Quartz or opaline silica solubility

The simplest process that might regulate the concentration of an element in solution is equilibrium with respect to a solid phase containing the element as a major component.

For example, at low pH, the following reaction is sufficient to describe the solubility of silica in water:

$$SiO_2\ (qz) + 2\ H_2O \leftrightarrow H_4SiO_4\ (aq)$$

The equilibrium constant for this reaction can be written as:

$$K^o_{eq}(qz) = a(H_4SiO_4)/a(SiO_2(qz))\ a^2(H_2O)$$

$$K^o_{eq}(qz) = a(H_4SiO_4) = 2 \times 10^{-4} \text{ at } 25^oC \text{ and 1 atm}$$

$$K^o_{eq}(opal) = a(H_4SiO_4) = 2 \times 10^{-3} \text{ at } 25^oC \text{ and 1 atm}$$

http://eps.mcgill.ca/~courses/c220/

Quartz or opaline silica solubility

Reactions	log K°	
SiO_2 (quartz) + 2 H_2O ←→ H_4SiO_4 (aq)	-3.7	(1)
SiO_2 (amorphous) + 2 H_2O ←→ H_4SiO_4 (aq)	-2.7	(2)
H_4SiO_4 ←→ $H_3SiO_4^-$ + H^+	-9.46	(3)
$H_3SiO_4^-$ ←→ $H_2SiO_4^{2-}$ + H^+	-12.56	(4)

The total dissolved silica concentration,

$[SiO_2]_T = [H_4SiO_4] + [H_3SiO_4^-] + [H_2SiO_4^{2-}]$

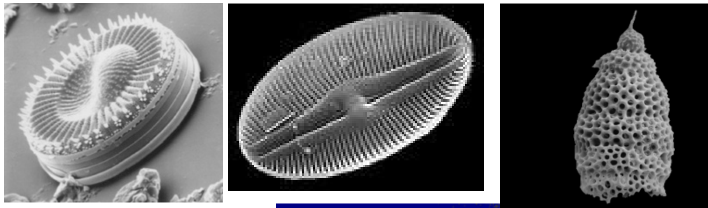
From the above equations,

$a(H_3SiO_4^-) = K^o_3\, a(H_4SiO_4)/a(H^+)$

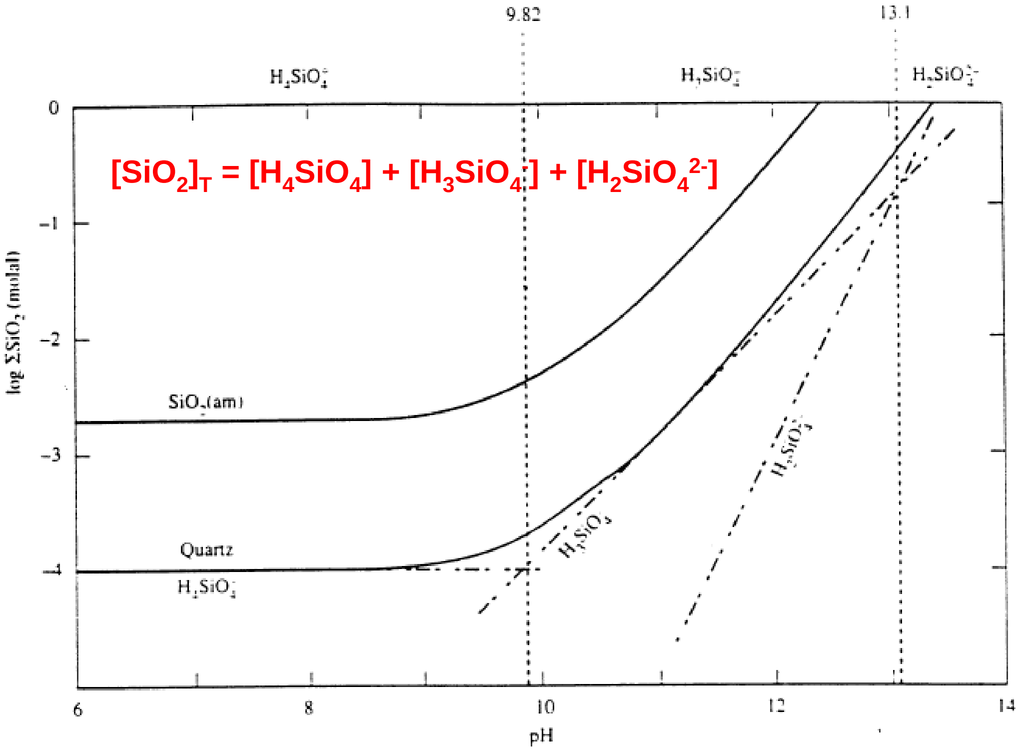
$a(H_2SiO_4^{2-}) = K^o_3\, K^o_4\, a(H_4SiO_4)/a(H^+)^2$

if we are dealing with an ideal solution (i.e., $a_i = [i]$),

$$[SiO_2]_T = [H_4SiO_4] + [H_3SiO_4^-] + [H_2SiO_4^{2-}]$$
$$= [H_4SiO_4]\,(1 + K^o_3/a(H^+) + K^o_3\, K^o_4\, /a(H^+)^2)$$

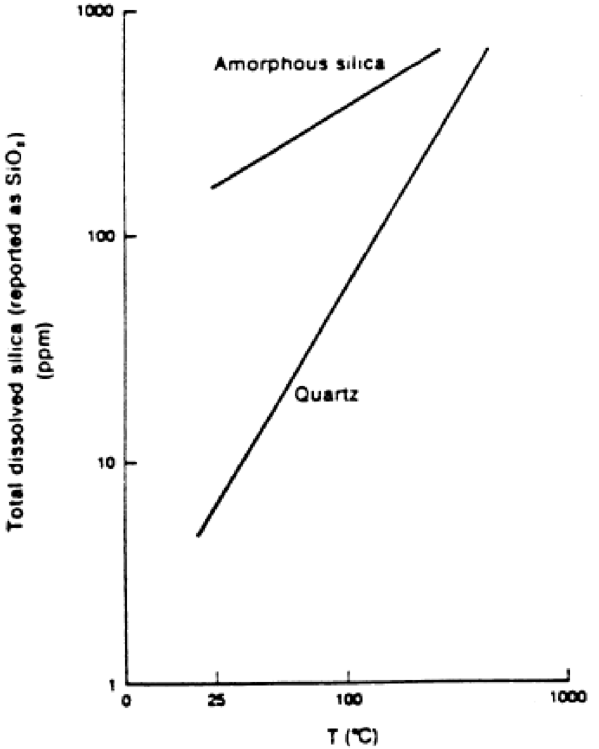


Quartz and opaline silica solubility



$[SiO_2]_T = [H_4SiO_4] + [H_3SiO_4^-] + [H_2SiO_4^{2-}]$

Figure 7.7 Solubilities of quartz and amorphous silica as a function of pH. Also shown are lines indicating the solubility of quartz due to the individual dissolved silica species $H_4SiO_4^\circ$, $H_3SiO_4^-$, $H_2SiO_4^{2-}$, and the fields of dominance of $H_4SiO_4^\circ$, $H_3SiO_4^-$, and $H_2SiO_4^{2-}$ as a function of pH.



