

Nearly monomineralic rocks of the two common calcium sulphates are exploited but in most applications, gypsum is preferred. Impurities in gypsum rock may be anhydrite, clay and carbonate, with accessory kerogen, bitumen, authigenic quartz and soluble salt. The same gangue occurs in anhydrite rock with soluble salts more common. Anhydrite rock is usually strong, massive and finely crystalline. Alabaster is a very fine-grained, massive and pure (>99%) gypsum rock that is used for ornamental purposes, preferably when it is snow-white and translucent. Alabaster originates by near-surface supergene solution and reprecipitation of gypsum. In arid and semiarid climate zones, ascending soil solutions may form gypcrete, similar to calcrete. Gypsite is an earthy variety of gypsum mixed with sand and soil. Selenite designates crystals of translucent and colourless gypsum.

Gypsum and anhydrite cannot be enriched by mine-site processing; therefore, run-of-mine material must meet buyers' stipulations. These include specification of purity (usually a minimum of 70–80% gypsum or anhydrite), carbonate contents (commonly <5%), MgO <2% and soluble salt contents ($\text{NaCl} + \text{MgCl}_2 + \text{MgSO}_4$) <0.02%. For many applications, white colour (low Fe-Mn concentration) is desired.

Gypsum is composed of 32.6% CaO, 46.5% SO_3 and 20.9% H_2O . When heated to $\sim 65^\circ\text{C}$, $1\frac{1}{2}$ moles of water are lost and the remaining solid is very reactive "plaster of Paris". The relic $\frac{1}{2}$ mole of water is retained strongly until 95°C , when dehydration is quickly completed and the structure of the solid transforms into a polymorph of anhydrite (Klein & Hurlbut 1999). This "dead-burned" gypsum sets (hardens) very slowly. Most gypsum is consumed in the building industry, in the form of the fast-setting semihydrate $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, for example for wallboards and mortar. An average house in the United States is said to contain 7 tonnes of gypsum. Uncalcined gypsum is used as a retarder in Portland cement and as a calcium soil conditioner and sulphur fertilizer in agriculture. Small amounts of high-purity gypsum are used for industrial processes, such as smelting and glass-making.

Anhydrite may be added to the cement powder instead of raw gypsum, in order to retard setting of concrete. In deep coal mines, anhydrite is used for fire prevention as a backfill and plugging material in galleries. Note that anhydrite hydrates strongly and fast under ambient conditions (eq. 3.4), resulting in a volume increase of $\sim 60\%$. This "heave" is quite a nuisance in mining, tunnelling and road building (Bell 1993).

Dehydration of gypsum and hydration of anhydrite:



3.13.1 Deposits of gypsum and anhydrite

Deposits of gypsum and anhydrite are formed as chemical sediments of evaporating marine or terrestrial water bodies. Therefore, common country rocks of the calcium sulphates include dolomite, saline claystone and salt rocks such as halite (cf. Chapter 4 "Salt Deposits – Evaporites"). With increasing concentration of seawater, calcium sulphates are precipitated after carbonate rocks and before rock salt. Gypsum is slightly soluble in fresh water (13.78×10^{-3} mole/L at 25°C and atmospheric pressure). Its solubility displays a positive correlation with temperature and salinity, but the maximum solubility at $\sim 58^\circ\text{C}$ does not change significantly with fluid salinity. Contrasting the behaviour of gypsum, the solubility of anhydrite is retrograde; it increases with falling temperature. The primary precipitate of calcium sulphate is gypsum; only at temperatures higher than $56\text{--}58^\circ\text{C}$, anhydrite is the thermodynamically stable phase. In sabkhas, conditions of gypsum and anhydrite stability switch easily so that multiple transformations are observed (eq. 3.4). With increasing overburden, however, already in early diagenesis anhydrite is the stable phase, at $50\text{--}70^\circ\text{C}$ (Jowett *et al.* 1993). Dehydration of gypsum mobilizes a considerable mass of water and most of the strontium is abstracted with the dehydration water. Somewhere along the flow paths, celestite (SrSO_4 , the principle ore of strontium) may precipitate and fill joints and rock cavities, replace beds or form irregular masses that

can be economically attractive (cf. “Barite”). Overall, textures, structures and geochemistry of gypsum and anhydrite include the heritage from sedimentary formation and diagenetic alterations, and therefore reflect conditions from basin palaeogeography to the history of burial and uplift (Kasprzyk & Orti 1998).

