precipitate marine-fed saline giants. Isostatic response explains why many regions of basinwide evaporites are underlain by thinned or transitional continental lithosphere, although in some cases hydrographically isolated parts of the basin floor can be underlain by oceanic crust (e.g. some South Atlantic Aptian salt basins; e.g. Jackson et al., 2000). Stages C, D and E of the Wilson Cycle encapsulate open marine settings where any deposited sediments are situated atop and surrounded by dense ocean lithosphere with a hypsometry that favours ongoing hydrographic connection to the ocean, so precluding subsealevel hydrographic isolation, unless the plate was elevated by the effects of local tectonism or migration over a mantle plume (hot spot).

An extensional basinwide evaporite succession typically passes up into marine carbonates as it is deposited in an extensional setting where a widening subsealevel rift opens into a hydrographically-isolated incipient ocean (Fig. 27). Evaporite deposition then ceases as the marine basin opens further into a passive margin with its continuous surface connection to waters of the open ocean. A compressional basinwide evaporite sequence typically overlies marine sediments and is in its turn overlain by continental sediments. Like epeiric periplatform evaporites, both these ancient tectonically-induced marine-fed deposits have no modern same-scale Quaternary analogues (Figs. 1, 23, and 25). They are the result of a combination of tectonic and climatic processes that are not present on the world's surface today. They have been in the past and they will be again in the future.

Brine inflow to these ancient tectonically-induced evaporitic lows tends to be maintained by continuous seepage of marine groundwaters into the depression (i.e. they are subsealevel marine-fed hydrologies), along with the occasional marine flood of the barrier. This ancient evaporite hydrology is tied to arid climates as these are the zones of the world's ocean surface where there is always the potential to lose more water from the basin than can actually enter via a combination of groundwater seepage and surface floods. And so, throughout time, evaporite sediment occurrence characterises the same two latitudinal belts that characterise Holocene evaporites (Fig. 22). But, what is not constant is the volume of evaporite sediment deposited in the horse latitudes (Fig. 21A, B).

This is why there are no Quaternary examples of megahalites. Our largest and thickest bedded modern halites are forming in suprasedalevel Quaternary collision belts as lacustrine “piggy-back” basins in the salars of South America (Bobst et al., 2001; Jordan et al., 2007). The only Quaternary examples of marine-fed subsealevel rifts are small-scale and include Lake Asal, Djibouti and the late Pleistocene marine-fed halites (with MgSO_4 bitterns) in the Danakil depression (Gasse and Fontes, 1989; Hutchinson and Engels, 1970). Modern inflow waters in the Danakil are continental/hydrothermal and not marine, so the modern bittern precipitates lack MgSO_4 . Earlier in the Pleistocene, the inflow to the same region was marine/hydrothermal seepage into the widening subsealevel rift, and kainite precipitated.

In the recent geological past the best example of a full-scale rift-associated marine seepage evaporite is probably the thick Middle Miocene salt layer beneath much of the Red Sea (Bosworth et al., 2005). Other well studied older examples of rift-associated evaporites include the Mesozoic circum-Atlantic salt basins (Manspeizer, 1982).

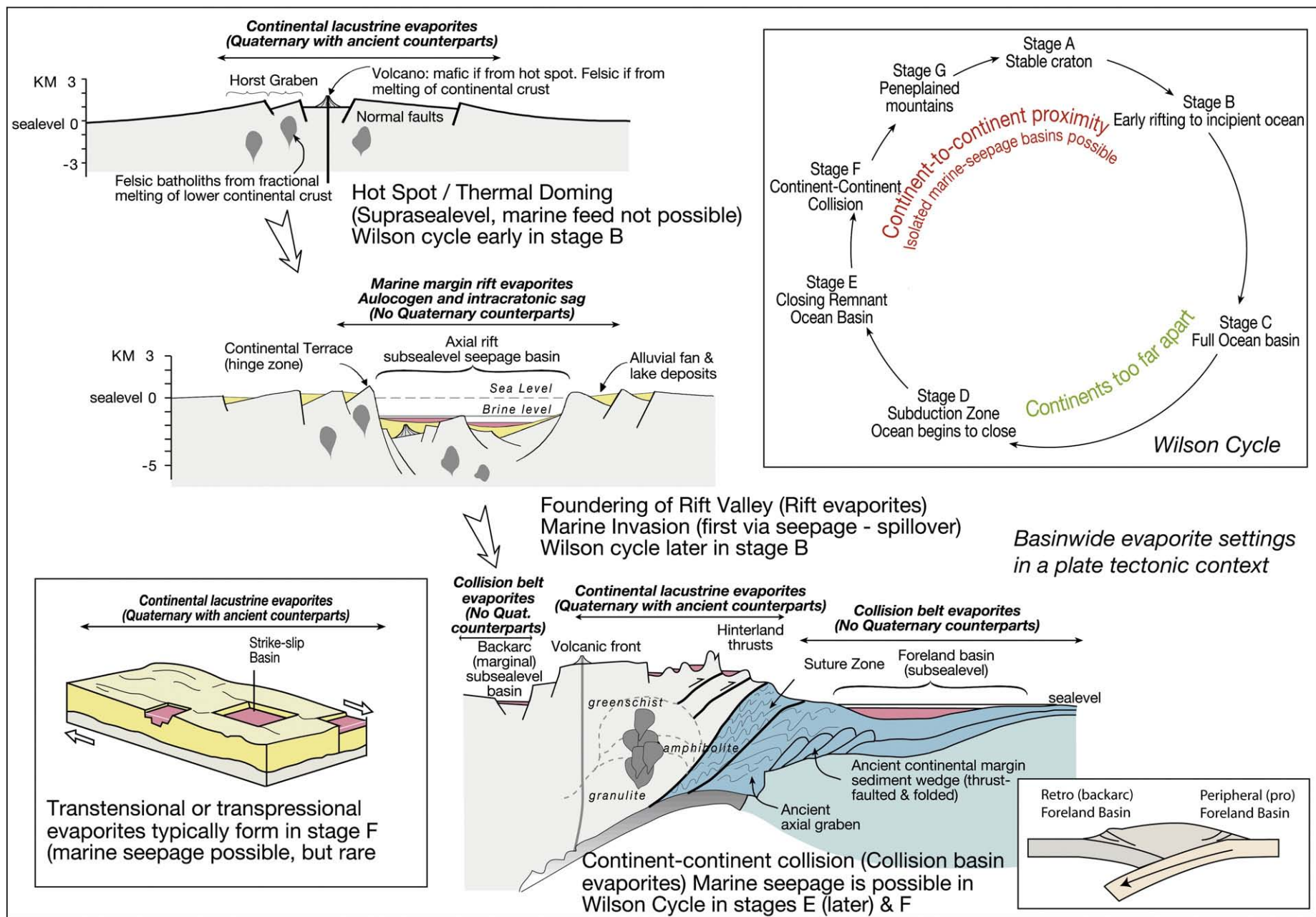


Fig. 27. Tectonic and hydrographically isolated (marine endoheic) situations where basinwide evaporites tend to accumulate (evaporite beds are shaded pink). Positions are largely tied to world-scale times of continent–continent proximity and so can be tied to the various stages of the Wilson cycle (Table 9; after Warren, 2006).

Table 9

Listing of tectonic setting of various halite-entraining basins at the time that thick halite was precipitated. It is based on an interpretation of the synprecipitatorial setting, so in basins with an ongoing polyphase tectonic history (like the various Zechstein sub-basins of Europe) it is not the same as the salt's current tectonic situation. See Fig. 18 for basin age and location, asterisk indicates postrift megahalite deposition.

Divergent	Abenaki (N. Scotian), Adelaide fold belt, Adriatic–Albanian foredeep, Apennine, Aquitaine, Arabian Basin (Gotnia Salt Basin), Arabian Basin (Hith Salt Basin), Atlas (Algerian–Tunisian, Atlas (Moroccan), Baltimore Canyon, Berrechid, Betic–Guadalquivir Basin, Brazilian Aptian Basin (Camamu), *Brazilian Aptian Basin (Campos–Santos), Brazilian Aptian Basin (Ceara), Brazilian Aptian Basin (Cumuruxatiba), *Brazilian Aptian Basin (Sergipe–Alagoas), Cantabrian–West Pyrenees, Carson Basin (Grand Banks), Chu–Sarysu (Devonian), Cuban, Danakil, Dniepr–Donets, Eastern Alps, Flemish Pass Basin (Grand Banks), Georges Bank, Gulf of Mexico (Northern; Gulf coast), *Gulf of Mexico (Southern; Salina–Sigsbee), Haltenbanken, Horseshoe Basin (Grand Banks), Ionian, Jeanne d'Arc Basin (Grand Banks), Jura/Rhodanian, Katangan, La Popa (Monterrey) Basin, Lusitanian, Maestrat, Majunga Basin, Mandawa Basin, Ma'rib–Al Jawf/Shabwah (Hadramaut), Moesian, Nordkapp Basin, Olduvai depression, Orpheus Graben, Palmyra, Red Sea (North), Red Sea (South), Rot Salt Basin, Ruvuma Basin, Sabinas Basin, Salar Basin (Grand Banks), Scotian Basin, Somalia–Kenya, South Whale Basin (Grand Banks), Tadjik Basin, Takutu Salt Basin, Tromsø Basin, *West Africa (Angola–Gabon), West Africa (Gambia–Guinea Bissau, West Africa (Mauritania–Senegal), West Africa (Morocco–S. Spain), Whale Basin (Grand Banks), Zechstein (NW Europe), Zechstein (onshore UK)
Convergent	Adavale, Amadeus Basin (Chandler), Andean, Arabian Basin (Hormuz central Saudi), Arabian Basin (Hormuz Gulf region), Arabian Basin (Hormuz–Kerman region) Bohai Basin, Cankiri–Corum, Carpathian foredeep, Chu–Sarysu (Permian), Cilicia–Latakia, Ebro Basin, Green River Basin, Haymana–Polatli, Holbrook Basin, Jiangnan Basin, Khorat Basin, Kuqa Foreland (Tarim Basin), Mediterranean–Western, Mediterranean–Adriatic, Mediterranean–Andros Basin, Mediterranean–Cretean Basin, Mediterranean–Samothraki Basin, Mediterranean–Tyrrhenian, Mediterranean–Central, Mediterranean–Eastern, Mediterranean–Sicilian, Neuquen Basin, Oman (Fahud Salt Basin), Oman (Ghaba Salt Basin), Oman (Ghuden Salt Basin), Oman (South Oman Salt Basin), Paradox Basin, Pricaspian Basin, Qaidam Basin, Qom–Kalut, Sachun Basin, Salt Range (Hormuz–Punjab region), Salt Range (Kohat Plateau), Sirjan Trough, Sverdrup Basin (Ellef Ringnes–NW Ellesmere), Sverdrup Basin (Melville Is), Tabriz Salt Basin, Transylvanian, Western Canada (Alberta Basin), Zagros (Mesopotamian Basin), Zipaquira Basin
Intracratonic	Amadeus Basin, Amazonas, Appalachian, Bonaparte (Petrel), Canning Basin, Carnarvon Basin (Yaringa), Hudson Bay, Mackenzie Basin, Maritimes Basin, Michigan Basin, Moose River Basin, Officer Basin, Oriente–Ucayali (Pucara) Basin, Parry Islands Fold Belt, Pripyat Basin, Saltville (Appalachian), Siberia–East, Solimoes, USA
Transform	Midcontinent, Williston Basin
	Dead Sea

Evaporites deposited in ancient continental rifts that passed into incipient ocean basins have a sediment fill that can be further subdivided in prerift, synrift and post-rift (Fig. 28A). Prerift accumulations are lithologies that predate the onset of the extensional

faulting that defines the rift. Synrift sediments are deposited in a subsiding zone that thickens toward active normal fault(s) along the rift margin. There is typically a well-defined rift onset unconformity at the lower contact of the synrift with the prerift sediments. The synrift sediment package typically expands over an ever-larger area with time, driven by subsidence related to ongoing normal fault activity. Expansion in the area of synrift sediments is associated with onlap of sedimentation surfaces and is a characteristic feature that is usually recognizable in associated seismic reflectors (Fig. 28A). Post-rift sediments are deposited when the rift-bounding normal faults are no longer active. These sediments tend to be deposited atop and over the rift graben edges.

