

Chert containing oxidised iron has a reddish colouration and is called jasper. Jasper may form on the seafloor near the spreading ridges. When water circulates through the spreading ridges it carries away iron which then oxidises in the seawater and produces the red colour. When mixed with silica which is precipitated mostly by organisms, chert is formed. Jasper is found on top of obducted ocean floor basalts in nappes of Ordovician age in western Norway.

Chert has also been found during ocean drilling, overlying present ocean floor of Cretaceous or Tertiary age. Although all amorphous silica has been converted to quartz, it is often possible in chert to detect the remains of organic particles, e.g. radiolaria, especially in Palaeozoic chert deposits. Younger silica deposits are chiefly precipitated by diatoms. In areas with upwelling, silica may also be deposited in relatively shallow water. The Monterey Formation in California is a well-known example of chert formed in an upwelling zone. Around the Pacific Ocean similar chert of Upper Miocene age is found. The Monterey Formation is both an important source and reservoir rock for oil in California, especially in the Ventura Basin. It is a source rock on account of the organic matter produced by the diatoms. After the transformation to opal C and quartz, the rock fractured due to tectonic folding, so that it became a fractured reservoir (Fig. 6.5).

Subjected to 1–2 km of overburden, amorphous silica is converted to quartz and the rock becomes brittle and fractures during folding and faulting to form good fractured reservoirs.

The Monterey Formation contains organic-rich shales and phosphate deposits. This is a very common



Oil seep in chert. Santa Maria, north of Santa Barbara

Fig. 6.5 Monterey chert with oil seeps, California

association when sediments have been deposited in upwelling areas with a limited clastic supply. Transformation of amorphous silica to quartz appears to depend on the chemical environment (temperature, pH, ionic strength, Mg concentration). Clay minerals reduce the conversion rate.

In soils, however, quartz may precipitate at low temperature near the surface, forming *silcrete* resulting in very hard ground.

Precambrian chert deposits typically occur in conjunction with banded iron formations (BIFs). It is uncertain whether there were organisms which could precipitate silica in Precambrian times, or whether Precambrian chert was chemically deposited. There are no definite indications of biological precipitation of Precambrian chert, and since silica must also have been added to the oceans, we must assume that the ocean was saturated with respect to silica, and that there may have been inorganic precipitation of silica.

Silica deposits may also be formed in lakes by freshwater diatoms. In lakes along the rift systems of East Africa, there are thick deposits of diatomite which are exploited for use in insulating materials. A great deal of CO₂ is taken from the lake water by diatoms and other algae for photosynthesis, and the water therefore becomes strongly basic (pH 9–10). This increases the solubility of silica, thus increasing the corrosion of silicate minerals. Examples of this are found, for instance, at Lake Turkana in Kenya. Volcanic rocks and water from hot springs are also important sources of silica.

Chemical precipitation of silica may also take place in evaporite basins, and in ephemeral lakes which dry up between rainy seasons.

6.4 Evaporites

Evaporites consist of minerals which have crystallised out through evaporation of water. This can happen in many ways:

1. Evaporation of seawater in completely or partly cut-off marine basins.
2. In lakes which have little or no outlet and a high evaporation rate.
3. Through evaporation of seasonal precipitation which collects in topographical depressions without outlets (playas).

4. In soil profiles or sandy sediments, through evaporation of groundwater.
5. In arctic areas, the sublimation of ice and the freezing of seawater to ice both increase the salt concentration of sea water, and evaporite minerals such as gypsum may be precipitated.
6. Through solution and precipitation of salts from older evaporite deposits.

The formation of evaporites is therefore not an unambiguous indication of a high temperature, but most evaporite deposits (salt) form in the climatically dry belts about 20–30° from the equator. Evaporites contain a number of salt minerals which are too soluble to be precipitated in normal marine or continental environments. The most important are:

Chlorides
Sulphates
Alkaline carbonates
Ca-Mg carbonates
Borates
Nitrates
Silica deposits
Iron deposits

6.4.1 Marine Evaporite Environments

Although the salt content of seawater varies somewhat in the different parts of the world's oceans, the composition of seawater is relatively constant. The table

below shows the percentage composition of dissolved salts in seawater which add up to a salinity of 35‰. To the right are the percentages of the various salts obtained through evaporation.