A. Solubility as a function of temperature at pH<7

Solubility of ionic salts

For an electrolyte that dissolves in water according to:

$$A_mB_{n\,(s)} \leftarrow\rightarrow mA^{+n} + nB^{-m}$$

A conventional equilibrium constant or solubility product is defined as:

$$K°_{eq} = K°_{sp} = (A^{+n})^m\,(B^{-m})^n/(A_mB_{n\,(s)}) = [A^{+n}]^m\,[B^{-m}]^n\,\gamma_{(A^{+n})}{}^m\,\gamma_{(B^{-m})}{}^n$$

Determining the solubility of a single ionic salt in pure water is trivial, if you assume that the components of the salt completely dissociate in solution:

Ex: $AgCl \leftarrow\rightarrow Ag^+ + Cl^-$

$K°_{sp} = (Ag^+)\,(Cl^-) = 1.80 \times 10^{-10}$, assuming ideal behavior

$\rightarrow [Ag^+] = [Cl^-] = (K°_{sp})^{1/2} = 1.3 \times 10^{-5}$ M

$CaF_2 \leftarrow\rightarrow Ca^{2+} + 2F^-$

$K°_{sp} = (Ca^{2+})\,(F^-)^2 = 3.08 \times 10^{-11}$, assuming ideal behavior

Since $[F^-] = 2\,[Ca^{2+}]$, $K°_{sp} = [Ca^{2+}]\,(2\,[Ca^{2+}])^2 = 4\,[Ca^{2+}]^3$

$\rightarrow [Ca^{2+}] = (K°_{sp}/4)^{1/3} = 2 \times 10^{-4}$ M and $[F^-] = 4 \times 10^{-4}$ M

Solubility of ionic salts:
The common ion effect

The presence of a common ion decreases the solubility of a sparingly soluble compound.

$$CaSO_4{\cdot}2H_2O_{(s)} \leftarrow\rightarrow Ca^{2+} + SO_4^{2-} + 2\ H_2O$$

$$K°_{sp} = (Ca^{2+})\ (SO_4^{2-}) = [Ca^{2+}]\ [SO_4^{2-}]\ \gamma(Ca^{2+})\ \gamma(SO_4^{2-}) = 2.4 \times 10^{-5}$$

For a pure salt solution at equilibrium

(assuming ideal behavior, i.e., $\gamma(Ca^{2+}) = \gamma(SO_4^{2-}) = 1$):

$$[Ca^{2+}] = [SO_4^{2-}] = (K°_{sp})^{1/2} = 4.9 \times 10^{-3}\ M$$

What happens if we add 1 mole of Na_2SO_4 to one liter of the gypsum-equilibrated solution?

Solubility of ionic salts:
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What happens if we add 1 mole of Na_2SO_4 to one liter of the gypsum-equilibrated solution?

$$K°_{sp} = [Ca^{2+}]\ [SO_4^{2-}] = 2.4 \times 10^{-5} = X\ (1.0 + X) = X + X^2 \approx X$$

$$\rightarrow X = [Ca^{2+}] \approx 2.4 \times 10^{-5}\ M \text{ if } [SO_4^{2-}] = 1.00\ M$$

Real solutions

Given that the solubility product of gypsum is approximately 2.4 x 10^{-5}, one can determine if a solution containing $[Ca^{2+}] = 1 \times 10^{-2}$ m and $[SO_4^{2-}] = 3 \times 10^{-2}$ m is saturated with respect to the salt, if we know that the total ion activity coefficients for the two species of interest in this solution are, respectively, 0.225 m^{-1} and 0.0843 m^{-1}.

$$\begin{aligned} \text{IAP} &= \text{ion activity product} = (Ca^{2+})\,(SO_4^{2-}) \\ &= [Ca^{2+}]\,[SO_4^{2-}]\ \gamma(Ca^{2+})\,\gamma(SO_4^{2-}) = \text{ICP} \times \gamma(Ca^{2+})\,\gamma(SO_4^{2-}) \\ &= (1 \times 10^{-2})\,(3 \times 10^{-2})\ (0.225)\,(0.0843) \\ &= 5.7 \times 10^{-6} \end{aligned}$$

$$\mathbf{\Omega = saturation\ state} = \text{IAP}/K^{o}_{sp} = 5.7 \times 10^{-6}/2.4 \times 10^{-5} = 0.24$$

since $\Omega < 1$, the solution is undersaturated with respect to gypsum in this solution, ...

Saturation indices are also often used to report the state of a solution with respect to a given mineral.

$$\boldsymbol{SI = saturation\ index = \log IAP/K^{o}_{sp}}$$

if SI = 0, the solution is in equilibrium with the mineral. If SI is positive, the solution is supersaturated with respect to the mineral and, if SI is negative, the solution is undersaturated.

Complexation and adsorption

The solubility of some salts or minerals is dependent on pH, although their solubility products are independent of pH. In other words, the amount of salt or mineral that can be maintained in solution is a function of pH but the K°_{sp} is a constant that is independent of solution composition (e.g., quartz and carbonate minerals).

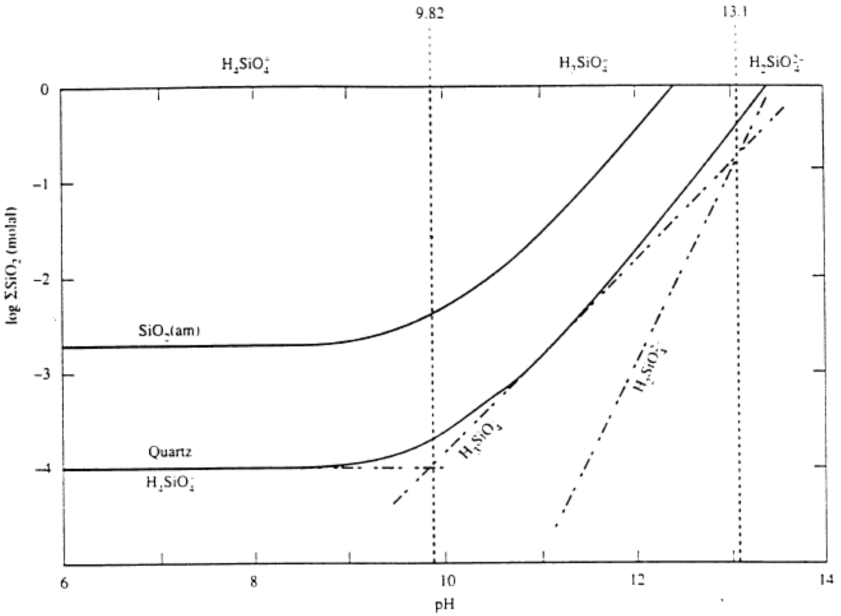


Figure 7.7 Solubilities of quartz and amorphous silica as a function of pH. Also shown are lines indicating the solubility of quartz due to the individual dissolved silica species $H_4SiO_4^\circ$, $H_3SiO_4^-$, $H_2SiO_4^{2-}$, and the fields of dominance of $H_4SiO_4^\circ$, $H_3SiO_4^-$, and $H_2SiO_4^{2-}$ as a function of pH.

