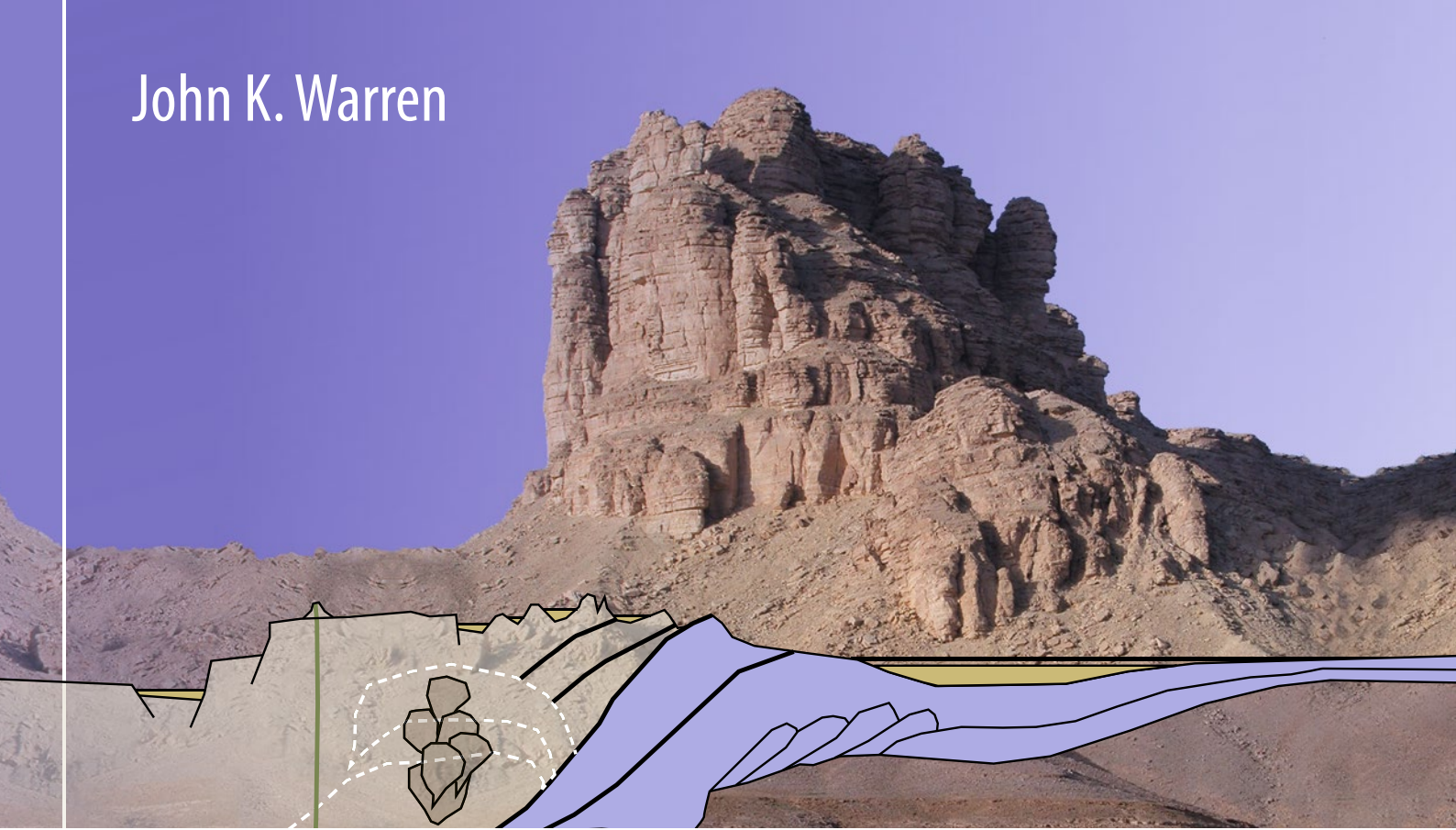



John K. Warren



# Evaporites

A Geological Compendium

*Second Edition*

 Springer

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A Geological Compendium

Second Edition

 Springer

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*For my wife, Jennifer  
my sons,  
Matthew and Tristan*

*Eppur si muove  
(And yet, it does move)  
Galileo Galilei after recanting Copernican beliefs*



---

## Preface

So here it is, most of the way through 2015, 8 years after my last effort on this topic, and I am writing yet another preface to yet another edition on evaporites. Once again, my aim is to give you, the reader, a timely overview of our current understanding of all matters evaporitic. That is why the reference list is now the length of a novella and I have added three new chapter topics compared to the 2006 incarnation. And, to massage my ego, I have included the word compendium in the title.

For the first time, the publishers have allowed me to compile an all-colour version, rather than grey-scale. As the use of paper copy for scientific publishing recedes, publishers are finally moving into the digital world, sometimes scratching and screaming. Then again, copyright and intellectual property issues related to information and intellectual property on the internet will be an earner for the legal profession for decades to come. A digital base to any scientific compilation allows a breadth of coverage in the topics and an accessibility to information that is unprecedented, as in all other scientific fields. You can see this evolution in information access in the page lengths in each of my four books on evaporites. The first, in 1989, was a few hundred pages long; the second in 1999, was over 500 pages; the penultimate effort, published in 2006 was over 1,000 pages long; and this current effort runs to more than 1,800 A4 pages.

Yet I now store and access the hi-res digital version of the complete volume, along with numerous other volumes, as a side issue of the use of my smart-phone. On the same device I can link to, search, review and download copies of all related digital information anywhere in the world I can access the net. Needless to say, this is one old-fart scientist who is impressed by this technology. It is a far cry from the 128k Mac that in the mid-1980s I lugged to a house on the coast of Denmark, along with three shipping cases of photocopied references in order to write the first book. On the downside, open internet access has led to a plethora of cacography, prattle and unsubstantiated opinion given as fact.

In this volume I make much more use of online sources, outside the various libraries and subscribed publishing websites. This makes many of the issues and data compilations discussed in this book, both more current and perhaps more relevant but also more readily dated and updatable at the same time. As I sift through much of the unscientific chaff that is presented as fact on the internet, I am very aware of both the strengths and current weaknesses of science conducted on the internet. Outside of the mainstream literature from subscribed publishers and some democratic government bodies, much online material is opinionated and/or uploaded with minimal peer review. As with much educational policy in the Western world these days, the internet approach is by its nature multicultural, largely non-judgemental, non-authoritarian and unfortunately, in terms of science, often phrased in terms of political correctness.

As a rationalist and a non-theist, I welcome the vast increase in freely available knowledge the internet brings. But I worry that logic and rationalism, which underpin all valid science is being lost in many places of education across the developed world. It is swamped in a tsunami of opinionated quasi-superstitious information. In science, not all points of view are equally valid, there are testable hypotheses and then there is opinionated bumpf. One expects the latter from politicians and religious zealots, unfortunately it has entered



matters that should be science-based, such as much of the current climate change discussion, as well as environmental discussions related, for example, to aforesaid climate change, hydrofracing in shale gas exploration, and other low-cost energy-recovery methodologies, as well as the relative merits of vaccinating children and the use of genetically modified crops. It says something about one's intellectual approach to a scientific problem if you tend to use the term skeptic as a pejorative.

Besides the scientific effort involved in writing this book, in order to give the volume broad utility and consistency, a good proportion of the blood, sweat and tears that I put into this volume involved preparing numerous colour illustrations and tables. I hope I have given improved value to the various authors listed, in my converting, compiling and revamping what were mostly their grey-scale and line drawings into Bezier-based colour outputs (all scaled figures with north to top, unless denoted otherwise). For this, thanks also to Saltwork Consultancy Pte Ltd for giving me permission to publish aspects of their evaporite GIS datasets as figures in this volume. In the digital form of this volume, figures should be extractable through any PDF reader and I hope will make a useful teaching and research resource for presentations and writings for anyone interested in matters evaporitic.

I would like to thank the various companies: Chevron Thailand, PDO, PTTEP, SaltWork Consultants Pte Ltd; Shell Brunei, Shell Oman and Statoil, who for the last 20 years have paid my salary allowing me to work as a company-sponsored academic in universities in interesting regions of the world where academic bureaucracy is subjugated to the peoples' thirst for education. So thanks as well, to my host universities of the past two decades: Universiti Brunei Darussalam, Sultan Qaboos University of Oman and Chulalongkorn University, Bangkok. This support has meant my academic teaching for the past 20 years has been based in developing world, in various places where you can be a full-time academic, publish and do research without being involved in the petty bureaucratic politics and political correctness that today plagues the efficiency of most federally and state-funded universities of the Western world.

Most importantly and most completely, my thanks to my wife Jennifer, who even after more than 40 years of marriage still manages to live with her at times abstracted other half.

Bangkok, Thailand

John K. Warren

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## What is an Evaporite?

I define an evaporite as a salt rock that was originally precipitated from a saturated surface or nearsurface brine in hydrologies driven by solar evaporation (Fig. 1.1a). This simple definition encompasses a wide range of chemically precipitated salts and includes alkali earth carbonates (Table 1.1). Some workers restrict the term evaporite to salts formed at the earth's surface via solar evaporation of hypersaline waters. To underscore the highly reactive nature of evaporites in the sedimentary realm I think of such evaporites as primary, that is, precipitated from a standing body of surface brine and retaining crystallographic evidence of the depositional/hydrological process set where they formed (e.g. bottom-nucleated or current-derived textures). Outside of a few Neogene examples, there are few ancient evaporite beds with textures that are wholly and completely "primary." Most in the subsurface exhibit "secondary" (burial-related) textures, while remnants that have been uplifted back to the surface show "tertiary" (exhumation-related) overprints (Figs. 1.2 and 1.9).

We can contrast the solar-driven set of precipitative processes with other surface and subsurface water-loss mechanisms that can form bodies and beds of mineral salts, with the same chemical compositions as rocks typically called evaporites as listed in Table 1.1. And yet, if applying the term evaporite in its strictest form (i.e., a response to solar-driven evaporation), this second group of mineral salts/sediments are not "true" evaporites; rather, they are mineral salts that crystallized in response to various cryogenic, hydrothermal and burial processes.