| Percentage by weight of salts in seawater | | | |
|---|------------------------|--------------------------------|--|
| Ion | Percentage in seawater | Salt | Percentage by weight of common salts after evaporation |
| Na | 30.64 | NaCl | 77.76 |
| Mg | 3.76 | MgCl ₂ | 10.86 |
| Ca | 1.20 | MgSO ₄ | 4.74 |
| K | 1.09 | CaSO ₄ | 3.60 |
| Cl | 55.21 | K ₂ SO ₄ | 2.47 |
| SO | 7.70 | MgBr ₂ | 0.22 |
| CO | 0.21 | CaCO ₃ | 0.35 |
| Br | 0.19 | | |
| | 100.00 | | 100.00 |

By evaporating seawater one can therefore determine the relative amounts of different salts. An evaporite basin will often have some supply of seawater, such that the evaporation is not total. As a result, evaporite deposits may accumulate carbonates and sulphates, while the chlorides remain in solution.

When seawater evaporates, carbonates are among the first salts to precipitate, but the amount of carbonate in solution is very small. When the volume of seawater is reduced to 1/3–1/5, both CaCO₃ (aragonite) and CaSO₄ · 2H₂O (gypsum) have precipitated. Only when the volume is down to 1/10 will NaCl (halite), quantitatively the main constituent, be precipitated (Fig. 6.6). MgSO₄ and MgCl₂ will be precipitated at the same time. Polyhalite (Ca₂K₂Mg(SO₄)₅ · 2H₂O) commonly

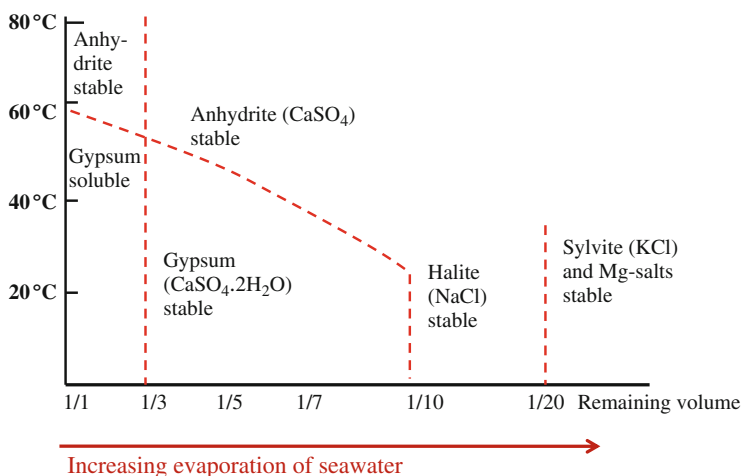


Fig. 6.6 Stability of salt minerals as a function of progressive evaporation of seawater and temperature

Fig. 6.7 Layers of gypsum in sabkha



precipitates when the seawater has been reduced to 1/20. KCl (sylvite) and bromides are among the most soluble salts, and are hence the last to precipitate. If the salt concentration increases with evaporation, this is the sequence of salt deposition. During periods with greater circulation and supply of normal seawater the salt concentration will fall, and there will be cyclic salt deposition and solution. Chlorides (NaCl, KCl) will dissolve in moisture from the air unless the humidity is very low.

Periods of increased evaporation and hence high salt concentration may alternate with influxes of seawater with a more normal salt concentration, producing cycles representing changes in salinity. These are called evaporite cycles. In many evaporite basins the salt concentration has been sufficiently high for gypsum to be precipitated, but not high enough for chlorides (see Fig. 6.7).

The stability of the various salts during evaporation can be determined experimentally, or estimated through physical chemistry calculations. However, it is clear that certain metastable mineral phases can also be formed. Calcium sulphate may precipitate both as a hydrated mineral, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum), and as a non-hydrated mineral CaSO_4 (anhydrite) (see Fig. 6.8). Which of these two phases forms as a result of oversaturation of calcium sulphate depends on the temperature, salinity and water vapour pressure. In a solution of CaSO_4 alone, anhydrite forms only at temperatures of over 60°C , but as the concentration of other salts increases, anhydrite may form at temperatures down to $25\text{--}30^\circ\text{C}$ (Fig. 6.6).



