GEOL 414/514

CARBONATE CHEMISTRY

Chapter 6

LANGMUIR

SOLUBILITY OF CALCITE

- $CaCO_3$ in nature: calcite & aragonite
- Reaction with strong acid:

$$CaCO_3 + 2H^+ \rightarrow Ca^{+2} + H_2O + CO_2$$

- Reaction with weak acid:

$$CaCO_3 + H^+ \rightarrow Ca^{+2} + HCO_3^-$$

- Summary of reaction in nature:

$$CaCO_3 + H_2CO_3 \leftrightarrows Ca^{+2} + 2HCO_3^-$$

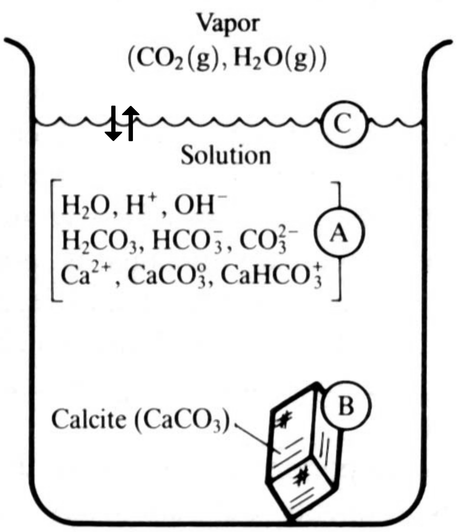
- Solubility depends on partial pressure of CO_2

$$H_2O(l) + CO_2(g) \leftrightarrows H_2CO_3(aq)$$

SOLUBILITY OF CALCITE - 2

CALCITE EQUILIBRIA

Equilibrium between calcite-water-air



SOLUBILITY OF CALCITE - 3

Natural Processes Affecting $CaCO_3$ Solubility

- **Dissolution & Exsolution of CO_2:**
  - **groundwaters contain more CO_2 than surface; are gen isolated from atmos**
  - **surface waters contain conc near atmos conc; may have higher amts when OM is present**
  - **see Fig 6.7(a)**
- **Evaporation:**
  - **occurs in soils & surface waters**
  - **significant in soils of arid & semi-arid regions; causes surface deposits & caliche to form**
  - **see Fig 6.7(c)**

SOLUBILITY OF CALCITE - 4

Natural Processes Affecting $CaCO_3$ Solubility

- **Temperature:**
  - **increase temp, decrease solubility of $CaCO_3$, some other carbonates & sulfates**
  - **what happens to solubility of CO_2 when temps increase?**
  - **increase temp, decrease solubility of CO_2, $CaCO_3$**
- **Pressure:**
  - **increase P, increase solubility of calcite (slightly)**
  - **in deep ocean, P increases solubility about 2X**

SOLUBILITY OF CALCITE - 5

Natural Processes Affecting $CaCO_3$ Solubility, continued

- **Organic Activity:**
  - **many organisms use $CaCO_3$ in construction of their shells, probably by affecting H_2O pH.**
  - **organisms are more abundant where waters are approximately sat'd with respect to $CaCO_3$**
    - **a minor pH change here would cause ppt'n**
- **Decay:**
  - **under aerated conditions: CO_2 produced & solubility of $CaCO_3$ increases**
  - **under anaerobic conditions:**
    - **if H_2S produced, inc H^+, & inc solubility**
    - **if NH_3 produced, inc OH^-, decrease solubility**

SOLUBILITY OF CALCITE - 6

Carbonate Equilibria Related to CO_2
(Summary reaction)

$$H_2O + CO_2$$
$$\downarrow\uparrow$$
$$CaCO_3 + H_2CO_3 \leftrightarrows Ca^{+2} + 2\ HCO_3^-$$

- increase CO_2, dissolve $CaCO_3$

- decrease CO_2, precipitate $CaCO_3$

CALCIUM CARBONATE: SOLUBILITY CALCULATIONS

- Calcium carbonate solubility is strongly influenced by the presence & availability of CO_2. Other influencing reactions may also be important.