## Solar-Heated Brine Concentration

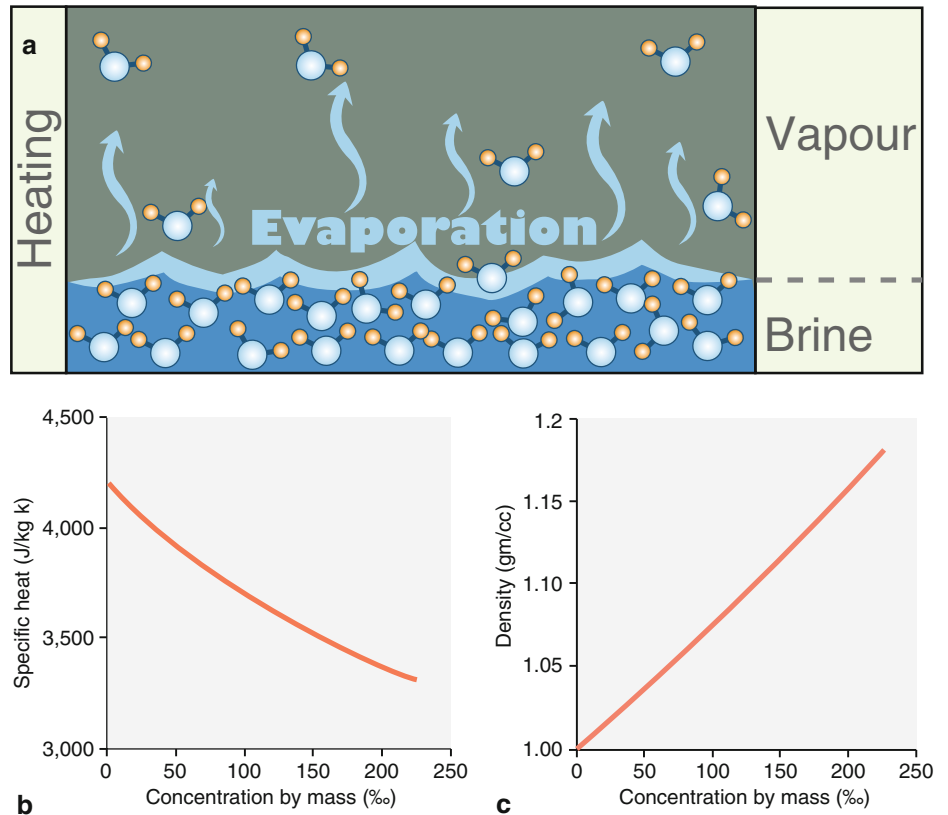
In its broadest definition, evaporation is the process by which molecules in a liquid (water) spontaneously become gaseous (water vapour) and escape the liquid state, while evaporites are the resultant mineral precipitates accumulating in and

around an increasingly saline residual brine that has reached a state of supersaturation with respect to a particular mineral salt or salts. Water molecules in the liquid phase are in continuous motion and so will collide. As they collide, they transfer energy to each other in varying degrees, based on how they collide. Evaporation, then, is a simple matter of solution kinetics in this milieu of molecular motion and is a response to varying degrees of heat absorption at the molecular scale.

On average, water molecules within a standing at-surface brine lake or in near-surface pore spaces, near a watertable and its associated capillary zone, do not have enough kinetic energy to escape the liquid phase and so cross the surface tension barrier. Otherwise, liquid water would turn to vapour spontaneously, any at-surface liquid phase would spontaneously disappear, while recharge to an underlying watertable would be an impossibility. Every so often, the level of solar energy transfer (heat absorption) at the molecular collision site is sufficient to give a water molecule (near the water-air interface) the heat energy necessary to pass into the vapour phase and so exit the liquid water mass (Fig. 1.1a). That is, for a water molecule to escape into the vapour phase it must absorb heat energy, be located near the liquid surface, be moving in the proper direction and have sufficient energy to overcome liquid phase intermolecular forces and pass through the surface tension interface. As the concentration of the residual brine increases the specific heat capacity decreases and the density increases (Fig. 1.1b, c). Specific heat is a measure of how much heat is required to raise the temperature of the brine by 1 °C.

In the absence of air movement, water vapour so created resides within the region immediately above the air-brine interface, or in the vapour phase in the gaseous portion near the top of the capillary zone, immediately below the land surface and above the watertable. Typically, the rate of evaporation atop a standing brine body, or in the uppermost few centimetres of a sabkha mudflat, increases with increasing temperature and decreases with increasing salinity (Bonython 1966). It also increases with the passage of dry winds over

**Fig. 1.1** Brine formation by loss of liquid water volume and can occur at any liquid water surface, either at the surface of a standing water body or in a pore. (a) Evaporation: the rate of evaporation and consequent rate of brine formation is controlled by rate of molecular passage of H<sub>2</sub>O across the vapour – liquid interface. (b) Decrease in specific heat with increase in concentration of NaCl solution. (c) Increase in density with increase in concentration of NaCl concentration



the brine lake or mudflat as this removes the overlying mass of an otherwise static water vapour cloud. If the water vapour layer is not blown away, it becomes increasingly saturated (humid) and so slows the rate of evaporation, even as the salinity of the underlying water mass increases (Chap. 2). In contrast, if the temperature atop the air-brine interface decreases, the vapour phase can pass back into the liquid phase via condensation. This explains the moisture droplets that form overnight in many saline arid settings and coat rock and salt crust surfaces in the early mornings in most coastal sabkhas. Condensation (not rainfall) explains many of the microkarst runnels that decorate the surfaces in intercrystal vadose contacts of subaerial halite crusts, so obvious in salars in the Andes and in the salt crusts that make up the Devil's Golf Course in Death Valley, California.

### Cryogenic and Other Non-solar Saline Mechanisms

In contrast to the formation of evaporite minerals by solar-driven evaporation (heating) of surface and nearsurface waters in hot arid and semi-arid climatic settings, cryogenic brines and associated salts require temperatures at or below the freezing point of the liquid phase. Cryogenic salts, such as hydrohalite, mirabilite, antarctite and epsomite, can then

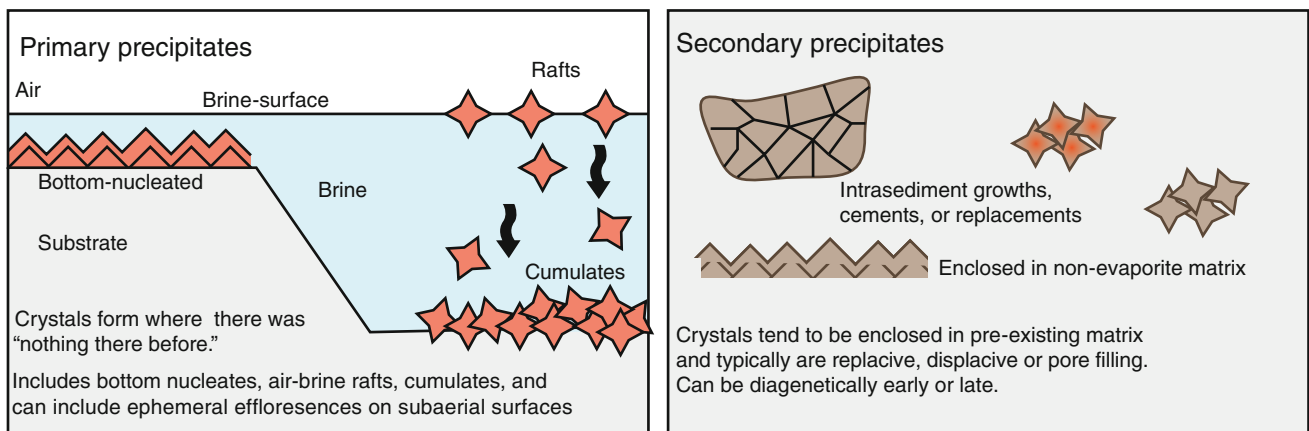
accumulate. They crystallize in a cold, near-freezing, residual brine as it concentrates via the loss of its liquid phase, which is converting/solidifying to ice (Fig. 1.3a). As brine concentration increases, the freezing temperature decreases (Fig. 1.3b). Hydrohalite is a stable precipitate in a freezing brine only when the water temperature is below 0 °C (Fig. 1.4a).

Hydrohalite (NaCl·2H<sub>2</sub>O) crystals have pseudo-hexagonal cross sections and are found in a number of modern cold saline lakes. Craig et al. (1974) collected hydrohalite from the lake bottom in saline Lake Bonney in Antarctica, where bottom water temperatures vary between +2.0 and -2.0 °C. Nikolaevsky (1938) observed hydrohalite forming in winter in the Baskunchak salt lake, northwest of the Caspian Sea (48°N latitude). It was seen to form on two occasions when formative brine temperatures were between -3 and -23 °C, while in summer halite precipitates. Hydrohalite also occurs in bottom sediments in salt-saturated cryogenic lakes in Saskatchewan, at about 51°N latitude, and has been observed in nearby saline springs sediments of the Northern Great Plains (Last 1989a). Hydrohalite pseudo-morphs occur as halite crystals with hexagonal cross sections in cores some 100–140 m deep, in Death Valley, California, indicating NaCl cryogenesis has occurred in the Pleistocene Death Valley Lake from brines with temperatures that were less than 0 °C (Roberts et al. 1997). The climatic significance