When this classification of pre-rift, synrift and postrift sediment packages is applied to thick salt fills that accumulated at divergent plate margins, it seems most megahalites in divergent settings were deposited as synrift packages within well-defined graben profiles, as exemplified by the various Triassic salt basins of the northern Atlantic rim. Permian and Triassic salt basins of Europe and the North Sea are also synrift deposits (Fig. 29; Table 9).

And yet, a plot of world salt basins at divergent margins shows the largest and thickest halite accumulations (remaining salt) are postrift, not synrift packages (Figs. 28B and 29). They formed in palaeo-Gulf of Mexico and in the South Atlantic Aptian salt basins of Brazil and West Africa. The lateral extent of the salt beds into the synprecipitatorial basin were not defined by a graben edge atop transitional crust, but in places thick postrift halites were in direct contact with seafloor basalts of the oceanic crust (Salvador, 1987; Jackson et al., 2000). It is very likely that the hydrographic barrier that facilitated the hydrology of these subsealevel megahalite basins was also an offset volcanic ridge (proto-Walvis Rise). It also implies that the northern and southern Jurassic salt masses of the Proto-Gulf of Mexico, and the Brazilian and Angolan Aptian salt masses were never in direct depositional contact, but were separated by a basaltic midoceanic ridge, even as they formed.

Recently, Huismans and Beaumont (2008) proposed that, compared with earlier one-dimensional depth-dependant models, the post-rift Mesozoic salt basins of the Atlantic are better explained by a model that includes notions of decoupling between upper and lower parts of the lithosphere during stretching, with contrasting wide and narrow extensional styles above and below the decoupling level and progressive focusing of crustal extension toward the rift axis. This would have facilitated the formation of widespread

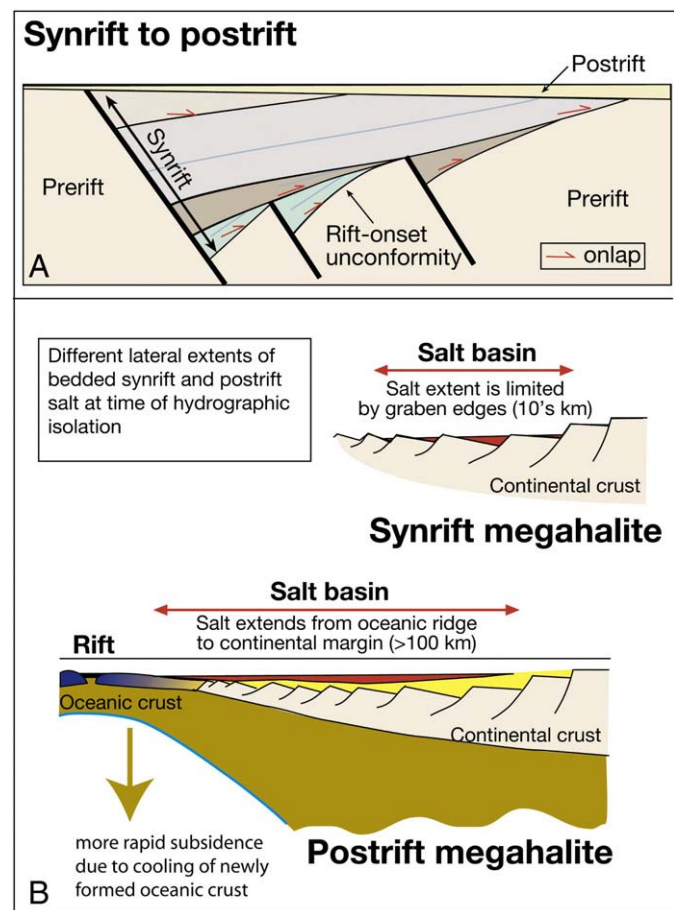


Fig. 28. Synrift to postrift associations. A) Stages in rift related sedimentation showing typical characteristics of prerift, synrift and postrift sediment packages. B) Lateral extents of megahalite basins in synrift and post rift settings.

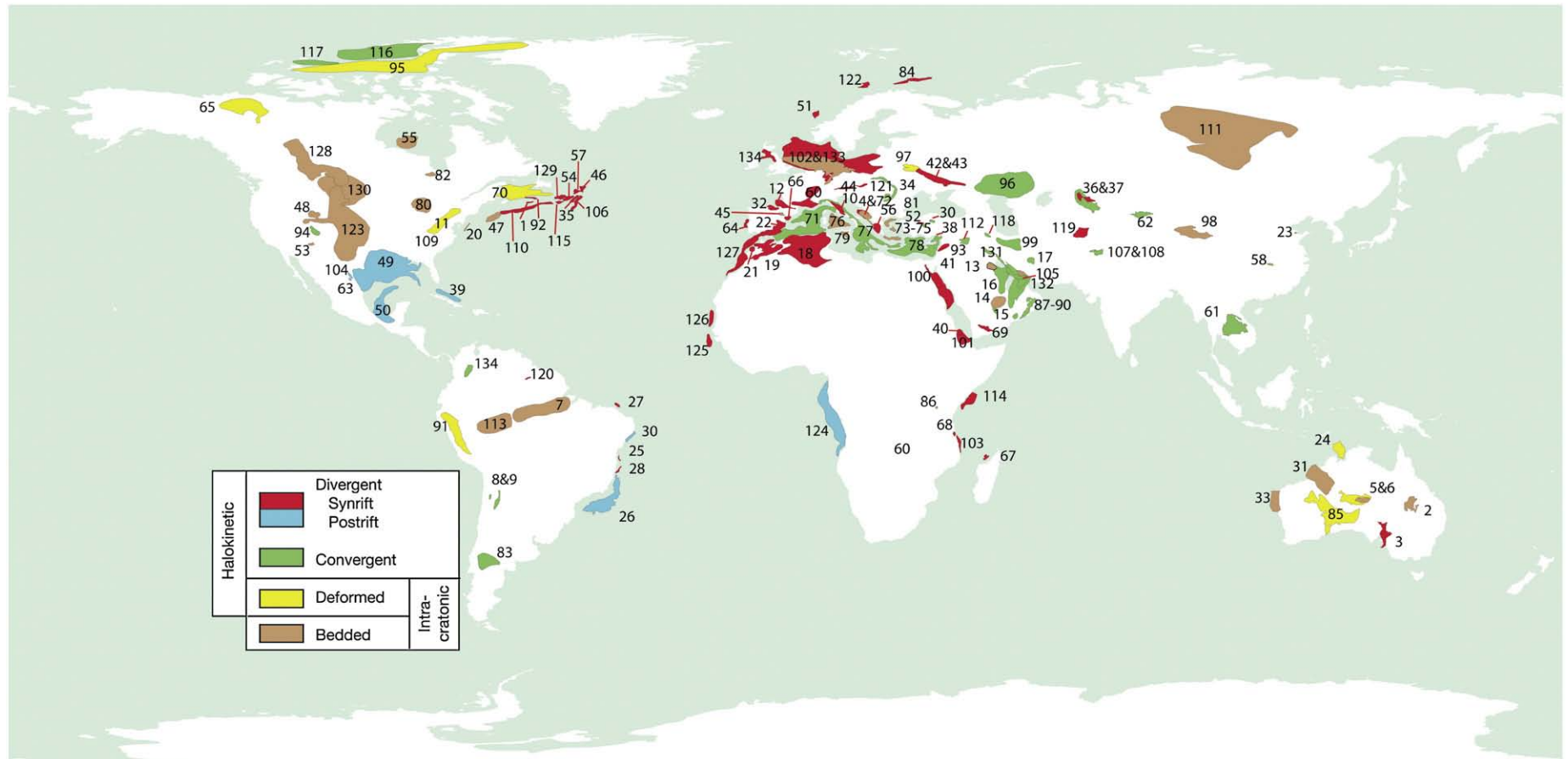


Fig. 29. Classification of selected NaCl-dominant basinwide evaporite deposits in terms of tectonic situation, including lacustrine associations. Numbers refer to listed basin key in Fig. 18.

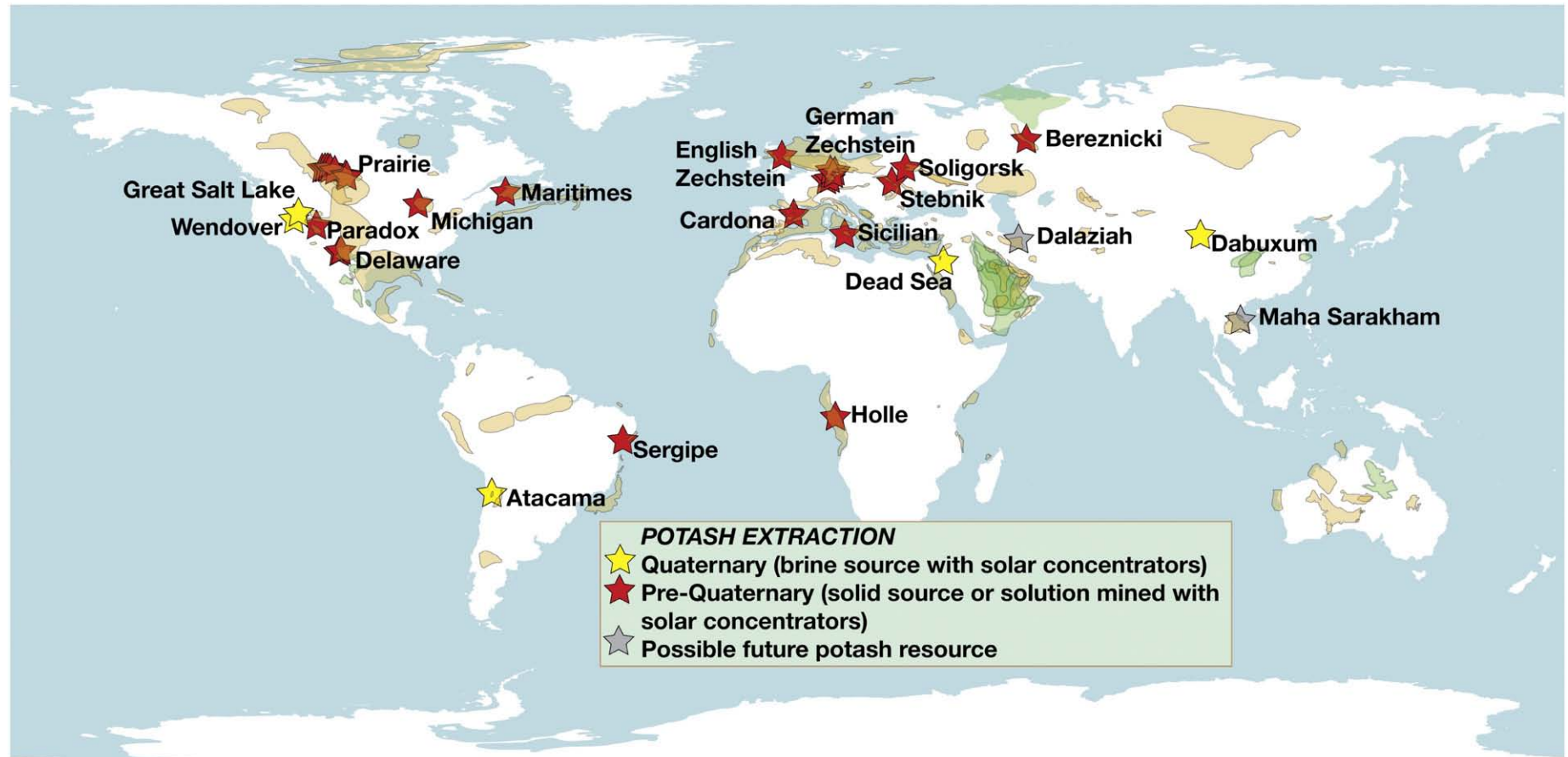


Fig. 30. World potash exploitation. Red stars indicate operations that are extracting (or have extracted) potash from a Pre-Quaternary bedded or halokinetic evaporite sequence. Yellow stars indicate operations exploiting Quaternary potash sources (lake brines). The brown and green shaded zones indicate the positions of ancient marine halite and sulfate basins, respectively (see Fig. 18 for basin names and Table 10 for deposit details).

postrift areas that were both subsealevel and hydrographically isolated.