Isotope data (D, O and S) provide a deeper understanding of gypsum and anhydrite formation. We have seen earlier that sulphur isotopes in seawater ($\delta^{34}\text{S}$ of sulphate) display strong variations with geological time (Figure 3.4). Also, stable isotopes allow deductions about conditions of sedimentation and diagenesis of calcium sulphate rocks. Gypsum and alabaster of the Paris Basin, for example, were not extracted from Tertiary seawater but leached from older Permian and Triassic evaporites. Messinian gypsum deposits in the Mediterranean region, by contrast, are direct precipitates from Neogene seawater. Sulphate ions in the Canadian McKenzie River system are derived from pyrite oxidation in the eroding mountains and not from sedimentary sulphate (Calmels *et al.* 2007). D and O isotope data usually allow a unique genetic attribution of associated water. Note that hydration water in gypsum is enriched in ^{18}O by $\sim 4\%$ compared to the water from which it is derived. The precise age of geologically young gypsum (and many other evaporite rocks) can be determined with the U-series disequilibrium method (Reich *et al.* 2009).

Many gypsum deposits originated by hydration of anhydrite rock, which was uplifted to the near surface by geological processes. Access of meteoric water initiates supergene gypsification that may reach a depth of several tens of metres. The anhydrite underneath often displays large karst cave systems. In the overlying gypsum, sinkholes and caves are ubiquitous and the surface resembles karst morphology of carbonate rocks (“gypsum karst”, Figure 3.19). The processes of gypsification and karst formation are a function of the groundwater system, morphology and the nature and spatial arrangement of rock bodies. Sinkholes and caves may be filled with collapse breccias comprising gypsum and dolomite, and often with earthy impurities. Breccias can be cemented by calcite. In that case, leaching of gyp-

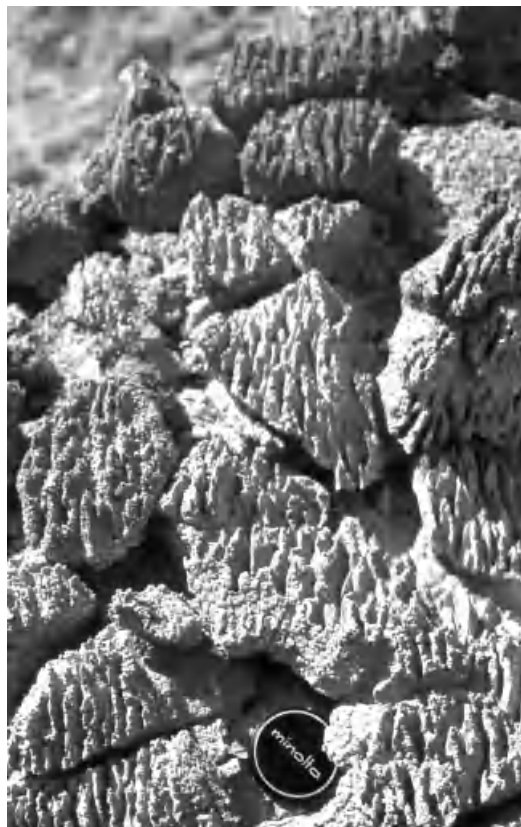


Figure 3.19 Gypsum outcrop at Wadi Essel, Red Sea Coast, Egypt, provides a model of full-scale gypsum karst morphology. Flutes and joint-controlled furrows also characterize the karst surface at the scale of tens to hundreds of metres.

sum fragments is the path to formation of cellular rocks termed “rauhwacke” (Schaad 1995).