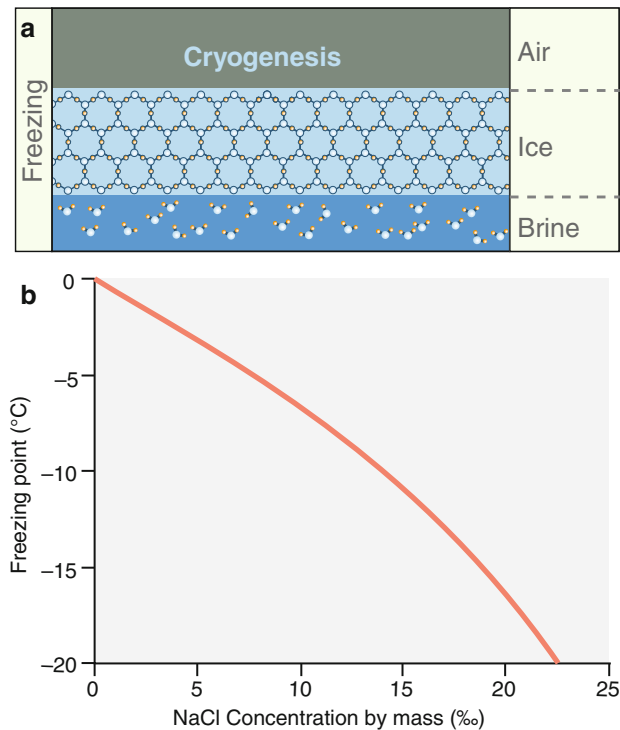
**Table 1.1** Major evaporite minerals: less saline alkaline earth carbonates or evaporitic carbonates are indicated by \*\*, the remainder are the more saline evaporite salts

Mineral	Formula	Mineral	Formula
Anhydrite	CaSO <sub>4</sub>	Leonhardtite	MgSO <sub>4</sub> ·4H <sub>2</sub> O
Antarcticite	CaCl <sub>2</sub> ·6H <sub>2</sub> O	Leonite	MgSO <sub>4</sub> ·K <sub>2</sub> SO <sub>4</sub> ·4H <sub>2</sub> O
Aphthitalite (glaserite)	K <sub>2</sub> SO <sub>4</sub> ·(Na,K)SO <sub>4</sub>	Loewite	2MgSO <sub>4</sub> ·2Na <sub>2</sub> SO <sub>4</sub> ·5H <sub>2</sub> O
Aragonite**	CaCO <sub>3</sub>	Mg-calcite**	(Mg <sub>x</sub> Ca <sub>1-x</sub> )CO <sub>3</sub>
Bassanite	CaSO <sub>4</sub> ·1/2H <sub>2</sub> O	Magnesite**	MgCO <sub>3</sub>
Bischofite	MgCl <sub>2</sub> ·6H <sub>2</sub> O	Meyerhoffite	Ca <sub>2</sub> B <sub>5</sub> O <sub>11</sub> ·7H <sub>2</sub> O
Bloedite (astrakanite)	Na <sub>2</sub> SO <sub>4</sub> ·MgSO <sub>4</sub> ·4H <sub>2</sub> O	Mirabilite	Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O
Borax (tincal)	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	Nahcolite	NaHCO <sub>3</sub>
Boracite	Mg <sub>3</sub> B <sub>7</sub> O <sub>13</sub> ·Cl	Natron	Na <sub>2</sub> CO <sub>3</sub> ·10H <sub>2</sub> O
Burkeite	Na <sub>2</sub> CO <sub>3</sub> ·2Na <sub>2</sub> SO <sub>4</sub>	Nitratite (soda nitre)	NaNO <sub>3</sub>
Calcite**	CaCO <sub>3</sub>	Nitre (salt petre)	KNO <sub>3</sub>
Carnallite	MgCl <sub>2</sub> ·KCl·6H <sub>2</sub> O	Pentahydrate	MgSO <sub>4</sub> ·5H <sub>2</sub> O
Colemanite	Ca <sub>2</sub> B <sub>5</sub> O <sub>11</sub> ·5H <sub>2</sub> O	Pirssonite	CaCO <sub>3</sub> ·Na <sub>2</sub> CO <sub>3</sub> ·2H <sub>2</sub> O
Darapskite	NaSO <sub>4</sub> ·NaNO <sub>3</sub> ·H <sub>2</sub> O	Polyhalite	2CaSO <sub>4</sub> ·MgSO <sub>4</sub> ·K <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
Dolomite**	Ca <sub>(1+x)</sub> Mg <sub>(1-x)</sub> (CO <sub>3</sub> ) <sub>2</sub>	Proberite	NaCaB <sub>5</sub> O <sub>9</sub> ·5H <sub>2</sub> O
Epsomite	MgSO <sub>4</sub> ·7H <sub>2</sub> O	Priceite (pandermite)	CaB <sub>4</sub> O <sub>10</sub> ·7H <sub>2</sub> O
Ferronatrite	3NaSO <sub>4</sub> ·Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	Rinneite	FeCl <sub>2</sub> ·NaCl·3KCl
Gaylussite	CaCO <sub>3</sub> ·Na <sub>2</sub> CO <sub>3</sub> ·5H <sub>2</sub> O	Sanderite	MgSO <sub>4</sub> ·2H <sub>2</sub> O
Glauberite	CaSO <sub>4</sub> ·Na <sub>2</sub> SO <sub>4</sub>	Schoenite (picromerite)	MgSO <sub>4</sub> ·K <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	Shortite	2CaCO <sub>3</sub> ·Na <sub>2</sub> CO <sub>3</sub>
Halite	NaCl	Sylvite	KCl
Hanksite	9Na <sub>2</sub> SO <sub>4</sub> ·2Na <sub>2</sub> CO <sub>3</sub> ·KCl	Syngenite	CaSO <sub>4</sub> ·K <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O
Hexahydrate	MgSO <sub>4</sub> ·6H <sub>2</sub> O	Tachyhydrate	CaCl <sub>2</sub> ·2MgCl <sub>2</sub> ·12H <sub>2</sub> O
Howlite	H <sub>5</sub> Ca <sub>2</sub> SiB <sub>5</sub> O <sub>14</sub>	Thernadite	Na <sub>2</sub> SO <sub>4</sub>
Ikaite**	CaCO <sub>3</sub> ·6H <sub>2</sub> O	Thermonatrite	NaCO <sub>3</sub> ·H <sub>2</sub> O
Inyoite	Ca <sub>2</sub> B <sub>6</sub> O <sub>11</sub> ·13H <sub>2</sub> O	Tincalconite	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·5H <sub>2</sub> O
Kainite	4MgSO <sub>4</sub> ·4KCl·11H <sub>2</sub> O	Trona	NaHCO <sub>3</sub> ·Na <sub>2</sub> CO <sub>3</sub>
Kernite	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·4H <sub>2</sub> O	Tychite	2MgCO <sub>3</sub> ·2NaCO <sub>3</sub> ·Na <sub>2</sub> SO <sub>4</sub>
Kieserite	MgSO <sub>4</sub> ·H <sub>2</sub> O	Ulexite	NaCaB <sub>5</sub> O <sub>9</sub> ·5H <sub>2</sub> O
Langbeinite	2MgSO <sub>4</sub> ·K <sub>2</sub> SO <sub>4</sub>	Vanthoffite	MgSO <sub>4</sub> ·3Na <sub>2</sub> SO <sub>4</sub>

Documented dolomite composition ranges from Ca<sub>1.16</sub>Mg<sub>0.84</sub>(CO<sub>3</sub>)<sub>2</sub> to Ca<sub>0.96</sub>Mg<sub>1.04</sub>(CO<sub>3</sub>)<sub>2</sub>. Less common evaporite minerals, such as borates, iodates, nitrates and zeolites are not listed here, but are discussed in detail in Chap. 12



**Fig. 1.2** What are primary and secondary precipitates?

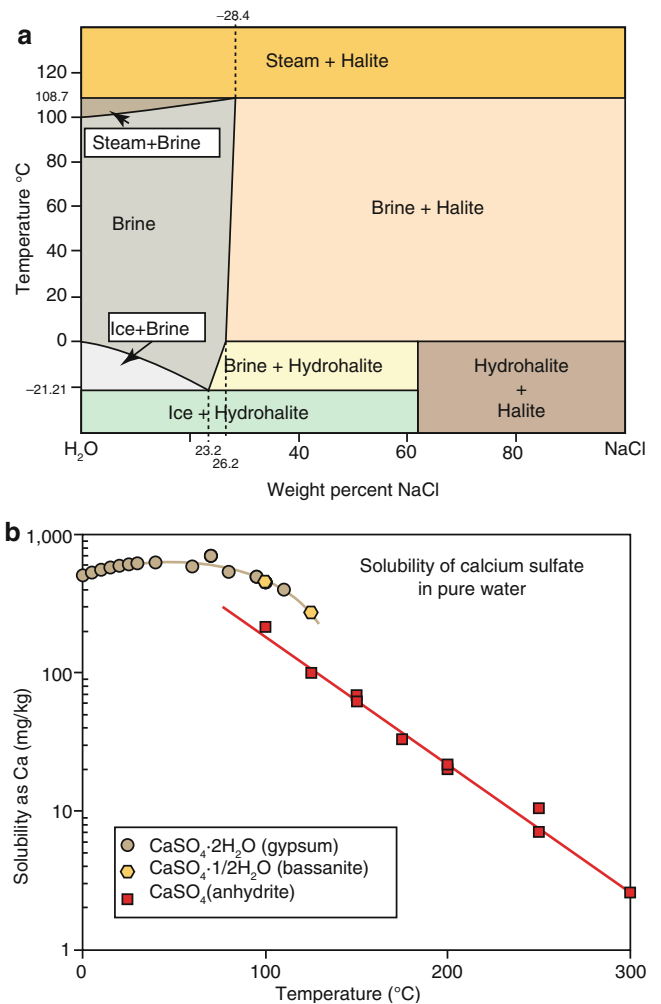


**Fig. 1.3** Cryogenesis: (a) Brine is formed and concentrated as cations and anions are excluded from the lattice structure of ice (pure water) as it solidifies. (b) Brine freezing temperature falls as the NaCl concentration increases

of such cryogenic salt is discussed in Chap. 2, while economic deposits of cryogenic lacustrine mirabilite are discussed in detail in Chap. 12.