Halokinesis in postrift evaporite-floored basins is characterised by well-developed allochthonous salt tiers, along with strong components of subhorizontal primary and secondary salt translation and formation of secondary minibasin-capped salt canopies (as in Aptian salt basins of the South Atlantic and the Jurassic salt basins of the Gulf of Mexico; Davison, 2007; Tari et al., 2003; Hudec and Jackson, 2007). Stronger vertical aspects of salt flow (c.f. lateral flow), both in extension and compression, characterise synrift salt basins such as the Permian Zechstein Basins of Europe and the Triassic salt basins of the circum North Atlantic (Warren, 2008).

A classification of ancient salt basins, as illustrated as the inset in Fig. 29, shows that halite sequences in intracratonic sag basins tend to be less subject to halokinesis than halite masses deposited in rift or collision basins. The NaCl remains as a bedded deposit unless an intracratonic basin is caught up in a subsequent deformation belt, as has affected Neoproterozoic halite in the Amadeus and Officer basins, the Cambrian salts in the Mackenzie Basin and the Silurian salts in the Appalachian basins. The lack of halokinesis prior to later superimposed deformation in intracratonic sag basins is in large part a reflection of their depositional style. As mentioned earlier, halite beds in these basins tend to be intercalated with anhydrites and marine platform carbonates. As such, the beds rarely attain the 80–100 m thicknesses of pure salt typically needed for syndepositional salt flow (Warren, 2006; Chapter 6).

6.4. Potash salts

Volumetrically most, if not all, Pre-Quaternary potash deposits are the bittern stages of marine-fed basinwide deposits (Fig. 30). The most common naturally occurring potash minerals are carnallite and sylvite, with sylvite the most economically important. Other common potassium-entraining evaporite ore minerals include: kainite, kieserite, langbeinite, leonite and polyhalite (Warren, 2000b, 2006). Natural potash evaporites are part of the bittern series precipitated at the surface or in the shallow subsurface at the higher concentration end of the evaporation series in marine and some continental waters (Fig. 19). Today, the deposition of thick beds of potash minerals at the earth's surface is a relatively rare occurrence and, with the possible exception of the Tuanje Lake region in China, occurs via brine processing and solar concentration in man-made salt pans (Fig. 30; Duan and Hu, 2001).

In 2007 there were 14 potash producing countries, including small extracted volumes from the Ukraine and Chile, constituting a total world resource of 254 billion tons (USGS estimate; <<http://minerals.usgs.gov/minerals/pubs/commodity/potash/>>). In 2007 Canada produced some 33% of the world's total potash production, eastern Europe and Russia some 36%, western Europe 11%, and the Dead Sea 10% (Fig. 30). Of total world potash production, just ten companies control 90%, and the five largest companies control more than 75%. Canada, the world's largest producer, holds more than 50% of the world's potash reserves and recovers potash mostly by conventional underground mining of bedded sylvinitic deposits. Production is centred on the Devonian Prairie Formation in the Elk Point Basin in Saskatchewan, with lesser production from the Carboniferous of the Maritime Provinces and Quebec (Fig. 30; Table 10). Devonian potash is mined in the Pripyat depression of Belarus. Permian potash is mined from bedded successions along the northern margin of the Delaware Basin in New Mexico, USA, from halokinetic intervals in the Zechstein of Europe (Germany, UK and the Netherlands), and from the Upper Kama Basin in the Russian Federation in the Solikamsk region west of the Urals. Oligocene potash has been extracted from bedded successions in the Rhine graben in France, while halokinetic Miocene potash is mined in the Stebnik area in the western Ukraine. In Spain, in the northern part of the Ebro Basin near the border with France,

potash is produced from Eocene-Oligocene transitional marine sediments.

In Utah, potash is solution mined from halokinetic Carboniferous Paradox Formation evaporites, or extracted from Great Salt Lake brines. Israel uses solar technology to produce large volumes of potash from modern lake brines created naturally from recycled marine Miocene evaporites and connate waters buried beneath the floor of the Dead Sea. In California, potash and coproducts, borax pentahydrate, soda-ash and salt-cake, are recovered from various subsurface playa brines using solar evaporation. Sylvite is also a byproduct of nitrate processing in the pedogenic nitrate terrane of the Atacama Desert.

The fertiliser industry uses more than 90–95% of produced potash and the chemical industry uses the remainder in the manufacture of soaps and detergents, glass, ceramics, synthetic rubber and numerous industrial chemicals. About 70% of the potash is produced as potassium chloride and sylvite is the preferred ore mineral in most mines. Potassium sulfate and potassium magnesium sulfate, required by certain crops and soils, comprise about 25% of potash production. Potash is a source of soluble potassium, which is one of the three primary plant nutrients; the others are fixed and soluble phosphorus and nitrogen. Mankind's use of these three nutrients, in commercial forms, started the "Green Revolution" in agriculture. Generally, nonagricultural uses of potash account for no more than 5–10% of annual world consumption.

Phanerozoic potash salts comprise two distinct associations: MgSO₄-rich and MgSO₄-poor (Fig. 20A). Potash deposits rich in MgSO₄ are composed of some combination of gypsum, anhydrite, polyhalite, kieserite, kainite, carnallite and bischofite. Potash deposits free of, or poor in, MgSO₄ are dominated by some combination of halite, carnallite, and sylvite. This latter group constitutes a majority of exploited Phanerozoic potash (Table 10, Fig. 30). Other than minor amounts in the Late Neoproterozoic–Early Cambrian Ara Salt of Oman, potash salt remnants have not been recognized in Precambrian sediments.

The extremely high solubility of potash means it can only accumulate today in highly restricted, some would say highly continental, settings (Hardie, 1991). Where potash does occur naturally today, it does so in transient volumetrically-minor lake strandzone (stratoid) beds about the northeastern margin of Lake Dabuxum and as Pleistocene bedded deposits in nearby Lake Tanje, both in the Qarhan playa region of the Qaidam Basin in China (Fig. 31), or in Pleistocene beds the Dallol pan in the Danakil Depression of Africa. In all examples carnallite, not sylvite, is the dominant precipitated salt (Table 10). Likewise, bedded carnallite, not sylvinitic, is the dominant bittern precipitate in the salt pans at the Southern end of the Dead Sea. Beneath the Lake Dabuxum margin the carnallite occurs not as beds but as vug-infilling cements in a chevron halite host (Casas et al., 1992). Similar vug-fill cement textures, but in sylvite not carnallite and without MgSO₄, typify the sylvite rich zones of the Aptian Maha Sarakham deposits of NE Thailand (Fig. 20A; Warren, 2006).

This time-related sylvite–carnallite–MgSO₄ dichotomy, as mentioned in our earlier discussion of the chemical evolution of seawater, is also part of an interesting split in the style of exploited potash deposits worldwide. All active potash extraction operations utilising a Quaternary-age source are brine processing facilities located in continental playa and saline lacustrine settings (e.g. Dabuxum, Dead Sea, Great Salt Lake; Table 10). Almost all pre-Quaternary potash operations extract ore from marine-fed basinwide deposits, not continental lacustrine deposits (Table 10). The dichotomy reflects the simple lack of basinwide marine deposits since the late Miocene. As for all ancient marine evaporites, the depositional system that deposited these ancient marine-fed potash deposits was one to two orders of magnitude larger and the resultant deposits were typically thicker stacks than any Quaternary potash settings. The last such

Table 10

Potash occurrences, listed by country, reserves listed in million tons (mt) or billion (Gt) metric tons of K₂O equivalent (for overviews see Garrett, 2004; Prud'homme and Krukowski, 2006; Warren, 2006 and references therein).