Fig. 6.8 Gypsum crystals growing on the sabkha surface

Gypsum is the mineral which normally forms in marine evaporites, but anhydrite is also observed in modern evaporites in supratidal zones. This is true, for example, of the sabkha deposits in the Persian Gulf. These are black algal muds in the supratidal zone, where temperatures may be up to 80°C , and anhydrite is deposited in the sediment. In patches of open water where the temperature is lower, gypsum forms instead.

Evaporite sediments have formed throughout geological history, but appear to have formed more abundantly during certain periods, particularly the Permian. In Northern Europe and the North Sea we find thick evaporites from this period in what is called the Zechstein Sea, which serve as a cap rock for the gas in the underlying Permian aeolian sandstones.

The lighter salt layers will flow upward and gradually form large mushroom-shaped or columnar structures. The prerequisite for initiating this salt dome formation, however, is that the salt beds must be at least 100–200 m thick. Salt domes are common in Northern Germany, Denmark and the southern part of the North Sea, where they may form oil or gas traps. During the Permian, NW Europe was in the dry belt 20–30°N, similar to the Sahara today.

Surveys of the bottom of the Mediterranean Sea have revealed the existence of considerable evaporite deposits in Upper Miocene sequences. Adjacent land areas also have numerous localities where salt beds of this age (Messinian salt) have been preserved. This can indicate that the Straits of Gibraltar were closed for large parts of the Tertiary and that the Mediterranean Sea was a vast desert inland sea 2,000–3,000 m below sea level at that time.

6.5 The Sabkha Model

“Sabkha” is the Arabic term for the large flat areas around the Persian Gulf. This area extends from the tidal zone, forming an 8–10 km wide belt with a very low seaward gradient of only c.0.4 m/km. The sabkha flats were created by carbonate sediments infilling lagoons, chiefly during the Holocene. For the last 4,000 years there has been a gradual regression in the area. The climate is very dry (30–100 mm annual precipitation), but this is nevertheless sufficient to cause groundwater from surrounding areas to flow out to the sea. The groundwater flow is extremely slow, only a few centimetres a year, but is nevertheless responsible for the diagenetic environment containing porewater of continental origin. During storms and high tides, marine water floods the sabkha. Some runs off, some evaporates and some filters down into the sediment and mixes with the groundwater. Relatively large amounts of gypsum are then formed. The remainder of the water is highly enriched in magnesium, and dolomite is formed. Evaporation will increase the salt concentration of the porewater, and if it is intense enough, chlorides (halite) are precipitated in addition to gypsum. However, halites will dissolve easily the next time salt water flows in over the sabkha. Moisture in the air

will also help to dissolve halite on the surface, so that it is not preserved in the bedding series.

The sediments which are deposited alternate between gypsum-carbonate and some clastics. A conspicuous lamination develops because of algal growth (cyanobacteria), which does not get destroyed because there is no bioturbation in this salt environment.

Although it is hot, up to 50–80°C on the sabkha, evaporation is limited where there is no open water because of the low permeability within the sediments. When the water table sinks, the evaporation rate rapidly declines. Thick layers of sediments with gypsum make up much of the Sabkha sediments (Fig. 6.8). Whereas the rate of evaporation from open water in the Persian Gulf is about 124 cm/year, it is only about 6 cm/year in the sabkha. We therefore have only moderate “evaporite pumping” where chlorides are precipitated above the water table and sulphates below the water table. The chlorides deposited will, however, redissolve as the overburden increases and the relative position of the water table rises. In some semi-arid regions, e.g. the Coorong region of Australia, dolomite lakes form which evaporate to dryness in the summer (ephemeral lakes). Evaporite minerals deposited in summer will redissolve during the winter rains, and will not be preserved in the bedding series.

6.6 Marine Evaporites

Evaporation from the surface of the sea will cause the salinity of the water in a basin to increase. If there is little wave or current action, the warm surface water will not mix quickly with the underlying, colder water. If the salt concentration increases, the density will increase and the surface water will sink to greater depths and mix with the water there, despite being warmer. To create a high salinity basin we must have physical barriers reducing or totally blocking the connection to the open ocean, and the evaporation must be greater than the total amount of freshwater added to the basin by precipitation, rivers and groundwater. If the evaporation is lower than the supply of freshwater it will develop into a freshwater basin.

An evaporite basin with a limited connection to the open sea may not dry out; it can then accumulate large amounts of gypsum, but not more soluble salt like