When polar seawaters freeze on Earth, hydrohalite and mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) precipitate from the residual marine brines and accumulate in ice sheet fissures, or in load-induced fractures in the ice understory wherever an increasingly saline brine sinks into rocks fractures beneath ice sheets. For example, there are numerous mirabilite beds on the ice floes of the Ross Ice Shelf near Black Island. Likewise, there are dense residual saline brines in interstitial waters extracted from deep cores in sediments of McMurdo Sound (Brady and Batts 1981; Frank et al. 2010). It seems that when ice sheets retreat, the at-surface cryogenic salts dissolve in the freshened at-surface hydrology, but the dense hypersaline brines remain behind in deep fissures, held and preserved in the rock fractures (Starinsky and Katz 2003). In the extreme setting of at-surface brine freezing in small saline depressions in the Dry Valleys of Antarctica, a solid form of calcium chloride, antarcticite, grows cryogenically in what is probably the most saline perennial natural water mass in the world (47 % salinity in Don Juan Pond, Antarctica; Horita 2009).

Extraterrestrially, cryogenesis explains sulphate salt phases that typify ice crack fissures crisscrossing the surface of Europa (a moon of Jupiter) and growing seasonally in



**Fig. 1.4** Temperature dependence of (a) hydrohalite and, (b)  $\text{CaSO}_4$  (After Cohen 1989)

soils of Mar. Widespread gypsum is also forming via ice ablation in the circumpolar Martian dunefield (McCord et al. 1998; Wentworth et al. 2005; Masse et al. 2012). On Earth, as ground temperatures increase, cryogenic salts tend to deliquesce or convert to their high temperature daughter salts (thenardite, glauberite and halite). Worldwide, in appropriate cold climatic settings, there are also numerous examples of cryogenic hydrated calcite (ikaite-glendonite after  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  – see James et al. 2005).

Silica is not normally considered an evaporite salt, but some forms of chert (finely crystalline silica) do accumulate as primary chemical/biochemical precipitates in evaporitic settings. For example, there are hypersaline chert-filled vugs in magnesite crusts in some of the hypersaline alkaline lakes of the Coorong region, Australia (Peterson and Von der Borch 1965) and there are abundant chert co-precipitates (early diagenetic) in Miocene lacustrine beds in the Ebro Basin, Spain (Orti et al. 2007). Then there are thermalitic opal-A cherts associated with hot springs about the edges of

many saline lakes, exemplified by the hot spring precipitates of the East African rift lakes (Owen et al. 2008). These likely-biomediated carbonate and silica terrestrial precipitates crystallize as mineral salts in somewhat saline settings, but unlike other evaporitic mineral salts, these syndepositional calcite and silica cements are not considered a possible variation on an evaporitic theme by the majority of the sedimentological scientific community.

I will leave it up to the purists to decide which of the various “heated” and “freeze-dried” salts, carbonates and silica cements that form at or near the earth’s surface, in environments influenced by variations in solar radiation, are “true evaporites.”

I am quite happy to call them all variations on the evaporite/mineral salt/brine theme. If not, then the classic thick widespread Quaternary-age cryogenically-formed mirabilites that evolved into the glauberite beds that underlie and typify Karabogaz Gol, and the extensive mirabilite bed in the shallow subsurface of Great Salt Lake, Utah, in two of what are considered by many to be better-known evaporite systems of the Quaternary, are not “true” evaporites. Nor are the mirabilites forming today on the floors and in the mudflats of modern salt lakes across the Canadian Plains.

## Burial and Hydrothermal Salts

Substantial volumes of mineral salts, with compositions typically considered evaporite mineralogies, such as anhydrite and even halite, can precipitate in the deep subsurface of the earth in response to heating, cooling, or to increases in pore fluid salinity. None of these process sets, which can typify large parts of the crustal subsurface, are directly solar-driven. Perhaps the resulting mineral precipitates are best classified as hydrothermal or burial salts rather than “true” evaporites. In the sabkha chapter we shall see how retrograde solubility of anhydrite may drive its precipitation as modern sabkha thermalites; the same retrograde precipitation mechanism also drives the formation of burial anhydrites.

The term burial salt is a general descriptor (as defined by Warren 1999, 2006) that encompasses a set of mineral salts created by diagenetic and metamorphic processes that can precipitate mineral salts in the vicinity of a dissolving and altering subsurface salt mass (salt beds, diapirs and allochthons). This is especially so in zones where two brines mix, which premixing had different salinities and chemical constituent proportions. In the sabkha chapter we shall see how retrograde solubility of anhydrite may drive its precipitation as modern sabkha thermalites; the same retrograde precipitation mechanism also drives the formation of burial anhydrites different salinities and chemical constituent proportions. In the subsurface, such burial salts tend to form pore or fracture fills, located wherever the most permeable

subsurface conduits were at the time of brine mixing and precipitation. A burial salt is not a true evaporite in that it is not formed by solar evaporation but, the fact that its ionic constituents are typically derived by the dissolution/alteration of a nearby evaporite, means most geologists consider burial salts in sedimentary basins to be evaporites. The precipitative processes driving formation of burial salts are typically heating, cooling or mixing of basinal waters of two salinities, typically derived by the dissolution of subsurface salt masses or relict hypersaline pore brines (see Chap. 2 for detailed discussion of the relevant literature).

The most common burial salt forming within or near a mass of buried evaporites is a sparry poikilotopic anhydrite, as typifies porosity-occluding cements in many reservoir sands in the North Sea (Sullivan et al. 1994). Halite cements can also be burial salts and both minerals are derived by the subsurface flushing of the nearby evaporites, as in carbonate-silver reservoirs encased in Infracambrian Ara Salt in the South Oman Salt basin (Schoenherr et al. 2009). Timing of the onset of such subsurface dissolution and reprecipitation as burial salts can be late or early (e.g. Schoenherr et al. 2009; McNeil et al. 1998; Kendall 2000).

Hydrothermal salt is a broader descriptor than burial salt and encompasses a higher temperature range for mineral precipitates than the diagenetic realm. Such salts typically formed in heated subsurface fractures or at seafloor vents where hydrothermal waters are escaping, mixing, degassing heating and cooling. Hydrothermal anhydrite crystallizes due to anhydrite’s retrograde solubility, whereby  $\text{CaSO}_4$  becomes less soluble with increasing temperature (Fig. 1.4b). This is why, in the vicinity of active basaltic ridges on the deep seafloor, anhydrite is the dominant component of “white smokers” and is commonplace in other hydrothermal vent mounds; it is also why anhydrite is a major early component of many VHMS seafloor mounds (e.g. TAG Mound where it can constitute more than 50 % of the rock mass; Chap. 16). Hydrothermal anhydrite precipitates in response to the heating of seawater in regions where magmatically-driven hydrothermal fluids are escaping onto the seafloor. In contrast, baryte, another marine hydrothermal precipitate, has prograde solubility and precipitates when an escaping barium-bearing brine is cooled by interacting and mixing with seawater (accordingly the S and Sr isotope signatures in the two precipitates reflect their origins – Paytan and Kastner 2002).

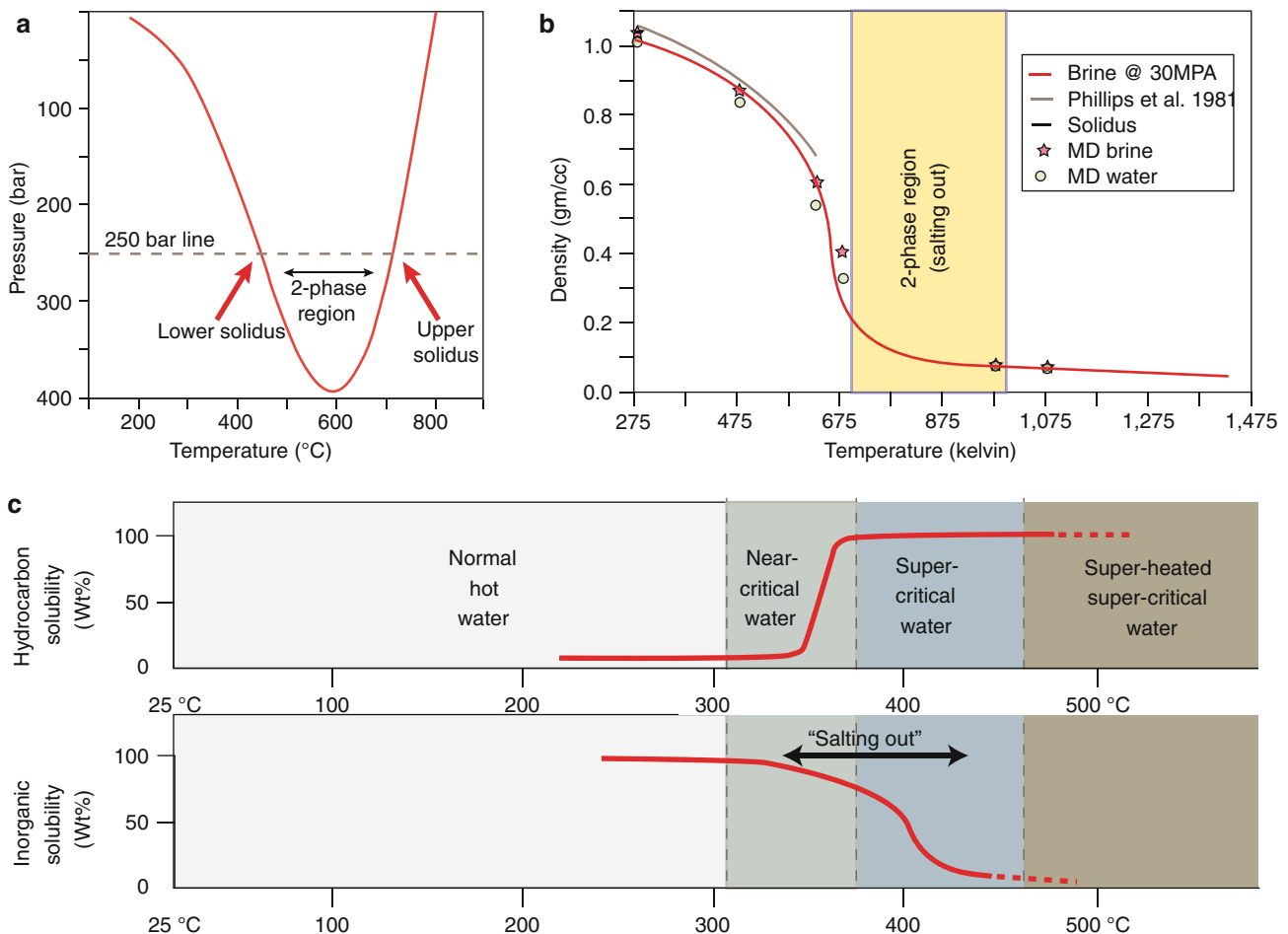
Hovland et al. (2006a, b) and Hovland and Rueslatten (2009) introduced the concept of substantial volumes of hydrothermal halite precipitating from subsurface brines at supercritical temperatures, especially in deeply buried rift-related sedimentary basins. The model relies on heated subsurface waters becoming supercritical and so transforming to a fluid that does not dissolve but precipitates salt (within specific temperature and pressure ranges). A supercritical fluid

is defined as any substance at a temperature and pressure above its critical point; in such a state it can effuse through solids like a gas, and dissolve materials like a liquid. In addition, close to the critical point, small changes in pressure or temperature result in large changes in density. The critical point (CP), also called a critical state, specifies the conditions (temperature, pressure and sometimes composition) at which a phase boundary ceases to exist. Under certain pressure/temperature conditions, supercritical water is unable to dissolve/retain common sea salts in solution (Josephson 1982; Simoneit 1994; Hovland et al. 2006a).