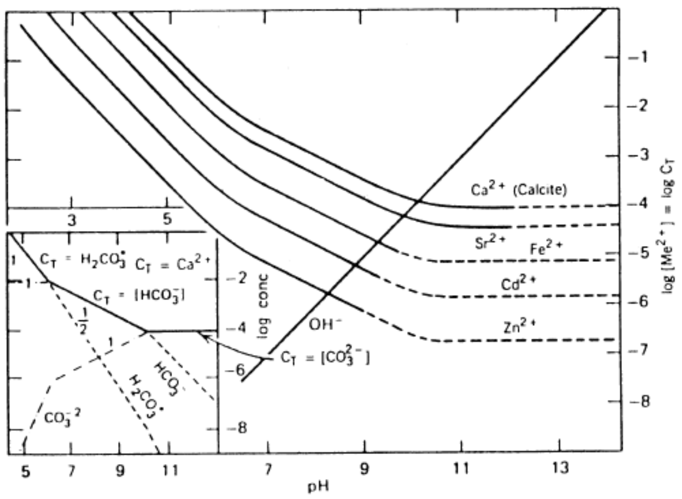


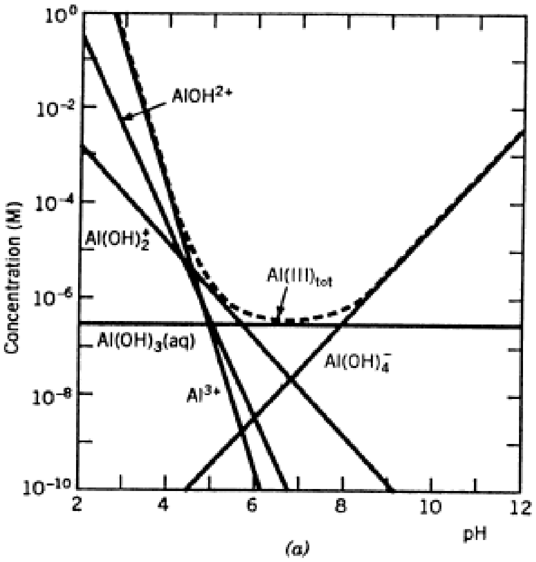
Figure 7.9. Models I*b* and I*c*. Solubility of metal carbonates in a closed system: $[Me^{2+}] = C_T$. The inset gives the essential features for the construction of the diagram for $CaCO_3(s)$ and equilibrium concentrations of all the carbonate species. A suspension of pure $MeCO_3(s)$ ($C_B - C_A = 0$) is characterized by the intersection of $[OH^-]$ and $[Me^{2+}] = C_T$. Dashed portions of the curves indicate conditions under which $MeCO_3(s)$ is not thermodynamically stable.

Complexation and adsorption

Likewise, the presence of a ligand or the adsorption of one of the solid constituents to another substrate will lower the effective concentration of this solute and increase the solubility of the solid.

Ex: $Al^{3+} + 3\ Ox^{2-} \leftrightarrow Al(Ox)_3^{3-}$

$$\Sigma\,[Al] = [Al^{3+}] + [AlOH_2^{+}] + [Al(OH)^{2+}] + [Al(OH)_3^{\circ}] + [Al(OH)_4)^{-} + [Al(Ox)_3^{\ 3-}]$$



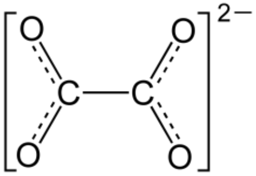
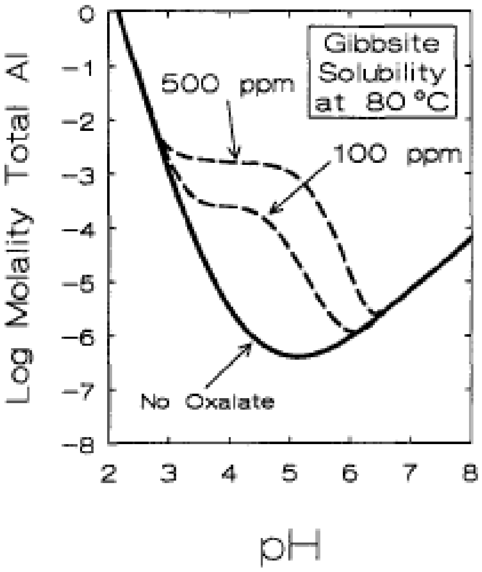


Figure 2. Calculated gibbsite solubility, as function of pH, in 0.1 molal NaCl fluids at 80 °C. Solid curve represents fluids that do not contain oxalate; dashed curves represent systems containing oxalate.



Evaporites deposits

Evaporites are formed in closed or semi-closed basins where evaporation exceeds precipitation (+ runoff).

Rogers Dry Lake, Mojave Desert, California

The Salar de Uyuni lake in Bolivia (more than 9,000 km^2) is the largest salt playa in the world. The salar (salt pan) has about a meter of briny water (blue). In addition to sodium chloride (NaCl - rock salt), and calcium sulfate ($CaSO_4$), the lake also contains lithium chloride, LiCl, making this the largest source of lithium in the world.

Chemical Fractionation and the Chemical Divide

As a result of evaporation, chemical fractionation takes place between the solutions and the remaining concentrated brines. The fractionation can be accounted for by a variety of mechanisms:

1) Mineral precipitation
2) Selective dissolution of efflorescent crusts and sediment coatings
3) Exchange and sorption on active surfaces
4) Degassing
5) Redox reactions

Mineral precipitation is the most important and the one that can most easily be modeled. The basic assumption of the model is that minerals will precipitate as the solution becomes saturated with respect to a solid phase. In other words, precipitation occurs when the ion activity product of the solution becomes equal to the solubility constant of the mineral and remains constant upon further evaporation. The fate of solution constituents upon mineral precipitation rests on the concept of **the chemical divide**.

Chemical Divides:

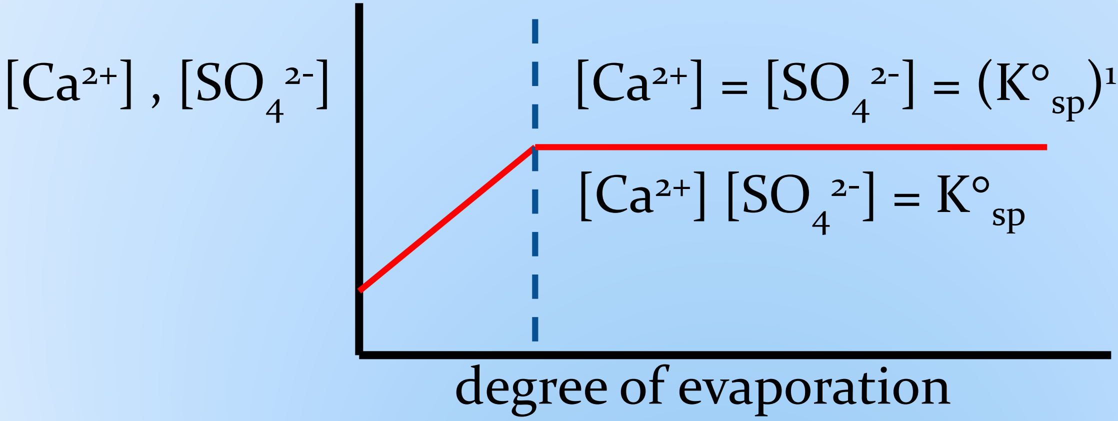
Branching points along the path of solution evolution

Brine evolution and chemical divides

If we monitor the evaporation of a dilute Ca^{2+} and SO_4^{2-} solution, their concentrations will increase until we reach gypsum saturation. From this point on, the evolution of the remaining solution will depend on the $[Ca^{2+}]:[SO_4^{2-}]$ ratio of the starting solution.

Two cases are possible:

1) $[Ca^{2+}] = [SO_4^{2-}]$, the ratio is equal to the stoichiometry of the solid, the ratio in solution will not change as evaporation progresses because they are both taken out of solution in equal amounts.