Location, country	Age	Koeppen	Brine source	Target unit	Comments/key reference
Potash in Congo and Gabon basins, Africa (Congo, Zaire, Angola)	Cret., Lower	–	Marine	Kouilou horizons	Carnallite, sylvinitic in halite host, variable tachyhydrite (Aptian). Previously mined at Holle Mine (Republic of Congo) in 2 variable layers of 1.9 m and 3 m thickness with K ₂ O contents of 18% and 38% respectively with mineable reserves of 17 mt and 26 mt K ₂ O respectively. Mine lost to flooding (breccia zone) in 1977. Future projected solution mine targeting of K and Mg brines in Kouilou evaporite horizons. (De Ruiter, 1979)
Neuquén and Mendoza Basins, Andes, Argentina	Cret.	–	Marine	Potash interval	Possible future solution mine. Sylvinitic ore divided into 2 zones, upper zone about 3 m thick and lower about 11 m thick, average grade 20–25% K ₂ O. A 1000 m depth and high formation temperature (>50 °C) precludes conventional mine (Prud'homme and Krukowski, 2006).
Pripyat Depression, Belarus	Dev., Upp.	–	Marine	Liven and Elets horizons	Livet (Frasnian) interval made up of four potash horizons with areas between 130 and 1500 km ² . Sylvite ore with minor carnallite in beds 4 cm to 1.5 m thick interbedded with muddy halite. Elets (Famennian) interval >60 potash beds over 5000 km ² at depth of 200 to 3000 m. Major potash production from Elets at average depth 480 m, grade 18% K ₂ O. (Zharkov, 1984)
Sergipe Basin, Brazil	Cret. Low.	–	Marine	Ibera member	Taquari–Vassouras mine targets sylvinitic beds in Muribeca Fm. found in association with halite host, variable carnallite, tachyhydrite (primary textures in unit up to 90 m thick) constituting some 9 evaporite cycles deposited in an opening rift (Aptian). Tachyhydrite present. (Wardlaw, 1972)
Amazonas Basin, Brazil	Upp. Carb.–Perm. Low.	–	Marine	Nova Olinda Fm.	Two potential sylvinitic deposits (sylvite cap to uppermost of 7 evaporite cycles) near Manaus ≈ 1000 m depth, with average thickness of 2.7 m and grade 16.5% K ₂ O. (Ufimian–Olenekian) (Szatmari et al., 1979)
New Brunswick Potash, Fundy Basin, Canada	Carb. Low.	–	Marine	Cassidy Lake Fm.,	Formerly mined at depths 300–100 m in halokinetic salt wall, Mississippian sylvinitic–halite sequence with local carnallite in Windsor Group in Moncton sub-basin. (Visean) (Anderle et al., 1979; Wilson et al., 2006)
Alberta Potash Basin, Canada	Dev., Middle	–	Marine	Prairie Fm	Actively mined, some ten mines (2 solution mines) at depths between 800 and 1000 m, region is world's major supplier of potash ore. Three potash horizons (sylvite, carnallite, halite) 20–25 m thick in upper part of Prairie Fm. (Esterhazy, Belle Plain and Patience Lake members). Dips gently to south at 1–8 m/km with potash level some 600–2500 m below surface. Prairie Evaporite basin is a marine-fed foreland basin situated behind foreland bulge created by Antlerian orogen. (Givetian) (see text)
Salar de Atacama brine, Chile	Quat.	BWk	Nonmarine	Rec.	Brine Processing. Sylvinitic is recovered as byproduct of lithium carbonate production (800 kt in 2004). Situated in Andean Altiplano at 2250 m above sealevel. (Garrett, 2004)
Dabuxum Lake (stratoid potash) Qahran Playa, Qaidam Basin, China	Quat.	BWk	Nonmarine	Rec.	Carnallite (via solar processing of lake brine along with bischofite). Transtensional basin at 2675 m elev. The Qahran playa region is main local supplier of potash to Chinese market (annual production of 1.2 mt K ₂ O). Other Quaternary K-rich lakes in Qaidam Basin include Seni Lake and Tuanje Playa (see text and Fig. 31).
Dalol Saline pan, Ethiopia	Quat.	BWh	Marine	Houston Fm.	Three members; uppermost is sylvinitic member up to 10 thick; intermediate is 3–24 m thick with carnallite throughout, (sylvite at its top and kainite at its base) and lower member is kainite that is 4–13 m thick. It is a Pleistocene marine-fed unit that now lies beneath continental halite in a subsealevel (–115 msl) hydrographically-isolated marine-fed rift valley, region of active volcanism and hydrothermal overprints. (Garrett, 2004)
Mulhouse Potash Basin, Rhine rift, France	Eoc.–Olig.	–	Marine	Upper Salt Group	Main potash target is primary sylvite bed in Salt IV in Oligocene Rupelian succession at depths between 420 and 1100 m. Basin was a consequence of Paleogene collision between European and African plates. Periodically mined for carnallite/sylvite ore. Subsealevel rift graben was active along western sidewall of the Alpine orogen during collision of the Apulian indenter with the European passive margin. (Sannoisan) (Cendon et al., 2008)
Zechstein Potash Basin, Germany	Perm. Upp.	–	Marine	Zechstein Group	Actively mined at depths between 300 and 800 m, Zechstein comprises four evaporite cycles, with potash as five ore horizons in lower three (Thuringen, Hessen, Stassfurt, Ronnenberg and Riedel) (Tatarian). Tachyhydrite present in Stassfurt. (Smith and Crosby, 1979; Richter-Bernberg, 1986)
Dead Sea brines, Israel and Jordan	Quat.	BSh	Nonmarine	Holocene anthrop.	Brine Processing (carnallite ppt. and converted to KCl) of lake brine pumped into a series of processing pans at southern end of Dead Sea. The Dead Sea brine contains an estimate 2 Gt of dissolved KCl, 1 Gt of MgBr ₂ and 20 Gt of MgCl ₂ . Annual production of KCl ≈ 3.4 mt (MgCl ₂ is coproduct) Subsealevel transtensional basin with brine surface some 415 m below sealevel. (Recent) (ZAK, 1997; Garrett, 2004)
Sicilian Basin, Italy	Mioc., Late	–	Marine	Solfifera Series	Inactive since mid 1990s. Kainite was dominant ore mineral (manufactured potassium sulfate). Other minerals in ore were sylvite, kieserite, and bischofite in 2–30 m thick beds dipping to 60°. Piggy-back basin in thrust belt. (Messinian).
Pricaspian depression, Kazakhstan	Perm. Low.	–	Marine	Potash interval	Not mined. Potash interval contains polyhalite–halite, bischofite–carnallite, carnallite–halite, interval is strongly halokinetic in central part of basin. Oil wells intersected several potash horizons in this region. (Kungurian). (Volozh et al., 2003; Garrett, 2004)
Solikamsk depression, Russia	Perm. Upp.	–	Marine	Iren horizon	Bezeneski and Solimgansk mines. potash interval lies at depths of 200–500 m and is divided into lower sylvinitic and upper sylvinitic–carnallite, little to no MgSO ₄ salts. Av. lower interval thickness 21 m, upper interval 60 m. (Kungurian) (Zharkov, 1984)
Eastern Siberia Potash Basin, Russia	Camb. Lower	–	Marine	Chara horizon	Potash lies at depths of 600–900 m and contains some ore-grade sylvite intervals (>30% K ₂ O) in Ussolye and Angara Fm. Not currently exploited. (Botoman–Amgan) (Zharkov, 1984)
Catalonia and Navarra Potash Basins, Spain	Eoc. Upper	–	Marine		Transitional from marine evaporite to continental, deposited in two depocentres in Southern Pyrenean foreland. Sylvite + halite at base of unit, carnallite + halite toward top (Bartonian). Lower sylvite member is ore bed. MgSO ₄ -free. (Rosell and Ortí, 1981; Cendon et al., 2003)

Table 10 (continued)

Location, country	Age	Koeppen	Brine source	Target unit	Comments/key reference
Khorat and Sakon Nakhon Potash Basins, Thailand, Laos	Cret. Upp.	–	Marine	Maha Sarakham Fm.	Possible sylvinitic target on basin margin. Widespread massive halite, carnallite (with local zones of sylvinitic), tachyhydrite and bischofite traces of priceite/boracite. Unconformable base, interbedded with three continental redbed successions and overlain by continental deposits. Variably halokinetic toward basin centre. (Albian–Cenomanian?) (Hite and Japakeset, 1979; El Tabakh et al., 1999; Warren, 2000b)
English Zechstein Potash Basin, UK	Perm. Upp.	–	Marine	Zechstein 3	Boulby Mine in UK extracts sylvinitic ore from two 6–8 m beds at depths between 1000 and 2700 m, essentially no MgSO_4 phases. Water inflow and instability problems (Tatarian). (Smith, 1996; Woods, 1979)
Carpathian foredeep, Ukraine	Mioc. Middle	–	Marine	Tyras Suite	Stebnik mine and Kalush–Golyn region. Four evaporite cycles upper three with potash; exploited potash units composed of kainite, langbeinite, kainite–langbeinite, sylvinitic and carnallite rocks with layers of rock salt or interbedded clays and carbonates. Fourth bed is polyhalite. (Burdigalian–Helvetian). (Hryniv et al., 2007)
Great Salt Lake region, UT USA	Quat.	Csa	Nonmarine	Rec.	Processing of lake brines in North Arm of lake and of shallow brines in Great Salt Lake desert (Bonneville Basin) at Wendover (MgCl is coproduct). Lake surface is 1270 m above msl. (Bingham, 1980; Colman et al., 2002; Garrett, 2004)
Paradox Potash Basin, UT, USA	Penn. Mid.	–	Marine	Paradox Fm.	Solution mining of Paradox Fm. in converted conventional mine on Cane Creek anticline at a depth of 850 m. Middle Pennsylvanian collision basin related to Marathon–Ouchita orogeny, 18 of 29 halite cycles contain potash, mostly sylvite. (Moscovian) Tachyhydrite present (Desmoinesian). (Hite, 1961; Williams-Stroud, 1994)
Salado Potash Basin, NM, USA	Perm.–Upp. Lower Trias.	–	Marine	Salado Fm.	Resource now largely depleted, 12 potash horizons in part of Delaware Basin known as McNutt Zone (sylvite ore), few mines still active. Ore zones contain sylvite, carnallite, lesser amounts of sulfate minerals such as polyhalite and langbeinite (Tatarian–Olenekian). (Lowenstein and Spencer, 1990)
Michigan Basin, MI, USA	Sil. Low.–Upp.	–	Marine	Salina A-1 Evap.	Sylvinitic and carnallite ore within central part of an intracratonic sag basin. Potash zone >30 m thick in central part of basin but ore concentration is erratic locally up to 40% K_2O and as deep as 2550 m but only solution mining is possible at these depths. (Wenlockian–Ludlovian). Tachyhydrite present. (Matthews and Egleson, 1974)

“saline giant” potash system was the Solifera series in the Sicilian basin, deposited as part of the Mediterranean “salinity crisis.” These evaporites are sufficiently young to be part of the MgSO_4 association as are the Eocene–Oligocene potash deposits of the Catalan and Mulhouse deposits.

Fig. 32 illustrates the geological setting and scale of the Middle Devonian Prairie evaporite of Canada, which is the world’s largest ancient potash system. This bedded evaporite was deposited in an intracratonic basin with the restriction probably created via the foreland bulge of the Antler Orogenic belt. Today its remnants constitute a halite unit some 500 m thick, which lies atop the irregular topography of the platform carbonates of the Winnipegosis Formation (Fig. 32A, B). Above the Prairie Evaporite Formation is a series of cyclic Devonian limestones, dolomites and evaporites that make up the Dawson Bay, Souris River, Duperow and Nisku Formations.

Devonian halite constitutes a large portion of the four formations that make up the Elk Point Group: 1) the Lotsberg (Lower and Upper Lotsberg Salt), 2) the Cold Lake (Cold Lake Salt), 3) the Prairie Evaporite (Whitkow and Leofnard Salt), and 4) the Dawson Bay (Hubbard Evaporite). At that time the Elk Point Basin covered most of Alberta, the southern half of Saskatchewan, southwest Manitoba and extended south into the USA (Fig. 32A). Its Pacific coast was near the present Alberta–British Columbia border, and the Elk Point Basin was centred at approximately 10°S latitude. The basin was bound to the north and west by a series of tectonic ridges and arches; but due to subsequent erosion, the true eastern extent is unknown (Mosso and Shetsen, 1994). Hydrographic isolation of the basin resulted in the deposition of a drawdown sequence of basinwide NaCl-dominant evaporites in an intracratonic sag that includes various potash-entraining intervals in the Prairie Evaporite Formation (Fig. 32B).

Potash deposits mined in Saskatchewan are all found within the upper 60–70 m of the Prairie Evaporite Formation at depths of more than 400 to 2750 m beneath the surface of the Saskatchewan Plains (Fig. 32C). Within the Prairie Evaporite there are four main potash-bearing members, in ascending stratigraphic order they are: Esterhazy, White Bear, Belle Plaine and Patience Lake members (Fig. 32B). Each member is composed of various combinations of halite, sylvite, sylvinitic, and carnallite (Fuzesy, 1982). The Belle Plaine member is separated from the Esterhazy by about 15 m of halite, its thickness

ranges from 0 to 18 m and averages around 9 m. The Patience Lake member is separated from the Belle Plaine by 3–12 m of halite its thickness ranges from 0 to 21 m and averages 12 m (Holter, 1972).

Bedded halite away from the various potash ore zones generally retains primary depositional textures (chevrons) typical of halite precipitation in shallow ephemeral saline waters (Brodylo and Spencer, 1987). Many of the chevrons are truncated by irregular patches of clear halite that formed as early diagenetic cements in syndepositional karst, much like textures currently forming beneath the strandzone of Lake Dabuxum.

In contrast, halite associated with Prairie potash ore lacks well-defined primary textures and is atypical when compared with the well-preserved depositional textures in the non-ore halite beds. From regional petrology and lower than expected Br levels in halite in ore zones in the Prairie Evaporite Formation, Schwerdtner (1964), Wardlaw and Watson (1966) and Wardlaw (1968) postulated a series of recrystallisation events that precipitated secondary sylvite due periodic flushing by hypersaline solutions. This origin as a diagenetic precipitate is supported by observations of intergrowth and overgrowth textures (McIntosh and Wardlaw, 1968), large-scale collapse and dissolution features (Gendzwill, 1978), radiometric ages (Baadsgaard, 1987) and palaeomagnetic orientations of the diagenetic haematite linings associated with the emplacement of the potash (Koehler et al., 1997).

Dating of clear halite crystals associated with the ore zone shows that the exceptionally coarse and pure secondary halites forming pods in the mined potash horizons may have precipitated as soon as early burial or have formed as late as Pliocene–Pleistocene. Even today, alteration and remobilisation of the sylvite appears to be an ongoing process, perhaps related to the encroachment of the current dissolution edge or the ongoing stopping of chimneys fed by deep artesian circulation (Warren, 2000b).