- There are five cases or sets of conditions that cover many situations of geologic interest; most other situations can be stipulated as combinations or permutations of these five

Case 1. Reactions involved when pure calcite is placed in pure water with negligible gas phase present
- used to determine the solubility of calcite – it is of little geologic utility

CALCIUM CARBONATE: SOLUBILITY CALCULATIONS - 2

Case 2. The reaction of calcite in pure water but with the system open to CO_2; i.e., in contact with a reservoir, the atmosphere, of fixed P_{CO2}
- of considerable geologic importance; this represents reactions in rivers, lakes, streams & other “dilute” natural waters open to the atmosphere where pH is controlled entirely by the carbonate equilibria

Case 3. Equilibrium relations in a system with a fixed quantity of dissolved carbonate species, but with pH arbitrarily fixed; i.e., controlled by other reactions in the system
- some situations of ground water
- surface waters with other sources of H^+

CALCIUM CARBONATE: SOLUBILITY CALCULATIONS - 3

Case 4. Equilibrium in a system connected to an external reservoir of fixed P_{CO2}, but with pH arbitrarily determined
- of considerable geologic interest
- need to determine P_{CO2}, pH, $[Ca^{+2}]$ in equilib with calcite; try to determine controlling substance
- can also use for hypothetical (model) calculations

Case 5. Equilibrium resulting from addition (exposure) of $CaCO_3$ to a system originally open to a CO_2 reservoir, but closed to that reservoir before addition of $CaCO_3$
- rain water in equilibrium with atmos sinks into the ground, through unreactive soil/rock before contacting calcite

CALCIUM CARBONATE: SOLUBILITY CALCULATIONS - 4

- Variables needed for solution of carbonate equilibrium
- For all systems mentioned, there is a maximum of 7 variables, at dT = 0 and dP = 0

$a_{CO2} = P_{CO2}$; a_{H2CO3}; a_{HCO3-}; a_{CO3-2}; a_{H+}; a_{OH-}; a_{Ca+2}

Note: activity = [x]

$[Ca^{+2}][CO_3^{-2}] / [CaCO_3] = K_{CaCO3} = 10^{-8.3}$

$[H^+][HCO_3^-] / [H_2CO_3] = K_{H2CO3} = 10^{-6.4}$

$[H^+][CO_3^{-2}] / [HCO_3^-] = K_{HCO3-} = 10^{-10.3}$

$[H^+][OH^-] / [H_2O] = K_{H2O} = 10^{-14}$

$[H_2CO_3] / P_{CO2} = K_{CO2} = 10^{-1.47}$

CALCIUM CARBONATE: SOLUBILITY CALCULATIONS - 5

Solubility of $CaCO_3$

$CaCO_3 \leftrightarrows Ca^{+2} + CO_3^{-2}$

- From Table A1.2:
  $K = [Ca^{+2}][CO_3^{-2}]/[CaCO_3] = 10^{-8.35} = 4.5 * 10^{-9}$
- Solubility = $(4.5 * 10^{-9})^{1/2} = 6.8 * 10^{-5}$ *m* (??)
- When CO_3^{-2} is present, hydrolysis occurs – this will affect pH & solubility

$CaCO_3 + H_2O \rightarrow Ca^{+2} + OH^- + HCO_3^-$

- Question: what will be the effect of the hydrolysis on the solubility of $CaCO_3$?

CALCIUM CARBONATE: SOLUBILITY CALCULATIONS - 6

Solubility of $CaCO_3$, continued

- **$K_{(3\text{-}6)} = [Ca^{+2}] + [OH^-] – [HCO_3^-]$**
- **$K = [Ca^{+2}] + [CO_3^{-2}] + [OH^-] – [H^+] * ([HCO_3^-]/[H^+][CO_3^{-2}]$**
- **$K = 10^{-8.3} * 10^{-14} * 1/10^{-10.3} = 10^{-12}$**
- **In pure H_2O, where γ's are ≈ unity, Ca^{+2}, OH^- & HCO_3^- should be formed in equal amounts (Eq 3-6), so**