$[Ca^{2+}]$, $[SO_4^{2-}]$

$[Ca^{2+}] = [SO_4^{2-}] = (K°_{sp})^{1/2} = 4.9 \times 10^{-3}$ M

$[Ca^{2+}]\,[SO_4^{2-}] = K°_{sp}$

degree of evaporation

2) $[Ca^{2+}] \neq [SO_4^{2-}]$??

Brine evolution and chemical divides

If we start with a solution in which $[Ca^{2+}] = 2\,[SO_4^{2-}]$, which upon evaporation has reached equilibrium with respect to gypsum. If we neglect activity coefficients and assume that the solubility product for gypsum is $10^{-4.61}$.

$[Ca^{2+}]\;[SO_4^{2-}] = 10^{-4.61} = 2\,[SO_4^{2-}]\,[SO_4^{2-}] = 2\,[SO_4^{2-}]^2$, then
$\rightarrow [SO_4^{2-}] = 3.5 \text{ x } 10^{-3}$ and $[Ca^{2+}] = 7.0 \text{ x } 10^{-3}$

If we evaporate this solution until the mass of water remaining is a fraction 1/n of the saturated solution (i.e., a concentration factor of n) which results in the precipitation of y moles of gypsum per kilogram of original saturated solution.

$[Ca^{2+}]_n = n\,(7.0 \text{ x } 10^{-3} - y)$ and $[SO_4^{2-}]_n = n\,(3.5 \text{ x } 10^{-3} - y)$

if the solution remains in equilibrium with gypsum

$$\begin{aligned} K_{sp} = 10^{-4.61} &= n^2\,(7.0 \text{ x } 10^{-3} - y)(3.5 \text{ x } 10^{-3} - y) \\ &= n^2\,(y^2 - 1.05 \text{ x } 10^{-2}\,y + 24.5 \text{ x } 10^{-3}) \end{aligned}$$

for any value of n, the quadratic equation can be solved for y and the concentration of Ca^{2+} and SO_4^{2-} calculated from above.

Brine evolution and chemical divides

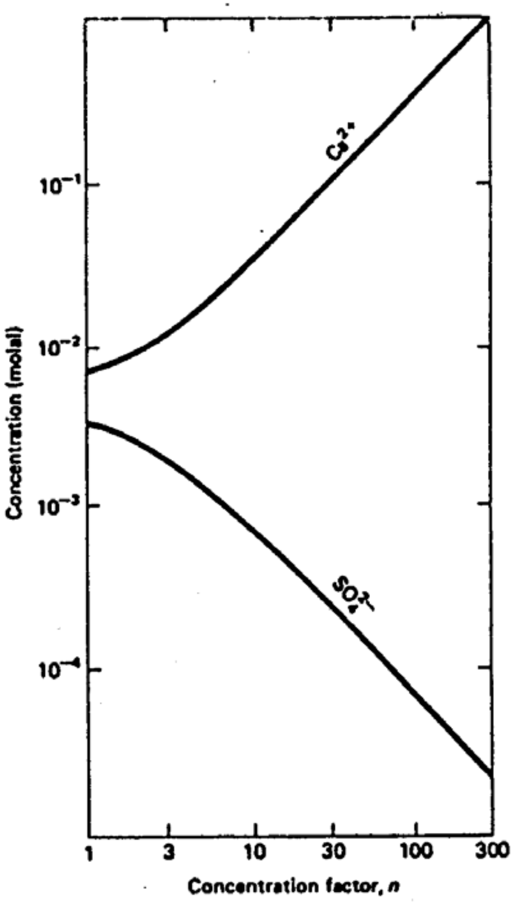
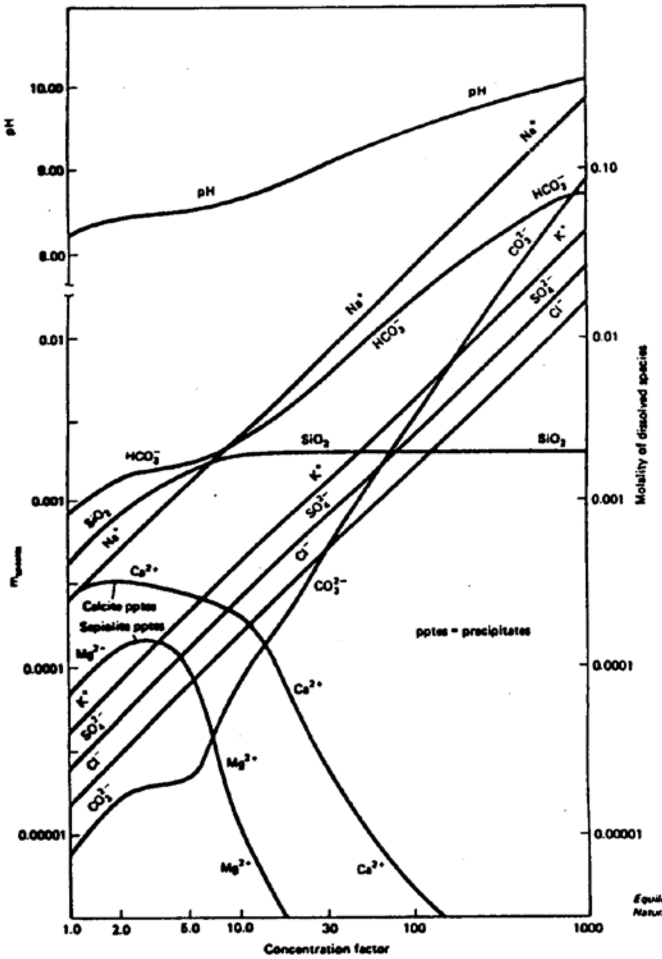


Figure 9-2 Concentrations of calcium and sulfate during evaporation of a solution in equilibrium with gypsum, assuming initial $m_{Ca^{2+}} = 2m_{SO_4^{2-}}$, and neglecting activity corrections.



Equilibrium Concepts in Natural Water Systems

Figure 9-1 Calculated result of evaporating Sierra Nevada spring water at 25°C and P_{CO_2} = $10^{-3.5}$. [Garrels, R. M. and Mackenzie, F. T. *Equilibrium Concepts in Natural Water Systems*, in Advances in Chemistry Series, no. 67, ed. Stumm, W. (Washington, D.C.: American Chemical Society, 1967)].

Brine evolution and chemical divides

The general principal being that "whenever a binary salt is precipitated during evaporation, and the effective ratio of the two ions in the salt is different from the ratio of the concentrations of the ions in solution, further evaporation will result in an increase in the concentration of the ion present in greater relative concentration in solution, and a decrease in the concentration of the ion present in lower relative concentration." …