The multiplicity of textures and overprints, so obvious in the Prairie potash, typifies multistage textural diversity seen in most ancient potash deposits (Warren, 2000b, 2006, Chapter 11). It indicates ongoing reactivity whenever a potash interval is flushed by basinal waters. Post depositional potash enrichment within a thick halite host often occurs at or near an intrasalt unconformity or disconformity (Warren, 2000b). It reflects times of brine fractionation

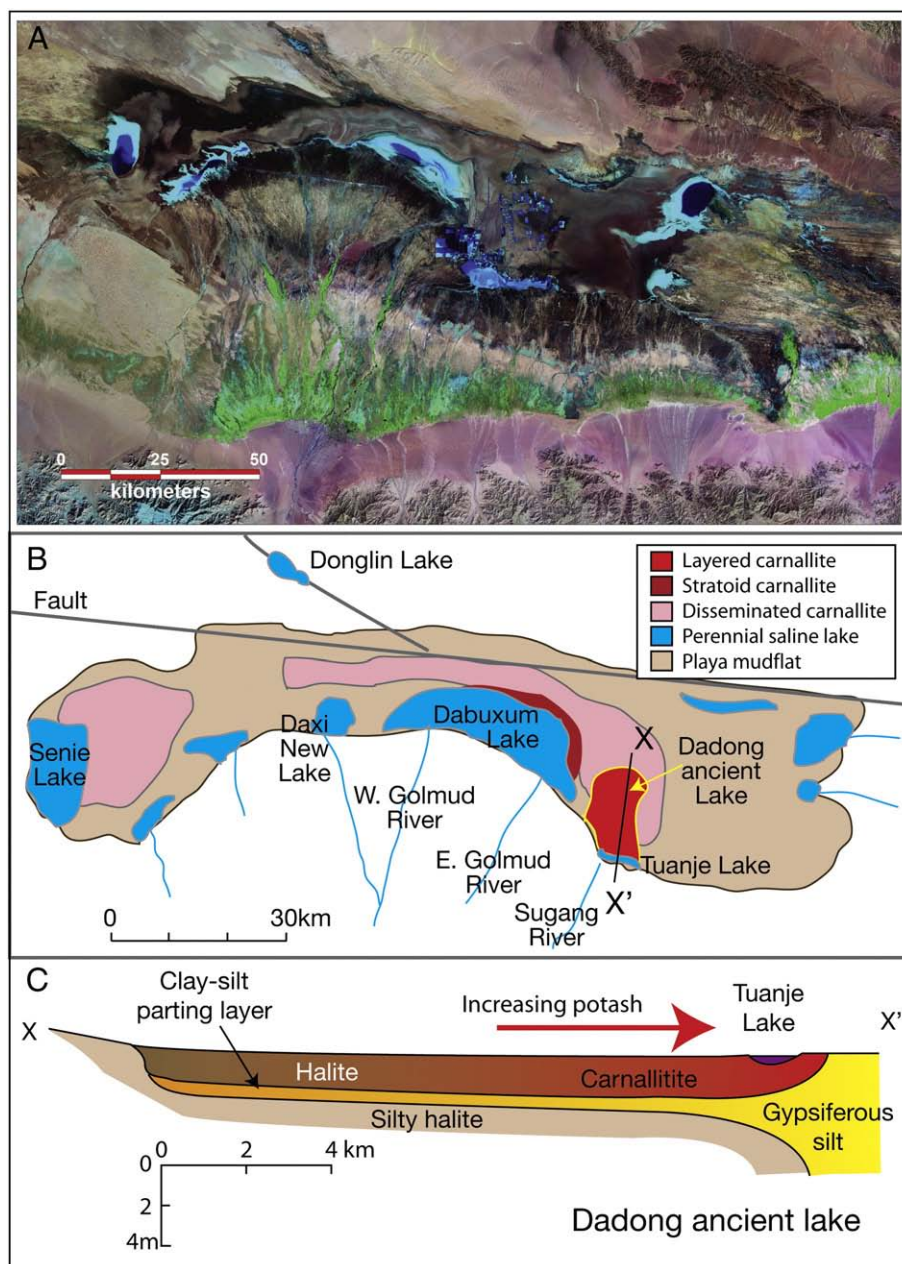


Fig. 31. Potash in the Lake Dabuxum region, China. A) locality map showing distribution of potash beds and lakes on the downflow side of the Golmud bajada (Landsat image courtesy of NASA <<https://zulu.ssc.nasa.gov/mrsid>>). B) Potash geological plan (after Duan and Hu, 2001). C) Cross section showing thickness and lateral extent of potash in ancient Lake Dadong (see b) for plan view and section location (after Duan and Hu, 2001).

and recrystallization related either to episodes of exposure and subaerial leaching/concentration, or to fault/fracture-related episodes of subsurface flushing of the more soluble salts followed by their reprecipitation. In some deposits, such as the Maha Sarakham, near Khon Khan Thailand and the Kueper salts of NW Europe, the potash concentration process was aided by early synprecipitational halokinesis and karsting of a bedded carnallite precursor (Warren, 2008).

7. Evaporite brines (lithium and CaCl_2)

So far, we have focused on evaporite deposits where the ore target is a mass of solid salt of the appropriate grade (as in conventional mines and managed solar pans) or it is a leaching program aimed at preferentially dissolving of a target salt horizon followed by recovery and solar enrichment of the resulting brine as a chemical feedstock (e.g. Laguna del Rey, the Dead Sea and Nedmag's solution mining of

Zechstein bischofite to recover MgCl_2 brine). But there are a number of Quaternary saline settings and their older buried counterparts where relatively unmodified pore brines (relict or connate waters), residing in permeable saline subsurface lithologies, are the feedstock targets. Such brines are not necessarily hosted in a salt mass. Lithium and calcium chloride brines are two commonly sought targets in this type of brine recovery operation (Fig. 33), other saline brine-enriched commodities include magnesia, bromine and iodine (Table 1). We shall focus on lithium and CaCl_2 , the interested reader is referred to Warren, 2006, Chapter 11 for detail on the others.

7.1. CaCl_2 brines and minerals

Most calcium chloride brines are derived from a hydrothermally-modified marine waters or from resurging deep basal brines/formation waters. Today, large volumes of relatively dilute, oceanic

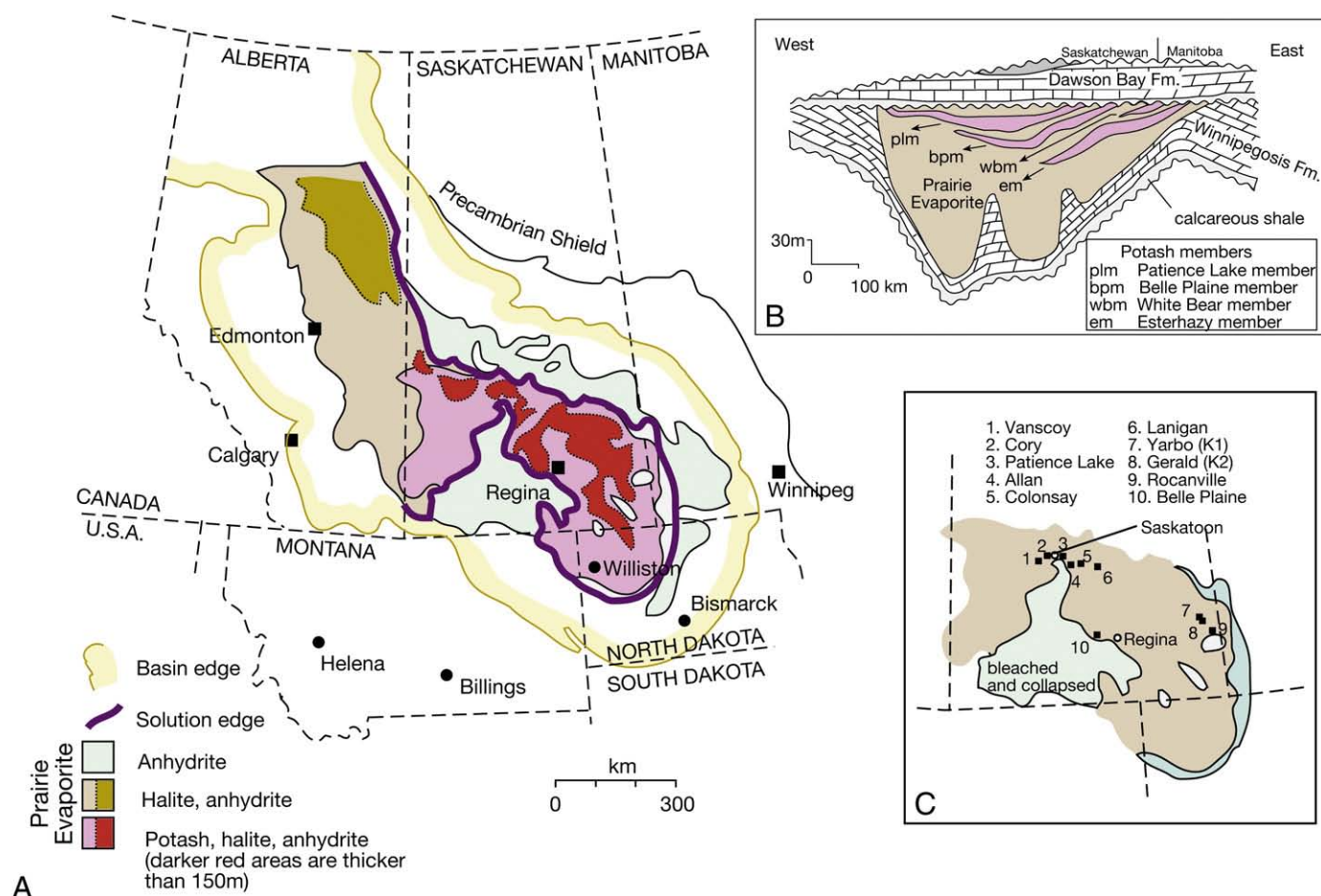


Fig. 32. Potash in the Devonian Elk Point Basin, western Canada. A) Regional geology showing thickest salt and potash intervals in the Prairie Evaporite and its dissolution edge. B) Cross section of basin showing distribution of potash members. C) Map of potash mines in the basin (compiled and modified from Worsley and Fuzesy, 1979; Fuzesy, 1982; Boys, 1993; Warren 2006).

CaCl_2 brines form via hydrothermal circulation and thermally-driven alteration of mid-ocean ridge lithosphere. These CaCl_2 waters occur in and near active fracture zones, wherever seawater interacts with labile basalt (oceanic crust) at elevated temperatures and converts it from a Na–Mg–Cl water into a low-salinity Na–Ca–Cl brine, depleted in Mg and SO_4 . Similar hydrothermally-driven alteration of continental basalts by deeply circulated seawater forms modern CaCl_2 brine feeds within the active continental Danakil rift valley. The only current commercially exploited CaCl_2 brine source is Bristol Dry Lake, California (Fig. 33, Table 11).

Pure CaCl_2 minerals are rare in today's hypersaline lakes and require a Ca-enriched mother brine that is depleted in sulfate. Otherwise, gypsum precipitates and in so doing removes all Ca from a concentrating brine, well prior to the bittern stage. There are only two known modern hypersaline saline deposits where the pure CaCl_2 mineral, antarctite ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$), is present; they are, Bristol Dry Lake in California and Don Juan Pond in the Dry Valleys, near Lake Vanda in Antarctica (Table 11; Dunning and Cooper, 1969). Both saline lakes possess similar CaCl_2 -enriched, MgCl_2 -depleted chemistries and are fed by hydrothermal waters. In Bristol Dry Lake the concentration process is driven by solar evaporation, while cryogenesis is the main driver in the Don Juan Pond. To form a pure CaCl_2 salt, a CaCl_2 brine must also be depleted in Mg, otherwise tachyhydrite ($\text{CaMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$) forms, along with carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$). These three chloride bittern salts are not part of the bittern suite of today's MgSO_4 oceans, as the sulfate and magnesium levels are too high relative to calcium, but they were more common in the bittern stages of ancient CaCl_2 oceans at times when

rates of seafloor spreading, and hence volumes of through-circulated seawater, were greater than today (Fig. 19A; Lowenstein et al., 2001, 2003).

Although it is highly soluble, halite-encased tachyhydrite, along with carnallite and bischofite, typify marine bittern assemblages in: Silurian potash of the Michigan Basin; Carboniferous potash in the Canadian Maritimes and the Paradox basin; Permian Zechstein 2 Stassfurt potash seam in Stassfurt, Germany; Triassic Saharan potash of North Africa; Cretaceous potash evaporites in Brazil, Gabon and Thailand and Oligocene potash in the Rhine Graben. Calcium chloride brines also typify pore waters associated with these evaporite assemblages, details of these deposits were discussed in the previous potash section and are listed in Table 10.