  $m_{Ca+2} = m_{OH-} = m_{HCO3-}$ and

  $m_{Ca+2} = (10^{-12})^{1/3} = 10^{-4}\ m$
- **pH should = 10; However:**

CALCIUM CARBONATE: SOLUBILITY CALCULATIONS - 7

Solubility of $CaCO_3$, continued

- **At high pH, the HCO_3^- is dissociated**
- **From Fig. 5-3, p. 156, $[CO_3^{-2}] / [HCO_3^-] \approx 0.5$**
- **The 3 ions are not present in equal conc's & more $CaCO_3$ must dissolve to maintain the ion product at 10^{-12}**
- **If $[CO_3^{-2}] / [HCO_3^-] \approx 0.5$, then conc's of HCO_3^- and OH^- should be ≈ $^2/_3$conc Ca^{+2}, so**

  $m_{Ca+2} = {}^3/_2\ m_{OH-} = {}^3/_2\ m_{HCO3-}$
- **From Eq 3-8, $mCa^{+2} = (9/4*10^{-12})^{1/3} = 1.3 * 10^{-4}\ m$ (orig est = $6.8*10^{-5} m$)**
- **OH^- slightly lowered and pH = 9.9**

CALCITE AND ARAGONITE

K_{sp} calcite = $10^{-8.35} = 4.5*10^{-9}$

K_{sp} aragonite = $10^{-8.22} = 6.0*10^{-9}$

- When aragonite is dissolved and an equilibrium is established between solid & solution (saturated), the K_{sp}, (product ion conc) is larger than the K_{sp} for calcite
- Q – why does calcite not precipitate (it doesn't)
- Calcite should precipitate; aragonite continue to dissolve and re-precipitate as calcite until the aragonite is gone - This does not happen (??)
- Aragonite is unstable with respect to calcite under ordinary conditions (thermodynamically speaking)

CALCITE AND ARAGONITE

- Aragonite is a high pressure form; pressures not found under surface conditions
- Question: why does aragonite form under surface conditions?
  - solution is slightly supersaturated with respect to calcite, perhaps there are no nuclei present for calcite precipitation
  - presence of Sr^{+2} & Mg^{+2} favor aragonite
  - some animals precipitate aragonite; some calcite; some precipitate both
- Over geologic time aragonite alters to calcite

SUPERSATURATION

- Supersaturated solutions can exist for long periods of time – calcite-aragonite example
- Supersaturated conditions are not uncommon
- Presence of submicron particles (higher solubility than well-crystallized phases used for K_{sp}
- Nucleation of precipitate seems to be a (the) key issue
- Common to find very high levels of supersaturation of waters with respect to calcite
- One key is rate of reactions
- Non-equilibrium processes have been cited as influencing factors but do not make good "geochemical sense"

EFFECT OF GRAIN SIZE ON SOLUBILITY

- Very tiny grains (mμ) show a greater solubility than do large crystals (apparent solubility)
- Only true for these extremely small particles
- May be the cause of supersaturation in nature
- Precipitation begins with formation of very small crystals, which are replaced by larger particles
- Solubility is a thermodynamic entity and is independent of grain size
- Rate of solubility is more of a function of grain size

EFFECT OF ION ASSOCIATION ON SOLUBILITY

- Formation of complexes might enhance solubilities

$$Ca^{+2} + CO_3^{-2} \leftrightarrows CaCO_3^{\circ}(aq)$$

$$K = a_{CaCO3(aq)} / a_{Ca+2} + a_{CO3-2} = 10^{3.2}$$

- As long as the a_{CO3-2} remains $<10^{-3.2}$, most of the calcium remains as Ca^{+2}.
- $CaCO_3^{\circ}(aq)$ is rarely important in enhancing $CaCO_3$ sol.
- Formation of other complexes may be important in enhancing $CaCO_3$ solubility: $CaHCO_3^+$, $CaCl^+$, $CaOH^+$ & $CaSO_4^{\circ}(aq)$.
- $CaSO_4^{\circ}(aq)$ is the most stable & may inc seawater sol by about 10%

EFFECT OF ORGANISMS ON SOLUBILITY

- Organisms appear to be able to precipitate $CaSO_4$ only from waters near saturation
- No evidence that organisms can precipitate carbonate at concs' far below saturation
- They prevent supersaturation, perhaps lower equilib sol slightly but do not greatly influence solubility
- Some organisms use precipitation reactions to provide energy for life processes (catalyze reaction)
- Incidental effects of life-processes:
  - water plants use CO_2, reduces H_2CO_3 (& H^+): ppt'n
  - organic decay: - cause alkaline conditions – ppt'n
    - cause acidic conditions – solubil.