Brine evolution and chemical divides

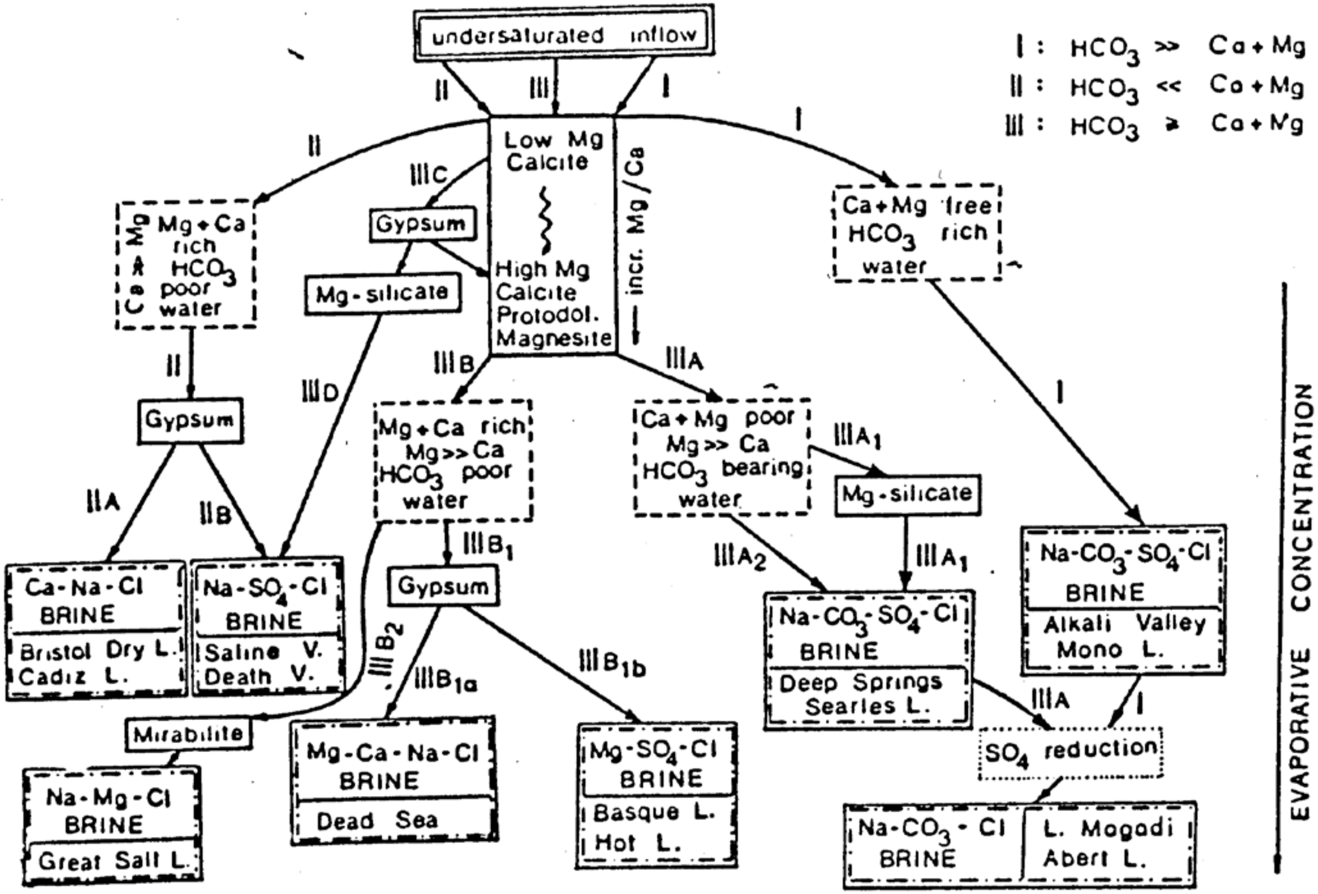
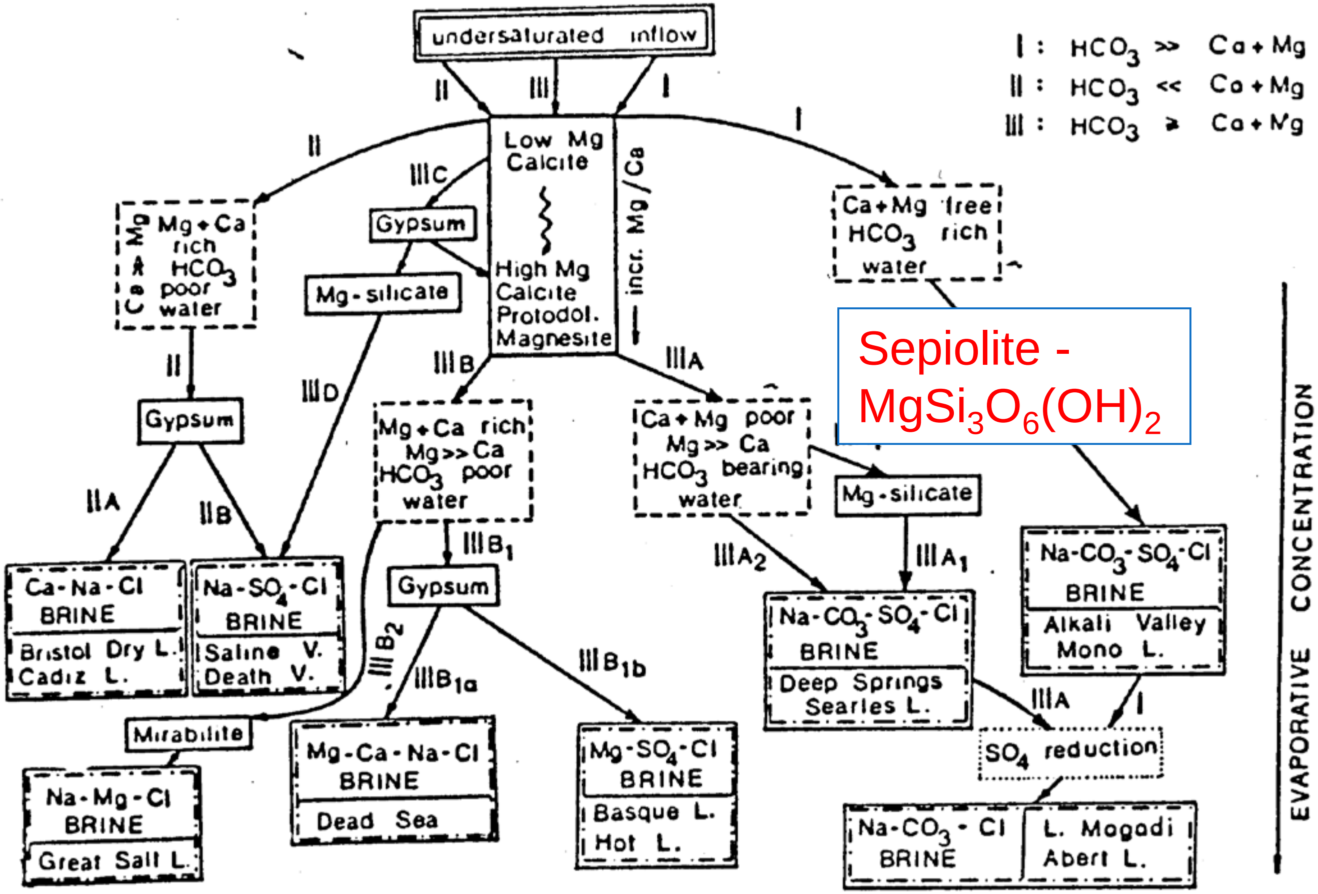


Fig. 2. Flow diagram for the geochemical evolution of closed basin brines from Eugster and Hardie (1978). The position of Mg–silicate precipitate in the scheme should be considered problematic.