Natural tachyhydrite is known from only one modern setting; it occurs as a minor interstitial cement along with carnallite, in the halite crusts of the Gavkhoni Playa, southeast of Isfahan, Iran (Ajallouian et al., 2000). Much of the ionic content in the various Iranian playas in the Great Kavir is derived by dissolution of the crests of at- or near-surface diapirs and namakiers, with the mother salt sourced in halokinetic Miocene marine salts in this tectonically-active collision belt (Warren, 2008).

Even in past times of CaCl_2 -rich oceans, calcium chloride minerals are relatively rare, in part due to their very high solubilities. On the other hand, CaCl_2 brines are commonplace basinal or formation waters in many Phanerozoic sedimentary basins. Historically, before micro-inclusion studies of chevron halite showed that the ionic proportions of seawater varied across the Phanerozoic, these CaCl_2 basinal brines were explained as an indicator of widespread



Fig. 33. Lithium and CaCl₂ brine occurrences. Red stars indicate operations that are extracting (or have extracted) lithium brines in a saline setting. Green stars indicate locations of possible future lithium brine resources. Blue square indicates an active CaCl₂ brine operation, green squares indicate other sites of CaCl₂ that may be a future possible CaCl₂ brine resource. The brown and green shaded zones indicate the positions of ancient marine halite and sulfate basins, respectively (see Fig. 18 for marine evaporite basin names and Tables 11 and 12 for deposit details).

Table 11

CaCl₂ brines in Quaternary saline settings; CaCl₂ brines and tachyhydrite in ancient evaporite deposits tend to typify times of CaCl₂ oceans, as listed in Fig. 20A and Table 10. For overviews of geology of deposits see Garrett (2004) and Warren (2006).

Location, Country (area)	Elev. (msl)	Koeppen	Comments
Don Juan Pond, Lake Vanda, Antarctica (<1 km ²)	90	EF	Very small saline lake (>1 km ²) and only of academic interest. Unusual association of low MgCl ₂ levels in this CaCl ₂ brine. Calcite, gypsum, mirabilite, antarctite are lake floor precipitates. See earlier mirabilite discussion for deposit detail. (Torii and Ossaka, 1965)
Lake Asal, Djibouti (54 km ²)	−155	BWh	Possible future resource. Lake precipitates halite and gypsum Is fed in east by hydrothermally-altered CaCl ₂ -rich modified seawater (Manda springs; 40–80 °C) seeping through recent fault zones in Dahla Basalt ridge (salinities >100,000 ppm). Lake waters are less enriched in Ca relative to springs due to widespread precipitation of subaqueous gypsum on perennial lake floor. (Stieljes, 1973; Castanier et al., 1992; Garrett, 2004)
Danakil depression, Ethiopia	−77 and −118 resp.	BWh	Possible future resource. Lake Giulietti (−77 m, 115 km ²) is largest perennial saline lake in Danakil depression, water depth of over 100 m situated in an actively rifted area in the center of the Danakil Depression and surrounded by active volcanic peaks. A number of calcium chloride-containing hot springs (40–50 °C) flow into the southwest edge of Lake Giulietti, and the lake appears to occasionally drain into the nearby Dallol Salt Pan (−118 m, 344 km ²). Inflow water is hydrothermally-altered seawater. In the northern portion of the Danakil Depression, bischofite and carnallite precipitate from a 130 °C MgCl ₂ brine that emerges from the Black Mountain hot spring, although bischofite quickly deliquesces to sylvite upon exposure to the atmosphere. (Hutchinson and Holwerda, 1968; Augustithis, 1980))
Dead Sea, Israel, Jordan (1023 km ²)	−415	BSh	Possible future resource. Ca and MgCl ₂ brine tied to carnallite and bischofite stage in artificial pans is used to manufacture MgCl ₂ . Dead Sea is a nonmarine, fault-bounded evaporite basin that contains CaCl ₂ -rich and SO ₄ - and CaCO ₃ -poor waters, supplied the Jordan River and a number of hydrothermal springs. Most of the solutes come from the hydrothermal spring waters that have leach earlier Miocene marine evaporites. These hydrothermal brines are enriched in CaCl ₂ , have a chlorinity that is 8 times that of sea water, and are rich in the heavy metals iron, manganese, lead and zinc. (Gavrieli et al., 2001)
Bristol Dry Lake, California, USA (	180	BWk	Active CaCl ₂ brine extraction and processing. Unusual nonmarine association of low MgCl ₂ levels in a CaCl ₂ lake brine. Main evaporites are gypsum, anhydrite, and halite with rare antarctite, celestite (SrSO ₄), bacterial calcite, and possibly chlorocalcite (KCaCl ₃). Bristol Dry Lake is mined for its chloride brines and is thus covered with pits and trenches. Antarctite was identified in one trench that was 3 m deep, 20 m long, and contained a 10 to 25 cm deep pool of CaCl ₂ brine. The base of the pit was a massive halite deposit with acicular groups of antarctite protruding outward from the halite and within the brine. Evaporative concentration of this brine in the arid cool climate with temperatures below 30 °C allowed antarctite to precipitate. (Dunning and Cooper, 1969; Garrett, 2004)

dolomitisation and other diagenetic reactions that preferentially extract magnesium from pore waters. Today, it is increasingly apparent that the CaCl₂ enrichment in many basinal brines is a partial leftover indicator of a CaCl₂ ocean at the time the enclosing evaporitic and marine sediments were deposited (relict or connate brines; Lowenstein and Timofeeff, 2008). Interestingly, since 1914, CaCl₂ brines have been targeted in Silurian strata of the Michigan Basin USA (Garrett, 2004). These brines were recovered from porous Detroit Group sediments that overlie the Silurian Salina evaporites, and the Silurian was a time characterised by a CaCl₂ ocean (Fig. 20A).

Hanor and McIntosh (2006, 2007), in contrast to Lowenstein and Timofeeff, 2008, argue that it is difficult if not impossible, to assign specific ages to basinal brines in sedimentary basins. Long time frames for subsurface reactions, variable rates of dolomitisation and dedolomitisation across time and the propensity for subsurface evaporite masses to mineralogically fractionate as they dissolve, greatly complicate a simple “connate” explanation for many ancient CaCl₂ formation waters. That is, other than volumetrically minor zones in a basin where relict rock-salt retains brine inclusions in primary halite chevrons, ongoing rock-fluid interactions mean it is impossible to determine ages of the ionic components in pore waters in any nearby deep subsurface aquifers. If the age and parentage of the components of the pore brine are not known, then the possible marine parentage of the pore waters, whether CaCl₂ or MgSO₄ type, cannot be determined.

Outside of the Michigan Basin, the only other active commercial CaCl₂ brine recovery operation takes places in the trenches and pits of Bristol Dry Lake, California (Table 11). There a poorly understood combination of dolomitisation, active hydrothermal circulation and rapid emplacement of basaltic magma has created unusual continental brines that are Ca-enriched and Mg-poor (Garrett, 2004).

As for potash deposits, there is a Quaternary continental/pre-Quaternary dichotomy in the nature of CaCl₂ brines. Brines in Quaternary Bristol Dry Lake and Don Juan Pond are not associated with a brine sourced in seawater or older (“connate”) marine evaporite successions. These two relatively small deposits contain natural antarctite due to inherently low Mg levels. All other CaCl₂

brine occurrences, as listed in Table 11 and Fig. 33, contain higher levels of Mg and are tied to deeply circulated marine/hydrothermal waters and/or are associated with dissolution of older marine evaporite beds (e.g., Lake Asal, Dallol Salt Pan, Dead Sea, Michigan Basin).

7.2. Lithium brines

Lithium compounds are consumed in the production of ceramics, lubricants, glass, and primary aluminium. Lithium is electrochemically reactive and has unique properties, so there are many ongoing commercial lithium usages in the new high tech fields of industrial production, including the rapidly expanding lithium battery technologies.

Lithium is widely distributed on Earth and is about as common as chlorine in the continental lithosphere (20–70 ppm). Its high reactivity means it does not occur naturally in elemental form but, like boron, tends to be concentrated the later magmatic phases of some granites or in saline lacustrine settings in tectonically and magmatically active terrains. So, exploited lithium resources either centre around rather unusual pegmatite mineralogies or a few highly-saline continental lacustrine brine sources. The latter are the focus of our discussion.

To the detriment of pegmatite-based producers of lithium, saline lacustrine salt systems are increasingly exploited as the world's major sources for lithium metal. Lithium-enriched brines typify pore waters formed in suprasedale saline lacustrine settings in many arid continental high altitude volcanogenic terrains, but only a few brines entrain sufficiently high concentrations of lithium over sufficiently large permeable areas in their salt hosts to make then suitable as brine extraction targets (Table 12). The move away from a pegmatite source for lithium is largely due to the presence of substantial volumes of cheaply produced lithium carbonate in a few Quaternary salars in South America and salt lakes in southwestern China. Production from pore brines in South American salars dominates current world lithium production, with Chile and Argentina producing 10,000 out of the world annual total of about 20,000 tons. Most lithium salts are highly

Table 12

Lithium-enriched brines, mostly in Quaternary saline settings (many lithium-rich brine occurrences are closely association with saline borate deposits, as listed in Table 3). For geological overviews see [Garrett \(2004\)](#), [Kunasz \(2006\)](#) and [Warren \(2006\)](#).