PRECIPITATION OF $CaCO_3$ IN SEAWATER

- Seawater is a very complex solution (Table 6-7)
- Activity product for $CaCO_3$ in seawater is

$$a_{Ca+2}a_{CO3-2} = 10^{-2.7} * 10^{-5.1} = 10^{-7.6} = 1.6 * 10^{-8}$$

This is ~5X greater than K_{sp} for calcite, and ~3X greater than K_{sp} for aragonite

- May precipitate as aragonite or calcite; through biotic or abiotic processes
- Diagenetic processes alter aragonite to calcite, increase crystal size, deposit calcite in veins, etc.

OTHER SIMPLE CARBONATES

$$MCO_3 + H_2CO_3 \leftrightarrows M^{+2} + 2HCO_3^-$$

Where $M^{+2} = Fe^{+2}$, Sr^{+2}, Mn^{+2}, etc.

- Equilibrium and solubility considerations are the same as for calcite
- Replacement of one carbonate by another is often observed in metamorphic & sedimentary rocks and in hydrothermal veins

$$CaCO_3 + Fe^{+2} \leftrightarrows Ca^{+2} + FeCO_3$$

$$K = [Ca^{+2}] / [Fe^{+2}] = [Ca^{+2}][CO_3^{-2}] / [Fe^{+2}][CO_3^{-2}] = 225$$

- If Fe^{+2} conc > 1/225 Ca^{+2}, siderite replaces calcite: rarely the case (later we will discuss effect of redox conditions on presence of Fe^{+2})

THE DOLOMITE PROBLEM

- Dolomite is one of most common sedimentary rocks
- Occurs in thick & extensive beds from Precambrian to the Cenozoic
- No geologic evidence that formation occurred under unusual conditions of temp or pressure
- No present day dolomite forming in nature in “normal” sedimentary environments
- Cannot prepare in lab under simulated surface condn’s
- Dolomite has been prepared under “extreme” conditions: high or low T, pH >9.5, high SO_4^{-2}; high NO_3^-
- Dolomite structure is regular & highly ordered- suggests a long time required for crystal growth

THE DOLOMITE PROBLEM - 2

Dolomite solubility

- How would we measure and verify dolomite solubility?
- It is difficult to obtain the K_{sp}; can measure the ion conc that forms upon dissolution but cannot re-precipitate to verify as with other minerals

$$K_{sp} = [Ca^{+2}][Mg^{+2}][CO_3^{-2}] \approx 10^{-17} \text{ to } 10^{-19}$$

$$CaCO_3 + Mg^{+2} + 2HCO_3^- \leftrightarrows CaMg(CO_3)_2 + H_2CO_3$$

$$2CaCO_3\ Mg^{+2} \leftrightarrows CaMg(CO_3)_2 + Ca^{+2}$$

- There are two possibilities of dissolution types

THE DOLOMITE PROBLEM - 3

Dolomite dissolution:

- **Process at ordinary temperatures:**

  $CaMg(CO_3)_2 \leftrightarrows Ca^{+2} + Mg^{+2} + 2CO_3^{-2}$
  (congruent dissolution)

- **Process at higher temperatures (partly both processes)**
  $CaMg(CO_3)_2 \leftrightarrows CaCO_3 + Mg^{+2} + CO_3^{-2}$
  (incongruent dissolution)

- **Dolomite seems to form relatively soon after deposition of the original sediment – entire beds replaced but adjacent beds of calcium carbonate**

- **Study Fig 3-5 in text – gives phase relationships between calcite – dolomite – magnesite**