Brine evolution and chemical divides



Sepiolite - $MgSi_3O_6(OH)_2$

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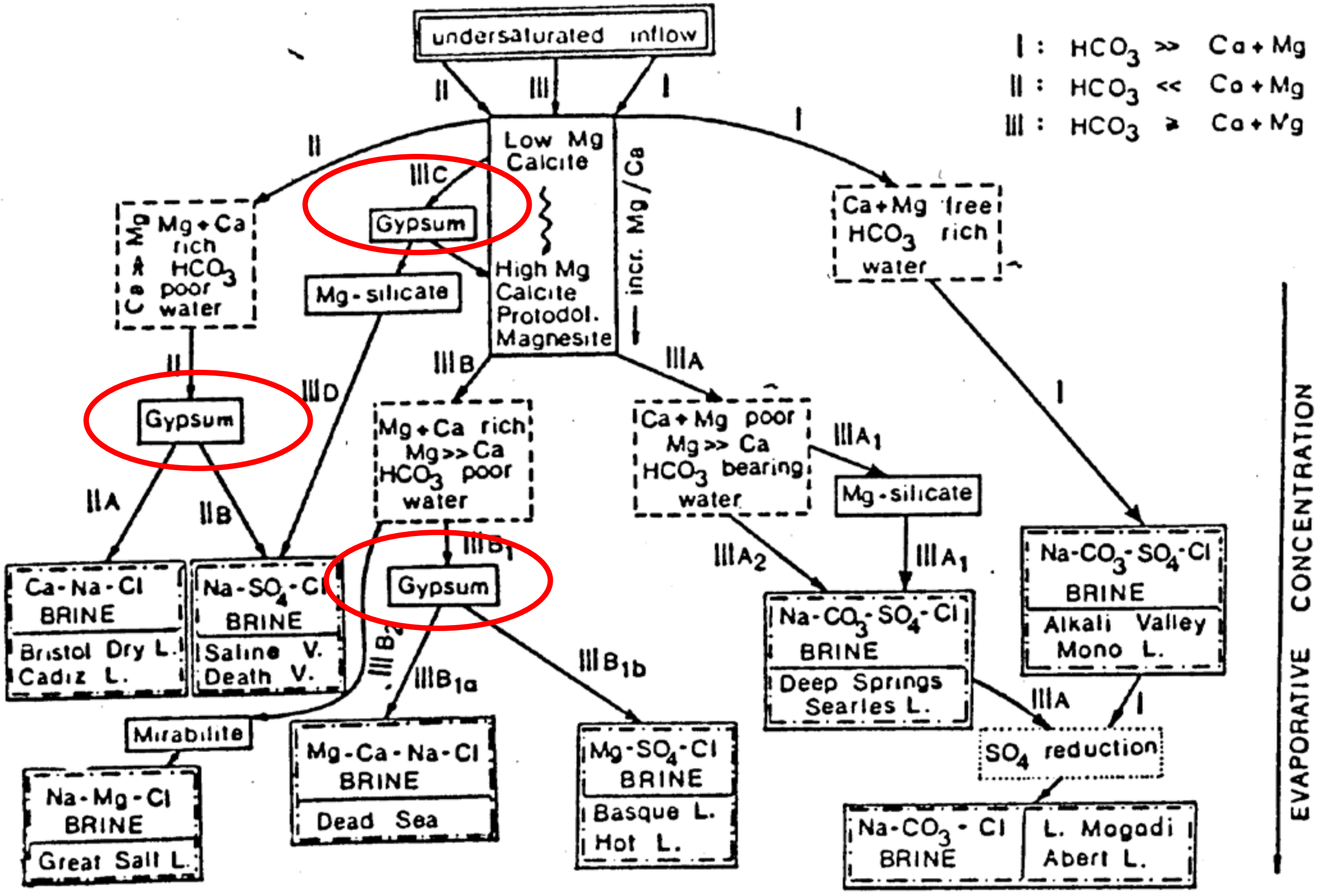
Brine evolution and chemical divides



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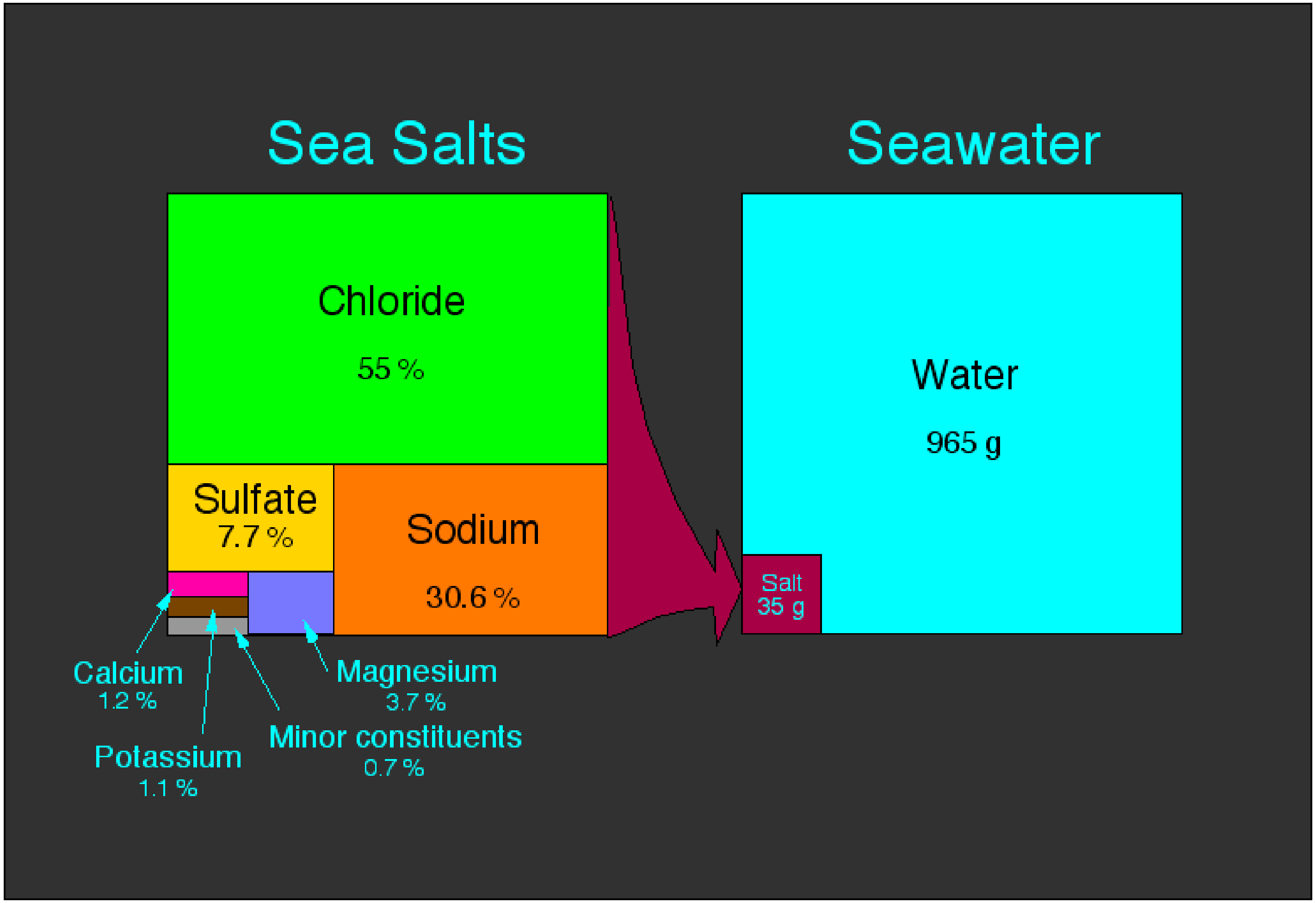
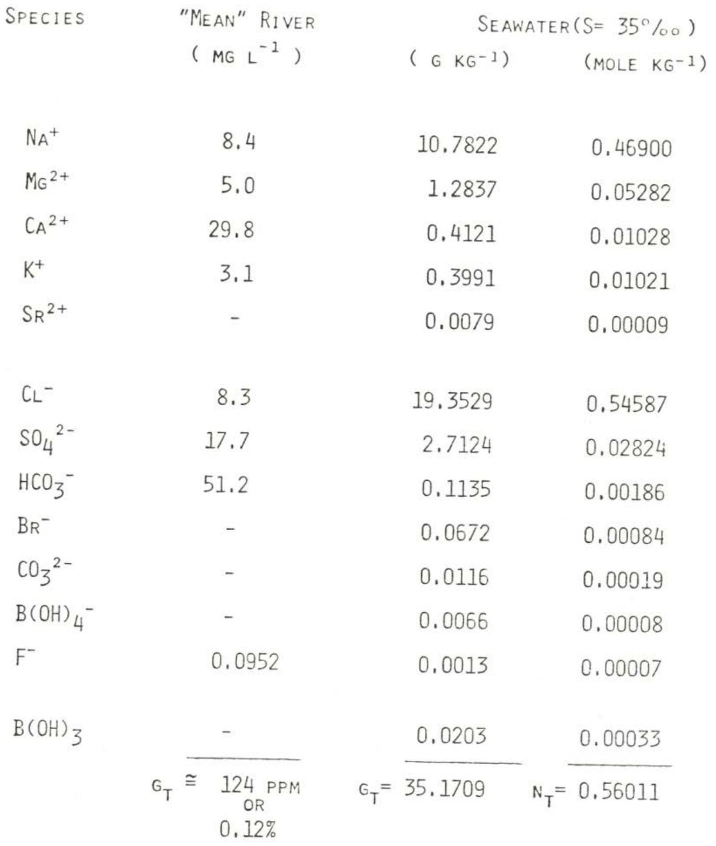
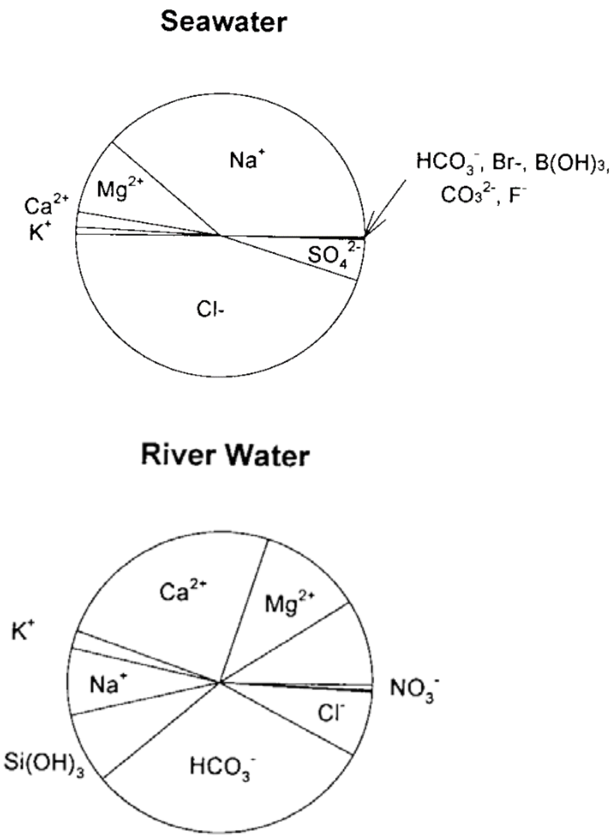
Seawater composition