Location, Country (area)	Elev. (msl)	Koeppen	Comments
Salar de Hombre Muerto, Argentina (565 km ²)	4300	ET	Lithium carbonate brine processing; Rather than solar evaporation, FMC use a proprietary alumina adsorption system to directly extract lithium from the salar brine. Nodular ulexite is commonplace on salar and in shallow subsurface. Porous halite bed (15% Ø) is more than 40–50 m thick across much of the salar. Pore brines principally sourced from lithium-containing hot springs and seeps. Average Li in brine ≈ 520 ppm. Brine in the salar is usually within 20 cm of the salar surface, and appears to be relatively constant in composition to depths of at least 15 m. (Vinante and Alonso, 2006)
Salar de Uyuni, Bolivia (9654 km ²)	3650	BWk	Planned lithium carbonate brine processing facility. Typical sediment thickness is 121 m, made up of 11 variably porous (0–30% Ø) halite beds separated by layers of mud and sand. Ulexite present. The upper halite bed is porous so targeted bed, it is around 11 m thick. Brine is always within 5–20 cm of the surface and contains 80 to 1150 ppm of lithium, averaging 321 ppm Li, a limited area in the southeast corner averages 625 ppm. Pore brines principally sourced from lithium-containing hot springs and seeps. Mg/Li ratios are three times that in salar de Atacama making brine processing to extract Li much more difficult. Similar problem occurs at the nearby Salar de Rincon, where Admiralty Resources plan to pretreat the raw brine with calcium hydroxide to reduce the magnesium content before evaporation commences. Compared to Atacama and de Hombre Muerto, the lesser thickness of porous halite (11 m versus 35 m), the lower Li, and higher Mg content in the brines have made this salar a less attractive resource. (Risacher and Fritz, 2000 ; Ericksen et al., 1978 ; Risacher et al., 2003)
Salar de Atacama, Chile (33065 km ²)	2250	BWk	Lithium carbonate extraction via solar concentration of extracted and ponded salar brine. Sediment fill of more than 950 m of intercalated halite and lacustrine muds. Nearsurface salt unit is very porous (30, 20, 15 and 5% at 0–0.5, 0.5–2, 2–25 and 25 m depth, respectively; average of 18% for the upper 25 m), and brine-filled from about 0.6–35 m. The porosity decreases rapidly to nearly zero after about 35–40 m. The brine is saturated with halite, and contains variable concentrations of lithium, potassium, magnesium, sulfate and borate in different locations in the Salar; Lithium concentration varies from about 1000–4000 ppm, and averages over 1500 ppm for the two commercial lithium operations on the Salar. Pore brines principally sourced from lithium-containing hot springs and seeps. Unusual of other Puna salars as it contains no borate beds. (Boschetti et al., 2007 ; Risacher et al., 2003)
Zabuye Salt Lake, western Tibet, China (251 km ²)	4426	Dwc	Currently under development and a 5,000 tpy LiCO ₃ plant began operations in 2005. Complex perennial brine; Li from 500 to 1,000 ppm, the lake centre brine is saturated with both halite and potassium sulfate, during solar evaporation lithium starts to crystallize around two-fold concentration. Unique saline lacustrine system in that LiCO ₃ is a natural precipitate about lake strandzone. (Zheng and Liu, 2009)
Dabuxum/East Taijinaier Lakes, China (350 km ²)	3200	Dwc	Potash brine operation via extraction and solar concentration since mid 1980s, a 35,000 tpy LiCO ₃ plant began operations at Golmud in 2007, but will not reach full capacity for a number of years. A 8–13 ppm Li brine is pumped into solar evaporation ponds where the final potash end-liquors (carnallite) contain around 120 ppm Li. (see text)
Dead Sea, Israel, Jordan (1023 km ²)	–415	BSh	Possible future resource. The MgCl ₂ -rich lake brine is currently pumped into large solar ponds to produce potash (carnallite) and magnesia in both Israel and Jordan (Mg and Br as byproducts), pond end-liquors contain about 30 ppm Li, but high Mg content make Li extraction problematic. (Garrett, 2004)
Clayton Valley Playa, Nevada, USA	1300	BWk	Lithium carbonate operation started in 1966 (then Li in brine was 360–400 ppm, today 230 ppm). Brine level (WT) was sometimes as low as 15–76 m beneath the playa floor. Brine wells were pumped into solar ponds where Li concentration reached 5,000 ppm, then sent to Li recovery plant. Current lower Li levels make this operation unattractive compared to South American salars. Hectorite clays (Na _{0.33} (Mg,Li) ₃ Si ₄ O ₁₀ (F,OH) ₂) in playa formed by interaction of playa brine with smectitic clays (Davis et al., 1986)
Great Salt Lake, USA (4998 km ²)	1280	Cfa	Possible future resource. The lake brine Li concentration varies widely with the climate cycle, the southern brine contains up to 18 to 43 ppm Li, and the northern brine from 40 to 64 ppm Li. The commercial magnesium plant's solar pond end-liquor often contains about 600 ppm Li, while the potassium sulfate plant has achieved values of 700–1600 ppm Li, but high Mg content make Li concentration and extraction problematic from either brine source. (Garrett, 2004)
Searles Lake, USA (100 km ²)	490	BWk	Lithium carbonate manufacture as byproduct from salt-cake and soda-ash processing via brine extraction from two porous halite layers and subsequent solar concentration. Li plant operated from 1951–1978. In the central section of the lake the brine contained an average of 50–80 ppm Li, which graded to 10–70 ppm Li near the lake edges. The high salinity brine resource beneath the lake is now largely depleted, Li contents is probably too low and volumes too small to make this a viable future LiCO ₃ resource. (Garrett, 2004)
Salton Sea, USA	–70	BWh	Possible future resource, situated in a very large geothermal brine field hosted in the porous sediments at a depth of about 500–3000 m. Brine is hot (100–400 °C) NaCl solution carrying elevated levels of metals including from 100–400 ppm Li (200 ppm average). Many difficulties to be overcome in terms of rigid environmental restraints, elevated Mg and other metal content in concentrated brines and land access to construct solar evaporators. (McKibben et al., 1987, 1988 ; Garrett, 2004)
Smackover oilfield brines, Arkansas, USA	–	–	Possible future resource, Smackover reservoirs in both Texas and Arkansas have Li content at 500–572 ppm, in one zone in Texas the brine averages 386 ppm Li, while Arkansas a brine averages 365 ppm. Brine occur at 1800–4800 m depth and are currently commercially processed to extract bromine before re-injection (these brines currently account for 40% of world Br production). (Garrett, 2004)

soluble in natural brines and tend stay in solution although some can be to be absorbed on playa clays, as in the hectorite beds in Clayton Playa, Nevada. Interestingly, lithium carbonate is a natural precipitate from the high-altitude hypersaline waters of Lake Zabuye in Tibet.

Chile produces from lithium-rich lake brines, largely through the exploitation of Salar de Atacama ([Fig. 34](#)). The salar lies on the Tropic of Capricorn at an altitude of 2300 m in the Desierto de Atacama, some 200 km inland from Antofagasto and adjacent to the Andean Altiplano. In its more central portions this salt-encrusted playa contains a massive halite unit (nucleus) that is more than 900 m thick, with an area ≈ 1100 km². Fringing saline muds, with an area ≈ 2000 km², surround this nucleus, especially to the north and east ([Fig. 34A](#)).

The current salt crust atop this halite nucleus contains a sodium chloride interstitial brine that is rich in Mg, K, Li, and B ([Alonso and](#)

[Risacher, 1996](#); [Carmona et al., 2000](#)). Lithium contents of the pore brines range from 200 to 300 ppm in the marginal zone, some 500–1600 ppm in the intermediate zone and 1510–6400 ppm in the salt nucleus. This central zone averages 4000 ppm lithium. Main inflows to the salar drain volcanic formations of the Andean Highlands located to the east of the basin. Salts dissolved in inflow waters have a double origin.

Weathering of volcanic rocks supplies K, Li, Mg, B and, to a lesser extent, Na and Ca. Leaching of ancient halokinetic evaporites from a mother salt layer that breaks through the volcanic formations that surround Salar de Atacama and from outcrops adjacent to the lake depression provides additional amounts of Na, Ca, Cl, and SO₄ to saline inflow waters ([Fig. 34B and C](#)). The mass-balance of the upper nucleus of the salar centre shows a strong excess of NaCl with respect to the bittern solutes Mg, K, Li, and B. According to [Alonso and Risacher \(1996\)](#) this suggests that the nucleus did not originate from

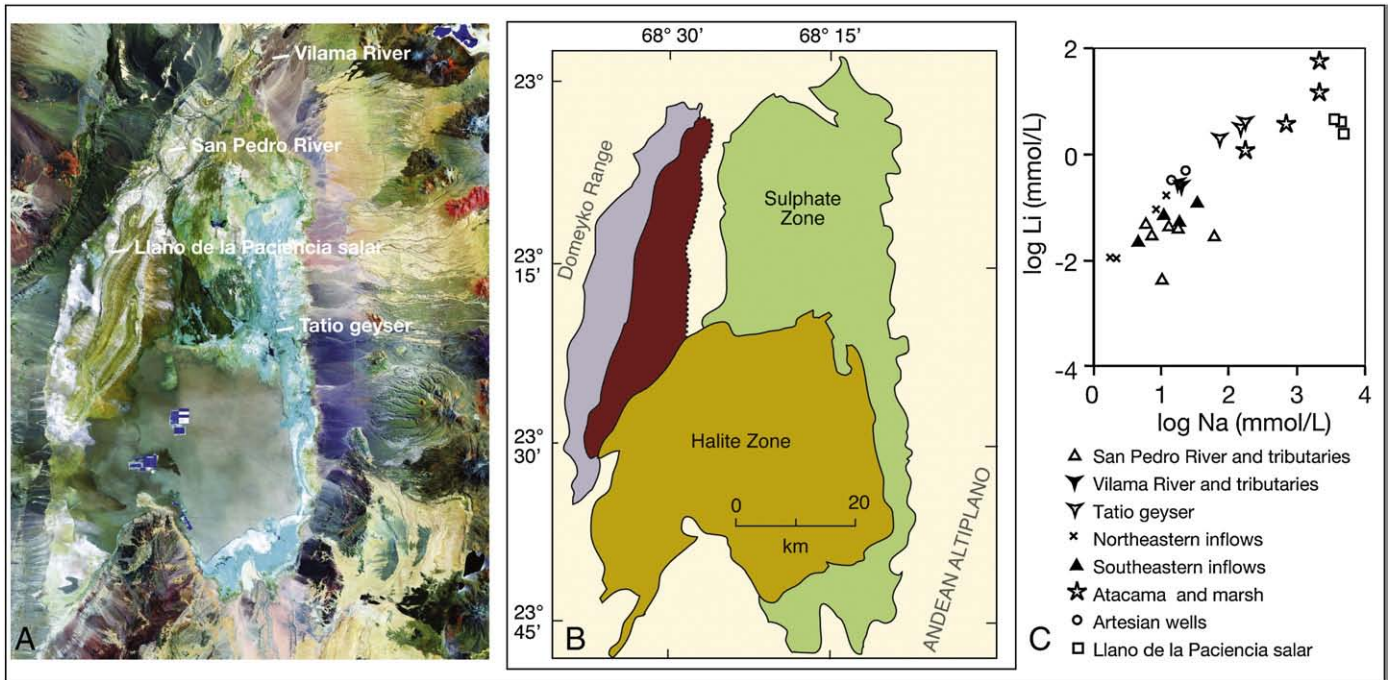


Fig. 34. Lithium brines in Salar de Atacama, Chile. A) Landsat image showing centripetal endoheic drainage (base image courtesy of NASA <<https://zulu.ssc.nasa.gov/mrsid/>>). B) Surface geology showing nearby Neogene evaporite outcrops in the Cordillera de la Sal (after Warren, 2006). C) Lithium content of wells in the halite nucleus and other nearby brine sources (after Carmona et al., 2000).

evaporation of inflow waters similar to the present. Rather, the excess of NaCl is due to NaCl-rich inflow waters that formerly drained the Cordillera de la Sal, a Tertiary-age evaporitic ridge along the western rim of the present-day salar.

The average sedimentation rate of halite in the lake centre is ≈ 0.1 mm/year, based on the age of an ignimbrite interbedded with the salt. This slow aggradation rate implies a climatic setting of long dry periods and inactivity alternating with short wet periods during which large amounts of saline water, and so large amounts of salt, accumulated in the basin centre. The lack of peripheral lacustrine deposits and the high purity of the salt also suggest that the main salt unit is not the remnant of an ancient deep saline lake, but originated mostly from evaporation of waters supplied by subsurface and subterranean saline seeps.

Brines are pumped from 30 metre deep holes in the salt nucleus into solar evaporation ponds. In the ponds they are concentrated by a factor of 25, generating a final brine strength of 4.3% Li. During evaporation processing and the production of potassium chloride and potassium sulfate the ion ratios are constantly monitored and adjusted to avoid the precipitation of lithium potassium sulfate. The high initial lithium content of the brines and the extremely arid setting (3200 mm pan evaporation and <15 mm precipitation) means that only 90ha of evaporation ponds are required for the current Atacama operation, this is only 5% of the area required at Clayton Valley, Nevada. Borate (as perborate) is recovered at levels of 0.84 g/l during lithium extraction. Increasing volumes of lithium are also produced by new salar brine processing facilities in Salar de Hombre Muerto, Argentina and Salar de Uyuni, Bolivia.

Porosity levels in the host halite aquifer are a major constraint on potential economics of any salar lithium brine resource. Most halite units lose their effective porosity and permeability by depths of 50–60 m (Fig. 35). Thus most Quaternary lithium brine operations hosted in a halite bed/aquifer will have an economic basement to brine recovery at around this depth. It is unlikely that recovery operations in Salar de Atacama and planned projects in Salar de Uyuni can recover economic brine volumes at much greater depths. There may be a

900 m thick halite-dominant succession infilling Salar de Atacama and a number of halite beds to a depth of 120 m in Salar de Uyuni, but economic porosities in the halite will likely only be present in the upper portions of the halite fill in both salars.