When seawater brines are heated in pressure cells in the laboratory they pass into the supercritical region at a temperature of 405 °C and 300 bar pressure (the CP of seawater). A particulate ‘cloud’ then forms via the onset of ‘shock crystallization’ of NaCl and Na<sub>2</sub>SO<sub>4</sub> (Fig. 1.5a). The sudden phase transition occurs as the solubility of the previously dissolved salts declines to near-zero, across a temperature range

of only a few degrees, and is associated with a substantial lowering of density (Fig. 1.5b). The resulting solids in the “cloud” consist of amorphous microscopic NaCl particles with sizes between 10 and 100 nm. The resultant “salting out” can lead to the precipitation of large volumes of subsurface salts, as well as the ability to carry high volumes of hydrothermal hydrocarbons prior to the onset of supercritical conditions (Josephson 1982; Fig. 1.5c). Supercritical water has enhanced solvent capacity for organic compounds and reduced solvation properties for ionic species due to its loss of aqueous hydrogen bonding (Simoneit 1994).

Hovland et al. (2006a, b) predict that some of the large volumes of deep subsurface salt found in the Red Sea, in the Mediterranean Sea and the Danakil depression, formed via the forced magmatically-driven hydrothermal circulation of seawater down to depths where it became supercritical. This salt, they argue, was precipitated deep under-ground via “shock crystallisation” from a supercritical effusive phase



**Fig. 1.5** Hydrothermal halite derived from supercritical seawater. (a) P-T projection of the monovariant solid-liquid-vapour saturation curve (solidus) for the NaCl-water system. *Arrows* indicate the two points of intersection with the section at 250 bar (defining the lower and upper solidus boundaries). (b) Density of water and brine as a function of temperature

along the 300 bar isobar. The two-phase region (or “out- salting region”) is indicated by the shaded region with onset indicated by a drastic fall in density over a narrow temperature range. (c) Ionic and hydrocarbon solubility in heated water at pressures of 200–300 bars (a–b After Hovland et al. 2006a, b; c after Josephson 1982; Simoneit 1994)

and so formed massive accumulations (mostly halite) typically in crustal fractures that facilitated the deep circulation. NaCl then flowed upwards in solution in dense, hot hydrothermal brine plumes, precipitating more solid salt beds upon cooling nearer or on the surface/seafloor. To date, the Hovland et al. model of hydrothermal sourcing for widespread halite from a supercritical brine source (in active magmatic settings) has not been widely accepted by the geological community (Talbot 2008).

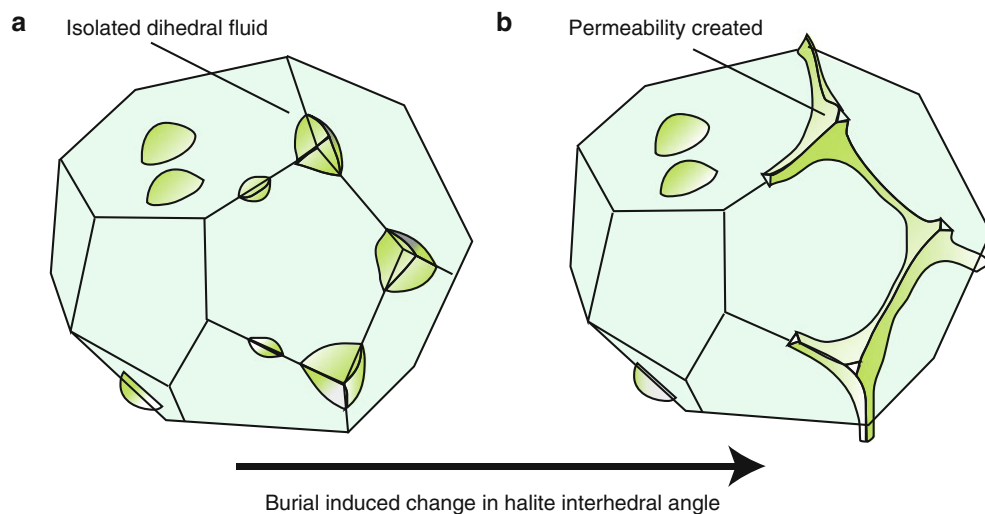
Another source of chlorine-rich hydrothermal fluid in the deep subsurface is the recycling of deeply buried sedimentary salt into the greenschist realm and beyond (Yardley and Graham 2002). In the metamorphic realm ( $T > 200\text{ }^{\circ}\text{C}$ ) the derived fluids do not precipitate halite, but a series of meta-evaporite indicator minerals (Chap. 14). Lewis and Holness (1996) demonstrated that buried salt bodies, subjected to high pressures and elevated temperatures, can acquire a permeability comparable to that of a sand. This is because the crystalline structure of deeply buried salt (halite) attains dihedral angles between salt crystals of less than  $60^{\circ}$  and so creates an permeable polyhedral meshwork. Such conditions probably begin at the onset of greenschist P-T conditions, whereby highly saline hot brines form continuous brine stringers around all such altered and recrystallizing salt crystals (Fig. 1.6; Chap. 14). This polyhedral permeability meshwork allows hot dense brines or hydrocarbons to migrate through salt and so ultimately dissolve the salt host, releasing a pulse of sodic- and chloride-rich fluid into the metamorphic realm (Chap. 14). It is why little or no evidence of masses of metamorphosed halite is found in subsurface meta-evaporitic settings where temperatures have exceeded  $250\text{--}300\text{ }^{\circ}\text{C}$ , even though the melting point of halite is  $800\text{ }^{\circ}\text{C}$ . Given the right subsurface conditions these halite-derived metamorphic brines may evolve into supercritical waters.

One of the most visually spectacular examples of hydrothermal precipitation is in the Naica mine, Chihuahua,

Mexico (Fig. 1.7a). There several natural caverns, such as Cave of Swords (Cueva de la Espadas) and Cave of Crystals (Cueva de los Cristales), which contain giant, faceted, and transparent single crystals of gypsum as long as 11 m (García-Ruiz et al. 2007; Garofalo et al. 2010). Crystals in Cueva de los Cristales are the largest documented gypsum crystals worldwide. These huge crystals grew slowly at very low supersaturation levels from thermal waters near the gypsum-anhydrite boundary. Gypsum is currently precipitating on modern mine walls.

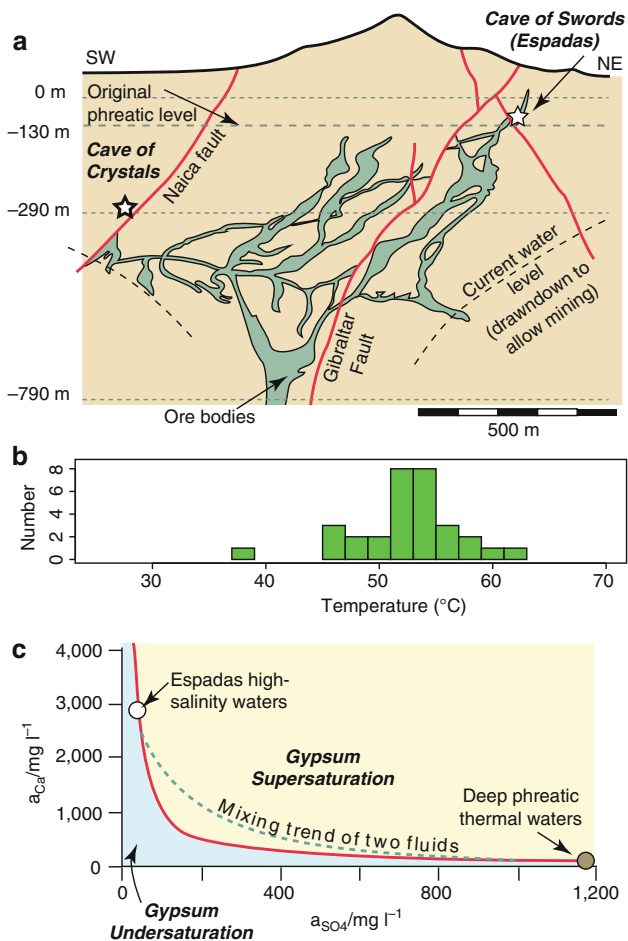
Fluid inclusion analyses show that the giant crystals came from low-salinity solutions at temperatures  $\approx 54\text{ }^{\circ}\text{C}$ , slightly below the temperature at which the solubility of anhydrite equals that of gypsum (Fig. 1.7b). According to García-Ruiz et al. 2007, the sulphur and oxygen isotopic compositions of these gypsum crystals are compatible with growth from solutions resulting from dissolution of anhydrite, which was previously precipitated during late hydrothermal mineralization in a volcanogenic matrix. The chemistry suggests that these megacrystals formed via a self-feeding mechanism, driven by a solution-mediated, anhydrite-gypsum phase transition. Nucleation kinetics calculations based on laboratory data show that this mechanism can account for the formation of these giant crystals, yet only when operating within a very narrow range of temperature of a few degrees, as identified by the fluid inclusion values. According to the paper's authors, these singular conditions create a mineral wonderland, a site of scientific interest, and an extraordinary phenomenon worthy of preservation.