Seawater composition



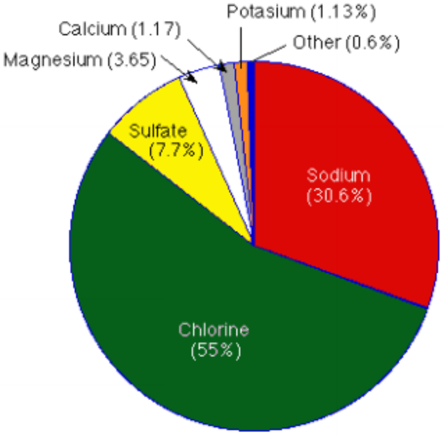
SPECIES	"MEAN" RIVER (MG L^{-1})	SEAWATER (S= 35‰) (G KG^{-1})	(MOLE KG^{-1})
Na^+	8.4	10.7822	0.46900
Mg^{2+}	5.0	1.2837	0.05282
Ca^{2+}	29.8	0.4121	0.01028
K^+	3.1	0.3991	0.01021
Sr^{2+}	-	0.0079	0.00009
Cl^-	8.3	19.3529	0.54587
SO_4^{2-}	17.7	2.7124	0.02824
HCO_3^-	51.2	0.1135	0.00186
Br^-	-	0.0672	0.00084
CO_3^{2-}	-	0.0116	0.00019
$B(OH)_4^-$	-	0.0066	0.00008
F^-	0.0952	0.0013	0.00007
$B(OH)_3$	-	0.0203	0.00033
	$G_T \cong$ 124 PPM OR 0.12%	$G_T =$ 35.1709	$N_T =$ 0.56011



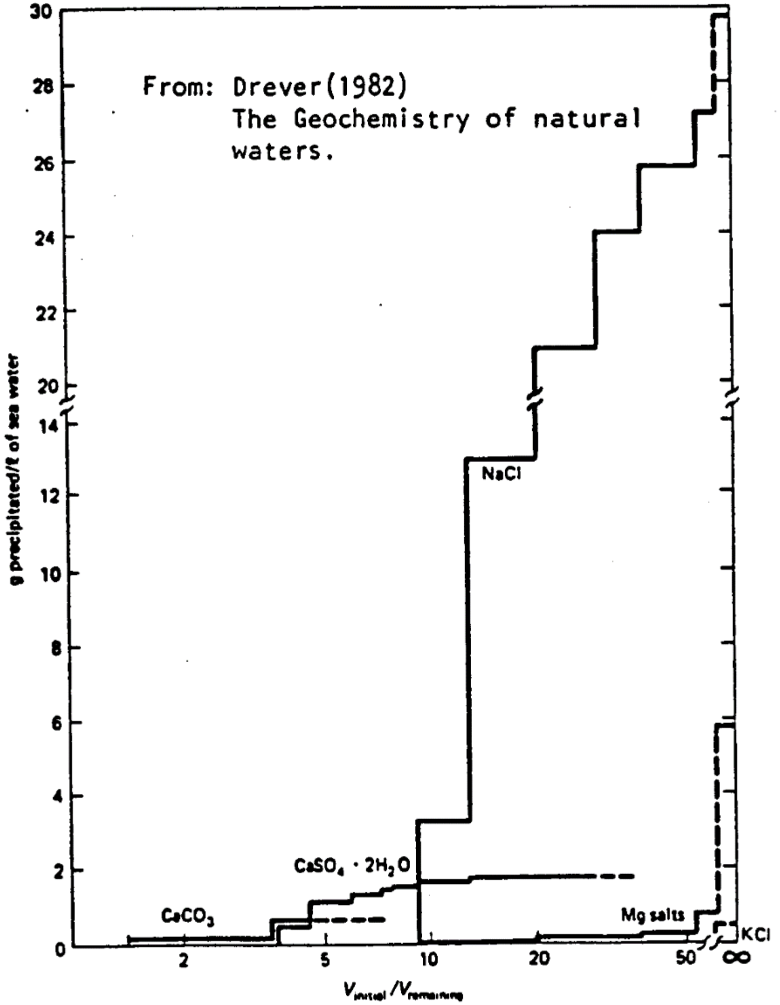
Law of constant relative proportions (Marcet's principle): the concentration ratio of major elements to each other or to the total salt content is a constant.