Postulating likely lithium resources in a salar to depths greater than 50–60 m should only be done after salar-hydrology-aware drilling has established the presence of economic permeabilities in the hosting halite aquifer. Such measurements require drilling and sampling equipment that facilitate reliable “in-situ” determinations of porosity and permeability in the halite mass and Li measurements in

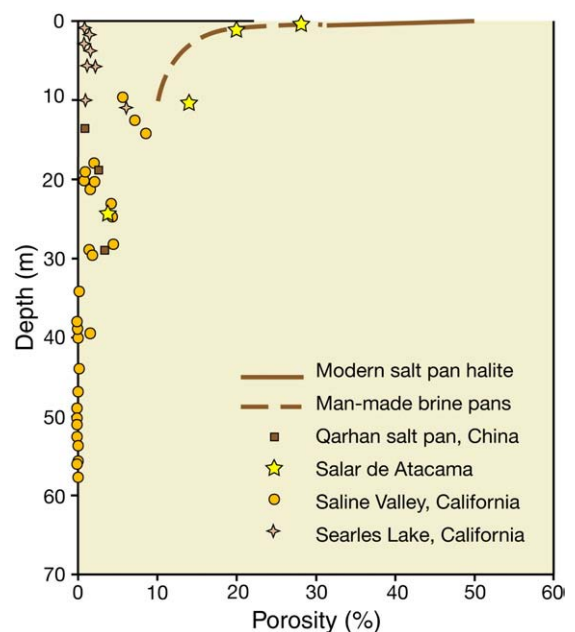


Fig. 35. Porosity loss with depth in bedded halite from saline pan and salar deposits (in part after Casas and Lowenstein, 1989).

Table 13
Summary of evaporite characteristics.

	Commodity	Hydrologic situation	Brine Source	Depositional Associations	Exploration Characteristics
NONMARINE (lesser ancient evaporite systems)	Borate	Suprasealevel intermontane hydrographically closed continental depressions ACTIVE SAME-SCALE QUATERNARY AND PRE-QUATERNARY COUNTERPARTS	Nonmarine brine, typically with volcanogenic leachates	Neogene lacustrine underfilled basin in cooler but arid conditions, generally in high elevation intermontane fault-bound depressions. A few borate deposits also found in older meta-evaporitic and igneous associations	Continental interior lacustrine. Best developed in Neogene continent–continent collision belts and/or continent/ocean plate subduction zones with active magmatism. Not located within or atop ancient marine mega-evaporite basins
	Sodium Sulfate (salt-cake)		Nonmarine brine	Neogene lacustrine underfilled basin. 1) Solar concentration of surface brines with associated increasing temperature in endorheic continental playa depressions, 2) The winter onset of saline brine cooling in local depressions	Continental interior lacustrine. Not located within or atop ancient marine mega-evaporite basins. Basin drainage must be high sulfate, e.g. from dissolution of older evaporites, cation exchange, volcanics or pyrite oxidation.
	Sodium Carbonate (soda-ash)		Nonmarine brine with elevated CO ₂ levels	Neogene lacustrine underfilled basin. 1) Eocene–Miocene intermontane depressions in actively subsiding foreland depressions with relatively high relief surrounding drainage terranes, 2) Quaternary lacustrine deposits at termini of hydrographically-closed drainages in: a) Intermontane depressions surrounded by relatively high topographic relief and, i) hot arid conditions or, ii) high altitude conditions. b) Terminal pans in lower-relief hot arid cratonic settings where NaCO ₃ resource resides within annually replenished NaCO ₃ brines, often in combination with NaSO ₄ .	Continental interior lacustrine. Not located within or atop ancient marine mega-evaporite basins. Sodium must be present (ionic exchange with appropriate labiles in abundant quantities along with elevated levels of CO ₂ . Nahcolite was a typical bedded co-precipitate with trona during the peak Eocene greenhouse period when atmospheric CO ₂ levels more than double those of today. Trona-nacholite, along with halite and not gypsum, were the dominant Early Archean evaporite salts.
	Lithium Brines		Nonmarine	As for borates	As for borates
MARINE (dominant ancient evaporite systems)	Mega-evaporite (especially thick halite intervals) but also mega-sulfate and mega-potash beds	Subsealevel, hydrographically-closed marine-seepage depressions, occasional breaching of barrier NO CURRENTLY ACTIVE SAME-SCALE QUATERNARY COUNTERPART	Marine brine. Alternating MgSO ₄ and CaCl ₂ ocean chemistry in the Phanerozoic tied to variable rates of seafloor spreading and platform dolomitisation	Continent–continent proximity. Megahalite and megasulfate beds deposited in: 1) Soft suture collision basin 2) Opening rift to incipient ocean basin 3) Intracratonic sag basin. 4) Strike-slip depression (smallest of the associations)	Marine mega-evaporite basins in zones of appropriate tectonics and climate, Late Neoproterozoic to Neogene at plate margins or intracratonic sags. Thick halite beds in this association subject to early halokinesis due to syndepositional tectonics, rapid subsidence and sediment loading (except in intracratonic settings where superimposed tectonism drives salt flow). Epeiric platforms favored by greenhouse eustasy.
	Mega-sulfate			1) Periplatform saltern and mudflat beds intercalated with open marine platform/shelf carbonates 2) Intracratonic sag with 10 m + thick sulfate typically intercalated with halite and evaporitic carbonates of equivalent or greater thickness	
HYBRID	CaCl ₂ brines	Subsealevel or basinal	Marine/ hydrothermal	Low Mg CaCl ₂ salts in underfilled continental lacustrine depression. High Mg CaCl ₂ salts in marine evaporite association	Typical subsurface connate association with marine evaporites, especially if ancient salts from a CaCl ₂ oceans are present.

the brine that are related to actual content at the level of measurement, with minimal contamination by waters from outside the measured horizon.

8. Summary

An understanding of the various exploited evaporite deposits in a framework of mineralogy and time can be summarized as (Table 13);

- 1) Primary evaporite minerals reflect the chemistries of their parent brines. Ancient marine evaporite deposits are dominated by large volumes of halite anhydrite and variable amount of potash and other bittern salts. Phanerozoic seawater composition has fluctuated between MgSO_4 oceans when carnallite and kainite/ MgSO_4 bitters dominated and CaCl_2 oceans when calcite seas dominated world ocean chemistry.
- 2) Large deposits of borate, salt-cake and soda-ash evaporites, and lithium-rich brines, require a brine chemistry that is not that of Phanerozoic seawater
- 3) Most exploited borate, salt-cake and soda-ash deposits are continental deposits that tend to occur in suprasediment tectonically active Neogene settings
- 4) Tectonics and climate, not eustasy, are the prime control of the distribution of most basinwide and nonmarine evaporites. Greenhouse eustasy (with associated epeiric seaways) favour the formation of platform evaporites.
- 5) The scale and diversity of marine evaporites show much greater diversity at particular times in the past when continents were in close proximity (aggregation of disaggregation of supercontinents) or epeiric seaways were widespread.

Appendix A

Evaporite minerals mentioned in this paper: less saline alkaline earth carbonates or evaporitic carbonates are indicated by **, the remainder in this list are more saline evaporite salts. Documented dolomite composition ranges from $\text{Ca}_{1.16}\text{Mg}_{0.84}(\text{CO}_3)_2$ to $\text{Ca}_{0.96}\text{Mg}_{1.04}(\text{CO}_3)_2$.

Mineral	Formula	Mineral	Formula
Anhydrite	CaSO_4	Leonhardtite	$\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$
Antarcticite	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	Leonite	$\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$
Aphthitalite (glaserite)	$\text{K}_2\text{SO}_4 \cdot (\text{Na},\text{K})\text{SO}_4$	Loewite	$2\text{MgSO}_4 \cdot 2\text{Na}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$
Aragonite **	CaCO_3	Ludwigite	$(\text{FeMg})_4\text{Fe}_2\text{B}_2\text{O}_7$
Bassanite	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$	Mg-calcite **	$(\text{Mg}_x\text{Ca}_{1-x})\text{CO}_3$
Bischofite	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	Magnesite**	MgCO_3
Bloedite	Na_2SO_4	Meyerhoffite	$\text{Ca}_2\text{B}_5\text{O}_{11} \cdot 7\text{H}_2\text{O}$
(astrakanite)	$\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$	Mirabilite	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
Borax (tincal)	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	Nahcolite	NaHCO_3
Boracite	$\text{Mg}_3\text{B}_7\text{O}_{13} \cdot \text{Cl}$	Natron	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
Burkeite	$\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$	Nitratite (soda nitre)	NaNO_3
Calcite**	CaCO_3	Nitre (salt petre)	KNO_3
Carnallite	$\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$	Northupite	$\text{Na}_2\text{CO}_3 \cdot \text{MgCO}_3 \cdot \text{NaCl}$
Colemanite	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$	Pentahydrate	$\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$
Danburite	$\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot 2\text{SiO}_2$	Pinnoite	$\text{MgB}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$
Datolite	$\text{Ca}_2\text{B}_2\text{Si}_2\text{O}_9 \cdot \text{H}_2\text{O}$	Pirssonite	$\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$
Darapskite	$\text{NaSO}_4 \cdot \text{NaNO}_3 \cdot \text{H}_2\text{O}$	Polyhalite	$2\text{CaSO}_4 \cdot \text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$
Dawsonite	$\text{NaAlCO}_3(\text{OH})_2$	Proberite	$\text{NaCaB}_5\text{O}_9 \cdot 5\text{H}_2\text{O}$
Dolomite**	$\text{Ca}_{(1-x)}\text{Mg}_{(1-x)}(\text{CO}_3)_2$	Priceite (pandermite)	$\text{CaB}_4\text{O}_{10} \cdot 7\text{H}_2\text{O}$
Eitelite	$\text{Na}_2\text{CO}_3 \cdot \text{MgCO}_3$	Rinneite	$\text{FeCl}_2 \cdot \text{NaCl} \cdot 3\text{KCl}$
Epsomite	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	Sanderite	$\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$
Ferronatrite	$3\text{NaSO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$	Schoenite	$\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
Gaylussite	$\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 5\text{H}_2\text{O}$	(picromerite)	

Table (continued)

Mineral	Formula	Mineral	Formula
Glauberite	$\text{CaSO}_4 \cdot \text{Na}_2\text{SO}_4$	Shortite	$2\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3$
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Suanite	$\text{Mg}_2\text{B}_2\text{O}_3$
Halite	NaCl	Sylvite	KCl
Hanksite	$9\text{Na}_2\text{SO}_4 \cdot 2\text{Na}_2\text{CO}_3 \cdot \text{KCl}$	Syngenite	$\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$
Hectorite	$[\text{Na}_{0.33}(\text{Mg}, \text{Li})_3\text{Si}_4\text{O}_{10}(\text{F},\text{OH})_2]$	Szaibelyite (ascharite)	$\text{Mg}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$
Hexahydrate	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$	Tachyhydrite	$\text{CaCl}_2 \cdot 2\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$
Howlite	$\text{H}_5\text{Ca}_2\text{SiB}_5\text{O}_{14}$	Thernadite	Na_2SO_4
Hydroboracite	$\text{CaMgB}_6\text{O}_{11} \cdot 6\text{H}_2\text{O}$	Thermonatrite	$\text{NaCO}_3 \cdot \text{H}_2\text{O}$
Ikaite**	$\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$	Tincalconite	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$
Inderite	$\text{MgB}_3\text{O}_3(\text{OH})_5 \cdot 5\text{H}_2\text{O}$	Trona	$\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3$
Inyoite	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 13\text{H}_2\text{O}$	Tunellite	$\text{SrB}_6\text{O}_9(\text{OH})_2 \cdot 3\text{H}_2\text{O}$
Kainite	$4\text{MgSO}_4 \cdot 4\text{KCl} \cdot 11\text{H}_2\text{O}$	Tychite	$2\text{MgCO}_3 \cdot 2\text{NaCO}_3 \cdot \text{Na}_2\text{SO}_4$
Kernite	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$	Ulexite	$\text{NaCaB}_5\text{O}_9 \cdot 5\text{H}_2\text{O}$
Kieserite	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$	Van'thoffite	$\text{MgSO}_4 \cdot 3\text{Na}_2\text{SO}_4$
Langbeinite	$2\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4$	Wegscheiderite	$\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$

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