Garofalo et al. (2010), accept the need for a limited temperature range during precipitation, but argue the precipitating solutions were in part meteorically influenced. Their work focused on Cueva de las Espadas. As for most other hypogenic caves, prior to their analytical work they assumed that caves of the Naica region lacked a direct connection with the land surface and so gypsum precipitation would be



**Fig. 1.6** Effect of dihedral angle on pore connectivity in texturally equilibrated monomineralic and isotopic polycrystalline mosaic halite. Shading shows position of dihedral fluid phase within the polyhedral intercrystalline porosity. (a) Isolated porosity for dihedral angle  $>60^{\circ}$ . (b) Connected polyhedral porosity for dihedral angle  $<60^{\circ}$  (After Lewis and Holness 1996)





**Fig. 1.7** Naica Mine, Mexico. (a) Cross section of Naica mine. Mine exploits a hydrothermal Pb-Zn-Ag deposit with irregular manto and pipe morphologies entirely enclosed in subhorizontally dipping carbonates. Cavities of gypsum crystals are located in carbonates close to main and secondary faults. Galleries have been excavated down to  $-760$  m, requiring average pumping rate of  $55$  m<sup>3</sup>/min to depress groundwater to  $-580$  m with respect to phreatic level located at  $-120$  m; Naica and Gibraltar faults act as main drains. (b) Homogenization temperatures of 31 fluid inclusions showing actual temperature of growth. (c) Solubility of gypsum calculated at  $55$  °C and  $105$  Pa and measured activities of shallow and deep cave fluids from fluid inclusion data. Mixing at equilibrium between these two fluids in any proportion generates a fluid with a composition would consistently supersaturated with respect to gypsum, as shown by the position of the mixing curve, indicated by a dashed line, in the gypsum supersaturation field (After García-Ruiz et al. 2007; Garofalo et al. 2010)

unrelated to climate variation, Yet, utilising a combination of fluid inclusion and pollen spectra data from cave and mine gypsum, they concluded climatic changes occurring at Naica exerted and influence on fluid composition in the Naica caves, and hence on crystal precipitation and growth.

Microthermometry and LA-ICP-Mass Spectrometry of fluid inclusions in the gypsum indicate that brine source was a shallow, chemically peculiar, saline fluid (up to  $7.7$  eq. wt.% NaCl) in the Cueva de las Espadas and that it could

have formed via evaporation, during an earlier dry and hot climatic period. In contrast, the fluid of the deeper caves (Cristales) was of lower salinity ( $\approx 3.5$  eq. wt.% NaCl) and chemically homogeneous, and likely was little affected by evaporation processes. Garofalo et al. (2010) propose that mixing of these two fluids, generated at different depths of the Naica drainage basin, determined the stable supersaturation conditions needed for the gigantic gypsum crystals to grow (Fig. 1.7c). The hydraulic communication between Cueva de las Espadas and the other deep Naica caves controlled fluid mixing. Mixing must have taken place during alternating cycles of warm-dry and fresh-wet climatic periods, which are known to have occurred in the region. Pollen grains from 35 ka-old gypsum crystals from the Cave of Crystals indicates a fairly homogenous catchment basin dominated by a mixed broadleaf wet forest. This suggests precipitation during a fresh-wet climatic period, the debate continues.

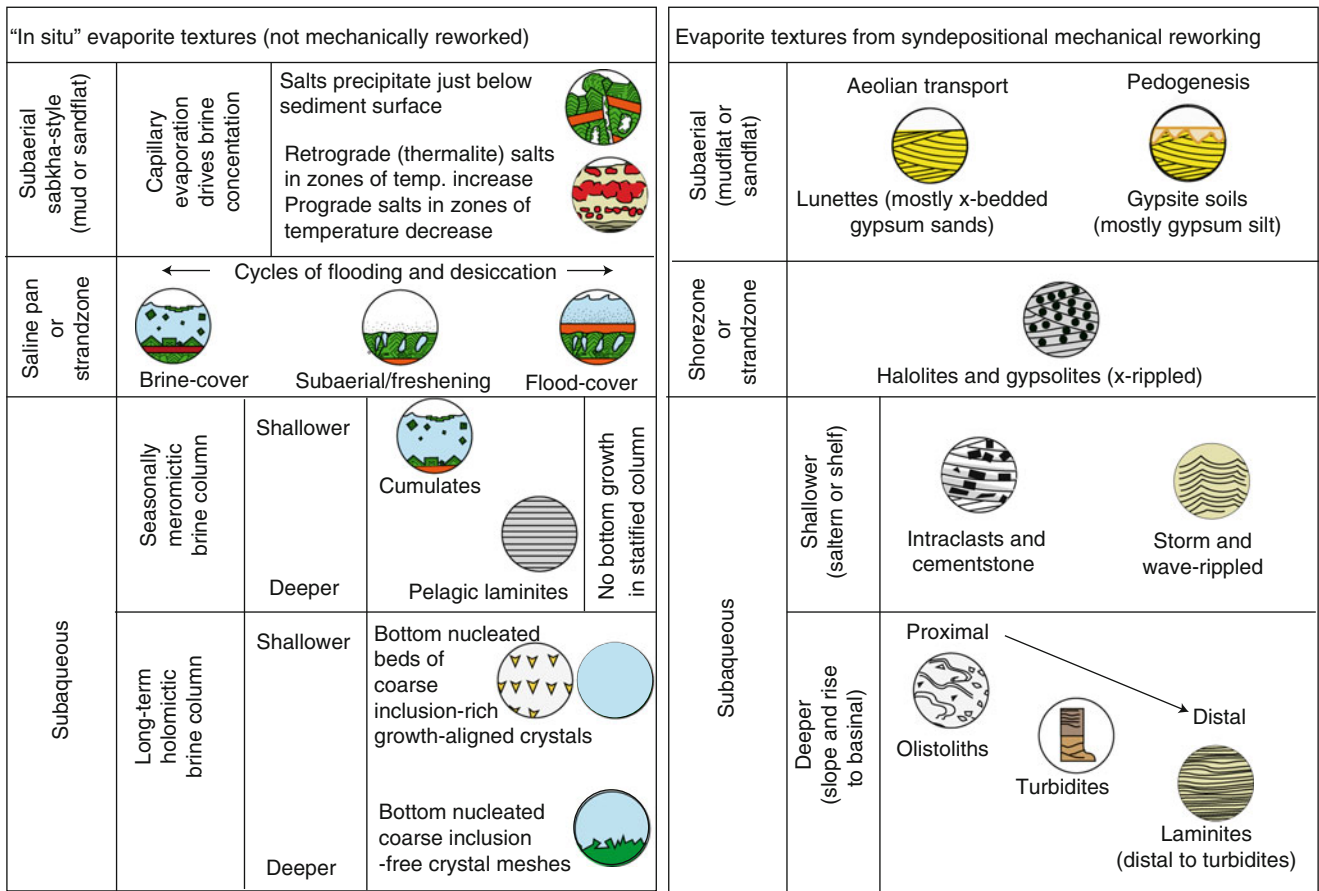
### So, What Exactly Is an Evaporite?

Now that we have discussed some possible complexities in interpretation created by the widespread occurrence of non-solar mineral salts, the remainder of this chapter deals with controls on distribution of “true” sedimentary modern and ancient evaporites (formed at or near surface by solar-driven brine concentration). My working definition for an evaporite is, as the name suggests, a sedimentary rock formed at sedimentary surface temperatures ( $>50$ – $70$  °C) and is typically precipitated by solar concentration (heating) of a near surface or at-surface brine to where the salinity of residual brine becomes saturated with respect to a particular set of mineral salts, which then drop out of the solution as a series of predictable crystallites, subject to near surface and later alteration, replacement and dissolution (Figs. 1.8 and 1.9).

So, what are the basic requirements to form and preserve an evaporite? We need; (1) a surface or near surface brine body that is saline enough to precipitate and preserve salt, this typically means an arid to semi-arid climatic setting with a drawdown hydrology capable of maintaining substantial volumes of saltsaturated brine at or near the landsurface, (2) accommodation space in a sedimentary depression that is not completely filled by other sediment, and (3) a burial environment that does not allow sufficient undersaturated porewater throughflow to completely dissolve the buried salts.