Seawater evaporation and marine evaporites

Zechstein Sea during the Late Permian period over the topography of present day North Western Europe.

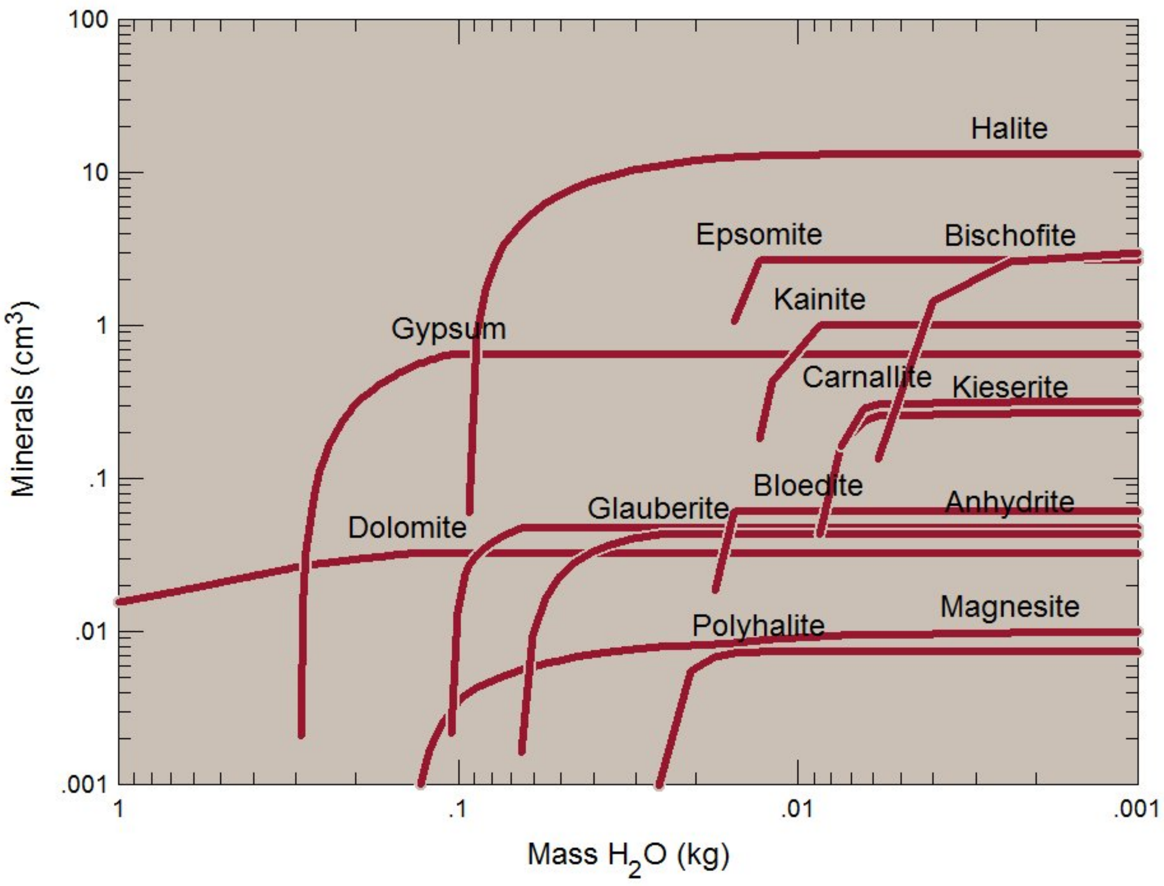


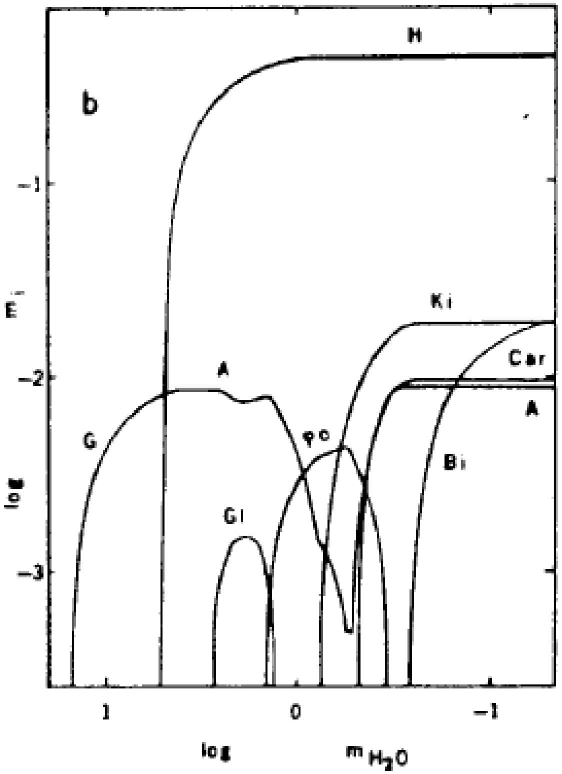
Salts in Seawater



From: Drever(1982) The Geochemistry of natural waters.

Equilibrium seawater evaporation

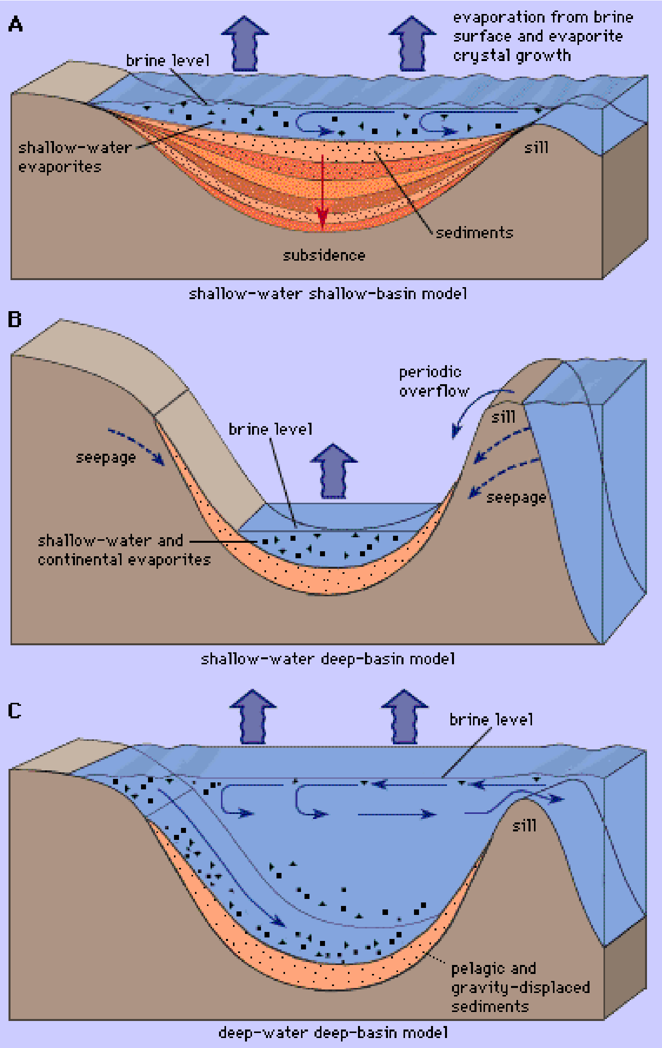




From: Harvie et al. (1980) Science 208, 498-500

Fractional seawater evaporation: salt pens

Marine evaporite deposits



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