Australia hosts a variety of young gypsum deposits. Its arid coasts are lined by numerous salinas (coastal salt lagoons), which originated due to the worldwide post-glacial rise of seawater levels. With rising oceans, valleys of Pleistocene dune belts were filled with seawater that evaporated (Figure 3.20). Sediments formed in these salinas consist mainly of gypsum, including solid masses of selenite near the base and banded gypsum sands. Near the margins, aragonite may occur. Holocene dry climate periods caused formation of gypsite dunes. All these varieties of gypsum are extracted

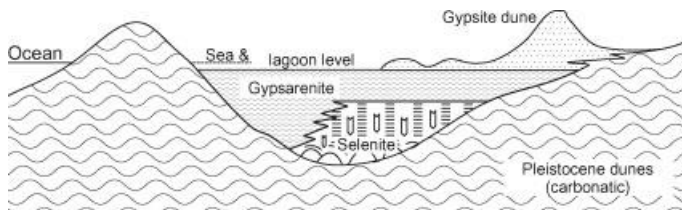


Figure 3.20 Schematic section of a Holocene coastal gypsum lagoon in South Australia (after Barnes 1990). Water level in the lagoon is lowered by evaporation.

and stockpiled for several years in order to reduce salt content by exposure to rain. Coastal Lake Macleod in Western Australia is essentially a dry lagoon of 100 by 30 km in size. Here, gypsum is extracted with a floating dredge, while salt brine is pumped from a deeper aquifer and harvested from evaporation ponds. In South Australia, gypsum was deposited in Pleistocene tidal Lake Alexandria that developed at a highstand mouth of the Murray River, today some 50 km from the coast. This gypsum is well drained and free of salt.

Gypsum is mainly exploited in quarries and exploration is limited to near-surface deposits. Geological maps provide first guides. In the field, karst morphology and sulphate in spring water (determined by reaction with BaCl_2 solution) may provide clues. Georadar and drilling are employed to define shape and nature of the karst surface underneath soil cover, of the base of gypsification and of waste material filling karst caves. Often, this can only be done with a very close spacing of drillholes. Gypsum karst landscapes are ecologically peculiar and mining intentions may therefore be resisted. It is advisable to obtain a valid mining licence as early as possible in the course of investigations.

Gypsum and anhydrite are low-cost raw materials and deposits are common. Most countries are self-sufficient. Nevertheless, considerable quantities are internationally traded. World mine production in 2009 was ~152 Mt. Largest producers were China, Iran, Spain, Thailand and USA (USGS 2010). Synthetic gypsum is a by-product of coal-fired electric power plants and other smoke-stack industries, of phosphate processing and of de-acidification of industrial waste water (e.g. TiO_2 -production). In the USA, synthetic gypsum accounts for ~22% of the total domestic gypsum supply. It is used like natural gypsum, except for special cases where elevated trace contents of heavy

metals, acids, chlorine, soot and its small grain size may be problematic. Still unsolved is the problem of phosphogypsum. The production of 1 tonne of phosphoric acid from phosphorite results in ~4.5 tonnes of calcium sulphate. Unfortunately, the processing of raw phosphate ore specifically concentrates radionuclide (^{226}Ra) radium in the sulphate phase. ^{226}Ra emits (^{222}Rn) radon by radioactive decay and this inhibits nearly all uses of phosphogypsum, except for those plants that process phosphate ore with very low contents of radionuclides.

3.14 KAOLIN

		Density (g/cm^3)
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	2.1 (aggregates) 2.6 (crystals)
Dickite	same as K.	2.6
Nacrite	same as K.	2.6
Halloysite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$	2.09
Allophane	$x\text{Al}_2\text{O}_3 \cdot y\text{SiO}_2 \cdot z\text{H}_2\text{O}$	~1.9

The four first listed kaolin minerals (“kandites”) are dioctahedral phyllosilicates made of 39.5% Al_2O_3 , 46.5% SiO_2 and 14% H_2O , corresponding to a formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. On heating, the structurally bound water escapes at different temperatures: 390–450°C for kaolinite and 510–575°C for dickite. Kaolinite forms generally by weathering and low-temperature weakly acidic hydrothermal alteration (50–150°C). Compared to kaolinite, dickite and nacrite are rare and originate at higher hydrothermal temperatures (~150–300°C). Macroscopically crystalline nacrite is a characteristic gangue of high-temperature gold and tin ore. Kaolinite may have a well-developed crystal structure