### Depositional Setting and Texture

Primary evaporites precipitate with distinct textures in a number of hydrologically-contrasted settings, contingent on brine stability and rates of temperature and salinity change in the mother liquor. Primary evaporite textures are direct indicators of the hydrology at the time of precipitation and



**Fig. 1.8** Significance of primary evaporite depositional textures as indicators of brine hydrology

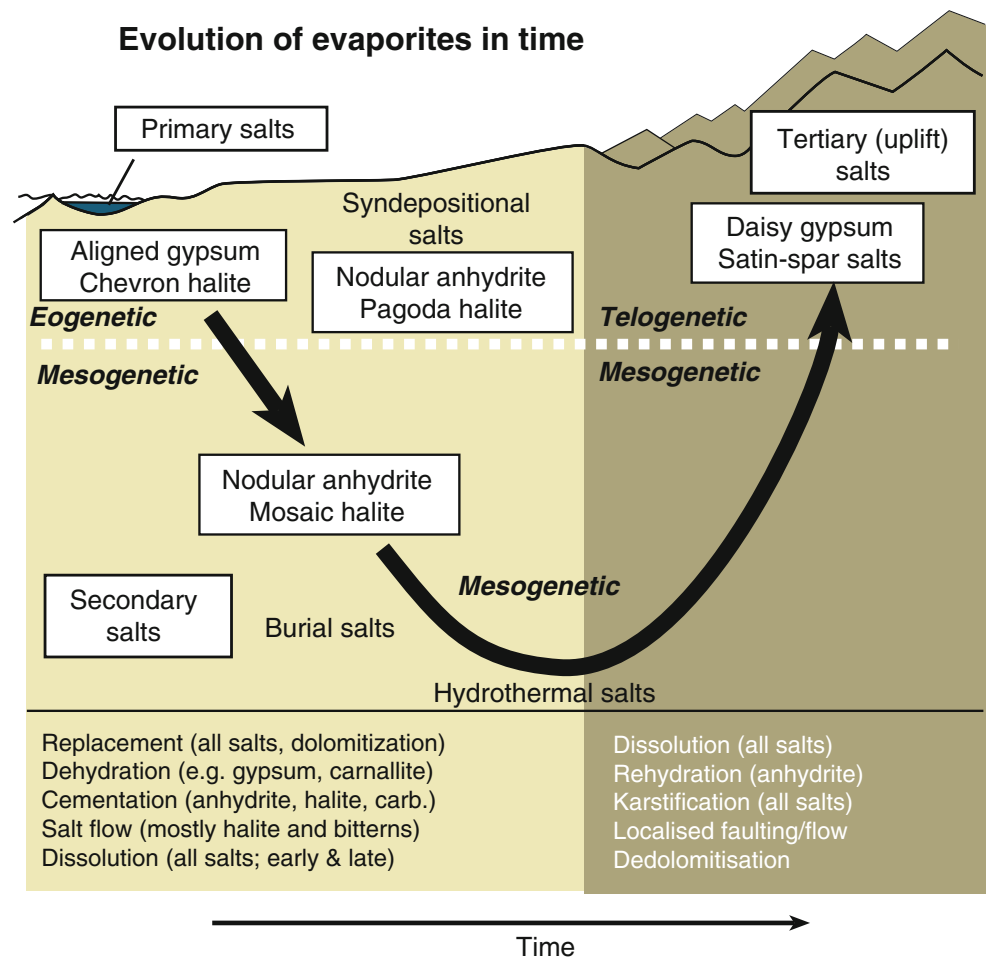
accumulation (Fig. 1.8). Sometimes crystals remain where they precipitate, other times they are mechanically or geochemically reworked, or undergo partial degrees of dissolution and fractional recrystallization.

Crystals may first precipitate at the air-brine interface in rafted crystal clusters that then sink to form cumulate beds, or can be blown to the strandzone (e.g., halite rafts crystallizing at the air-brine interface in Lake Guilietti in Ethiopia). Then again, immediately after they crystallize, precipitates can sink from the uppermost water mass to ultimately collect as pelagic accumulations (cumulates) on the shallow or deep brine floor "rain from heaven" deposits. Seasonal or longer term changes in the chemistry and salinity in the upper water column means many such pelagic deposits are mm-scale laminates made up of mineral doublet or triplet layers. In a holomictic shallow water mass, coarse cm-dm scale crystals can form as bottom-nucleated inclusion-entraining precipitates, typically at the base of a water column that is tens of centimetres to metres deep. Such crystals, be they gypsum swallow-tails or halite chevrons, tend to be composed of alternating inclusion-rich and inclusion-poor laminae and micro-laminae, reflecting rapid changes in chemistry or temperature of the overlying shallow holomictic water mass (Fig. 1.8).

If a brine column remains both supersaturated and holomictic to greater depths, then evaporites can accumulate at the deepwater base of a brine column that is hundreds of metres deep. This is the case today in the North Basin of the Dead Sea in the Middle East, where a salt bed, made up of a meshwork of inclusion-free, randomly-aligned cm-scale halite crystals, is accumulating and has been doing so since the North Basin brine column became holomictic in February, 1978. Prior to 1978 and for at least the preceding 400 years the brine column of North Basin (>370 m water depth) was a meromictic density-stratified hypersaline system, with pelagic mm-scale laminites accumulating on the same deep bottom, composed of alternating calcite and aragonite lamina, along with minor cm-scale gypsum crystal clusters or rosettes. The lack of inclusions in the halite mesh on the present-day deep bottom reflects the greater stability of chemical conditions on the bottom. The corollary is that growth-aligned evaporite crystals, rich in entrained inclusions of brine (e.g. chevron halite in Death Valley, California, or carbonate pellets encased in swallow-tail gypsum in Marion Lake, Australia) indicate precipitation in much shallower water depths (decimetre to metre depths). That is, inclusion-rich aligned bottom-growth

**Fig. 1.9** Classification of evaporite formation in the depositional-diagenetic realms emphasizing ongoing postdepositional evolution of mineralogy and texture

		Type	Precipitation process	Temp (°C)	Hydrological process
"An evaporite is a rock that was originally precipitated from a saturated surface or near-surface brine by processes driven by solar evaporation"	Remnant primary textures	"Primary" evaporite	An evaporite salt precipitated via solar evaporation from a brine pool at the earth's surface. Crusts, bottom nucleates & pelagic crystals accumulate on brine pool floor.	0-60 °C	Gravity and density effects at surface or in zone of active phreatic flow (brine reflux)
		"Secondary" evaporites (include sabkha nodules and the bulk of ancient evaporite beds)	An evaporite salt formed in the shallow subsurface in the zone of active phreatic flow. The concentration process of the brine and the associated gravitational reflux is driven by solar evaporation. May form displacive, replacive or cement textures.		
	Secondary texture dominant	Burial salts	Subsurface precipitation of evaporite as cements and replacements in non-evaporite matrix from a saturated brine derived from the dissolution of adjacent evaporite beds or zones of brine mixing.	60-200 °C	Burial effects compactional and thermobaric flow
		"Tertiary" evaporites	An evaporite formed by brine saturation related to partial bed dissolution via re-entry into the zone of active phreatic circulation. Often driven by basin uplift and reosion.		
??	No primary texture	Hydrothermal salts	Salts (anhydrite - retrograde; halite -supercritical) precipitated by heating of seawater or subsurface brines.	>150 °C	Hydrothermal circulation



textures form in well-mixed brines that are shallow enough to experience short term changes in saturation and growth rate, coupled to short term changes in water temperature or salinity.

If currents and waves rework the bottom crystals, then ripple structures and dune forms can be the dominant texture in the accumulating evaporite bed. The presence of evaporite equivalents of carbonate ooids, namely gypsolites and halolites, indicate oscillating bottom currents at the time the crystals grew. Brine floor instability, related to seismic events, halokinesis or tectonism, can also lead to the formation of slumps, brine escape and debris flow textures (seismites) in a salt bed deposited at any water depth (El Taki and Pratt 2010). The lowering of suprasalt brine column salinity or the lowering of the regional watertable can create karst cones and breccias in an evaporite bed. For more detail on the significance of the various evaporite textures the reader is referred to (Lowenstein and Hardie 1985; Orti et al. 2010).

Evaporite salts can crystallize as early diagenetic precipitates in the shallow subsurface some mm to cm below the sediment surface, as occurs today in the capillary zones of many marine coastal and continental mudflats and sabkhas (where displacive and poikilotopic crystals, nodules and efflorescent crusts are typical). Some initial crystals precipitates can be dissolved and recycled through the nearsurface sediment column, especially in arid and semi-arid settings, to create pedogenic profiles; as in the gypsum soils atop gypsum lunettes in southern Australia or in the nitrate-rich salt solid of the hyperarid Atacama Desert.

So, as for depositional textural associations in carbonate and siliciclastic sediments, a depositional model based on evaporite textures can encompass a spectrum of formative sites ranging from the pedogenic, to saline mudflats, to shallow and deep subaqueous brine settings. However, because evaporite salts are orders of magnitude more soluble than carbonate or siliciclastic sediments, they require particular postdepositional tectonics and hydrologies in order for large volumes of salts to be buried and textures preserved or no more than partially modified. This high degree of solubility and mobility at the time of precipitation and in their subsequent subsurface evolution is key to understanding deposition and diagenesis in both modern and ancient evaporite settings.

### Secondary and Tertiary Evaporites

As soon as an evaporite bed is formed it is subject to alteration, which continues at varying levels of intensity throughout the sedimentary history of the rock (Fig. 1.9). In a Pre-Quaternary, or certainly pre-Neogene evaporite, many textures are secondary; the rock has been diagenetically altered, frequently showing fabrics indicating early recrystallisation and perhaps some later crossflow of basinal waters.

Under this definition of a primary versus secondary salt, even the nodules in Holocene mudflats are secondary salts, including those in the various modern mudflats of the Arabian (Persian) Gulf, which is the type area for a sabkha. The nodules are a porewater overprint superimposed on a primary matrix of mud and sand. Ancient bedded anhydrites are typically dominated by secondary textures, although beds may still retain “ghosts” or partial relicts of primary textures such as indistinct laminae or aligned nodules after growth-aligned gypsum. In a halite bed there may be remnant patches of aligned halite chevrons floating in a matrix of mosaic halite spar. Even when evaporite beds are extensively recrystallised, most retain coarse stratiform layering made up of impurities that once defined primary depositional discontinuities.

What distinguishes evaporites, especially NaCl beds, from other types of sediment in the subsurface is their ability to flow via pressure-driven recrystallisation, even as they backreact or dissolve. Even earlier secondary textures can be syndepositional precipitates, formed as cements and replacements, while primary matrix accumulated around them. Early replacement sometimes preserves remnants of the original depositional texture, such as gypsum ghosts in nodular anhydrite or aligned halite chevrons outlined by secondary anhydrite. Nodular anhydrite ghosting of lenticular gypsum was recognised in Permian mudflats in the early 1960s by Kerr and Thomson (1963), they interpreted it as a subaqueous saline pan indicator. Unfortunately, for the next two decades their results were overlooked by workers in the Permian Basin who incorrectly applied supratidal capillary analogs to thick massive subaqueous anhydrite beds.

Early diagenetic overprints and effects of later compaction-driven flow and pressure solution can destroy much of the depositional evidence in an ancient evaporite bed. This means retention of primary crystal textures is at best patchy in both halite and anhydrite beds. Many ancient bedded halites are dominated by coarsely crystalline halite spar. Much of it was deposited in multiple episodes of early diagenetic (syndepositional) cementation, leaving less than 10–15 % of the bed as primary growth-aligned chevrons within a few metres to tens of meters below of the depositional surface. This syndepositional coarse sparry halite formed in multiple dissolution-precipitation events in microkarst pits and was precipitated between successive depositional episodes of chevron halite crust formation (Chap. 3). Other coarsely crystalline halite spar, especially in halokinetic beds, shows pervasive and multiple flow-aligned textures created by pressure-solution. Textures are driven by numerous salt creep and recrystallisation episodes, which occur millennia to millions of years postdeposition, and after hundred to thousands of metres of burial (Chap. 6).

Secondary evaporite textures form in subsurface settings equivalent to the eogenetic<sup>1</sup> and mesogenetic porosity realms, as defined for carbonates by Choquette and Pray (1970). Tertiary evaporite textures tend to form in the telogenetic realm (Fig. 1.9). And, as in carbonate diagenesis, the most pervasive alteration of evaporites is either early in the burial history (eodiagenesis) or it occurs much later during uplift (telo-diagenesis). Both the eogenetic and telogenetic settings are characterised by relatively permeable evaporites and hydrologies capable of high volumes of pore fluid cross-flow. Alteration of a salt mass in the mesogenetic realm consists largely of recrystallisation overprints within a flowing salt mass, but with substantial alteration and dissolution possible about the edge of a bed or a flowing salt mass. In carbonates, the mesogenetic overprint tends to be pervasive throughout the bed (Choquette and Pray 1970). In evaporites units, the pervasive early loss of porosity and permeability in the shallow diagenetic/eogenetic realm means that deep burial (mesogenetic) alteration, prior to halokinesis, tends to be first concentrated about the edges of a buried salt body (see discussion of dissolving salt “block of ice” model in Chaps. 7 and 8). Unlike carbonates and siliciclastics, the core of a subsurface bedded halite unit (nonhalokinetic) can be largely unaffected by fluid flow-driven processes of burial alteration due to its early loss of effective porosity via cementation. Preservation of the unaltered core of the salt unit is why viable Permian halobacteria can be cultured from brine inclusions in remnant chevrons in Permian salt beds from West Texas (Vreeland et al. 2000).

Unlike quartzose and aluminosilicate sediments, buried evaporite beds can flow as ductile masses from the surface down to 8–10 km of burial and even into the metamorphic realm. At the same time their dissolving edges supply ions to adjacent nonevaporitic sediments. Salt flow can be: (a) early diagenetic, coinciding with syndepositional fractionation, reflux or dissolution; (b) later diagenetic, associated with complex burial-stage bed dissolution or reprecipitation and driven by subsurface fluid flow in the zone of free convection below the zone of overpressure; (c) widespread and pervasive, as occurs during halokinesis (salt tectonics); and (d)

<sup>1</sup>In their original definitions Choquette and Pray (1970) focused their studies on carbonate sediments. Throughout this book I have expanded and slightly modified their original definitions (*as noted in italics*). So the modified definitions of eogenetic, mesogenetic and telogenetic are as follows: Eogenetic zone extends from surface of newly deposited sediment (*not just carbonates*) to depths where processes genetically related to surface become ineffective. Telogenetic zone extends from erosion surface to depths at which major surface-related erosional processes become ineffective. Below a subaerial erosion surface, the practical lower limit of telogenesis is at or near watertable (*and the related surface driven zone of phreatic meteoric water movement and includes both unconfined and confined aquifers*). Mesogenetic zone lies below major influences of processes operating at surface. The three terms also apply to time, processes, or features developed in respective zones.

postdiagenetic and extending well into the metamorphic realm where daughter minerals, such as scapolite and tourmaline, can act as a source of volatiles and lubricants long after the precursor salts have gone.

Exhumed or uplifted evaporite beds also undergo pervasive alteration, dissolution and replacement as they re-enter the zone of active phreatic flow (telogenesis) and regain permeability along internodular and intercrystalline boundaries. Once again, alteration tends to occur from the edges inward. Soluble components from the altering and dissolving bed can be reprecipitated in adjacent shales as alabastrine and satinspar gypsum or fibrous halite veins. Exhumed evaporite textures are termed tertiary (Fig. 1.9) and are varying combinations of competitive crystal alignment and geopetal void fills. The resulting fabrics can duplicate “primary” crystal alignments, especially when parts of a cavern fill can only be studied at a limited scale, as in core or a mine face. Not recognising a telogenetic overprint typically misidentifies tertiary evaporite textures as primary and so creates interpretive confusion (Chap. 7). This is why interpretations of depositional setting are not reliable if based on observations in an evaporite outcrop where that unit is the remnant of a once more massive and thick primary unit that has passed through the mill of burial and uplift. Adjacent nonevaporitic sandstones, shales and limestones also undergo diagenetic reactions when flushed by evolving pore fluids, but the diagenetic rock/fluid framework is slower to respond and requires years to millennia to overprint an original depositional texture. But, given enough time, the textures of many other sediments evolve during burial, just at much slower rates (Table 1.2).

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## Primary Evaporitic Carbonates

The simplest subdivision of evaporite minerals is into evaporitic alkaline earth carbonates – aragonite, dolomite, low-Mg calcite and high-Mg calcite – and evaporite salts – gypsum, anhydrite, halite, trona, carnallite, etc. (Table 1.1). Primary evaporitic carbonates tend to form in the initial stages of brine concentration, whereas the other primary evaporite salts are precipitated in the more saline stages of concentration (Chap. 2). Evaporitic carbonates can contain and preserve elevated levels of organic matter that subsequently generate hydrocarbons or act as reductants for base metal sulphides (Chap. 9).

Evaporitic alkaline earth carbonates are the first evaporite minerals to precipitate from a concentrating hypersaline surface water and are usually composed of aragonite, high- and low-Mg-calcite, magnesite or even primary dolomite. The essential hydrology of any evaporite depositional setting is that evaporative outflow exceeds inflow. This results in two characteristics of the carbonate depositional system, which hold also for the more saline evaporite salts. First, rapid

**Table 1.2** Characteristics of siliciclastic and carbonate depositional systems

	Siliciclastic: (continental, fluviodeltaic, shelf, submarine)	Carbonate: humid-oceanic/marine tropical/subtropical	Carbonate-evaporite: arid, land-locked subtropical/temperate
Early marine cementation	Rare	Local occurrence	Pervasive (especially in mesohaline platform)
Dolomitisation	Rare	Locally in mixing zones (?)	Pervasive (brine reflux and burial)
Leaching	Uncommon, mostly related to freshwater leaching, rare in burial diagenesis	Common, related to subaerial exposure and karstification	Intensive, related to hypersaline brines
Calcite cementation	Uncommon, locally common (mostly related to burial)	Common	Rare to local occurrence (mostly burial)
Anhydrite-halite	Uncommon	Rare to absent	Common to pervasive
Porosity types	Intergranular	(1) Mouldic, vuggy and chalky microporosity (common) (2) Fracture and intercrystalline porosity (local occurrence)	(1) Intergranular, mouldic, vuggy, and intercrystalline (dolomitic) porosity (very common) (2) Fracture and chalky microporosity (locally common)
Controls on reservoir quality	(1) Stratigraphic position (2) Depositional facies	(1) Stratigraphic position (2) Depositional facies (3) Karst in zones on meteoric influx	(1) Depositional facies (2) Accessibility of sulphate- and chloride-bearing and later corrosive fluids (karstic or deep)
Geometry	Layered	Layered	(1) Carbonate-basinwide evaporite: Massive, irregular, halokinetic (2) Carbonate-saltern-mudflat evaporite: layered
Reservoir distribution	High energy shoreline or channel fills with position related to lowstand, transgressive and highstand system tract	Highstand reef or bank carbonate immediately beneath subaerial unconformity	(1) Carbonate-basinwide evaporite: near faults and fractures where late corrosion is most intensive (2) Carbonate saltern-mudflat evaporite (a) Within grain-supported facies where primary porosity is preserved or mouldic porosity was created through leaching (b) Within coarsely crystalline dolomite (c) Within highly fractured limestone

In part after Sun and Esteban (1994)

changes in water level are possible, especially in the more marginward facies, leading to interlayering of strandzone and subaqueous units. Under such a regime any subaqueously precipitated sediment is liable to subaerial exposure and syndepositional subaerial diagenesis. Second, the solute content, especially the Mg/Ca ratio, of shallow hypersaline water fluctuates as the salinity fluctuates. For example, the Ca content of any freshened water is depleted by the early precipitation of calcite or low-Mg calcite. Subsequent carbonate precipitates drop out of increasingly saline waters that will have a higher Mg/Ca ratio and so saline carbonate precipitates tend to be dominated by high-Mg calcite, aragonite, magnesite, or even dolomite.

### Carbonate Laminites (Subaqueous?)

Mm-scale lamination is volumetrically the dominant sedimentary texture in modern and ancient evaporitic carbonates as well as in higher salinity salts, but its origins are varied and complex (Fig. 1.10). Sometimes it is an inorganic cumulate, other times it is biologically structured (biolaminite –

see next section). Beds dominated by finely laminated, regular alterations of two or more sediment types are called laminites or rhythmites. Many evaporitic carbonate laminites form couplets or even triplets by the regular superposition of micrite with siliciclastic clay, organic matter or evaporite salts. Such couplets and triplets are frequently referred to as varves, yet are not necessarily “true” varves in that the layers may not define annual couplets.

As an example of a contemporary carbonate laminite, consider deep bottom pelagic sediments deposited prior to 1979 in the Northern Basin in the Dead Sea, Israel (Fig. 4.51). They are made up of alternating light and dark mm laminae that accumulated beneath a density-stratified brine column more than 350 m deep. The whitish laminae are composed of stellate clusters of aragonite needles (5–10 µm diameter), which precipitated each summer at the air-brine interface and then sank. The darker laminae consist of clay minerals, quartz grains, detrital calcite and dolomite that washed in as suspended sediment from the surrounding highlands during occasional storm floods (Garber et al. 1987). Thus laminites in the Dead Sea are not annual layers, but indicate flood events that occur every 3–10 years.