

### Lecture 3: Chemistry of Natural Waters

1. Electroneutrality and charge balance – water is net neutral, so the sum of all positive charges must be matched by the sum of all negative charges; charge is measured in units of equivalent concentrations (eq/L)
  - a. Equivalent/L =  $m_i$  (ion concentration, mol/L)  $\times z_i$  (ion charge)
    - i. E.g.,  $\text{CaCl}_2 \rightarrow \text{Ca}^{2+} + \text{Cl}^-$
    - ii. If there are 3 moles/L of  $\text{CaCl}_2$ , there are 6 eq/L of  $\text{Ca}^{2+}$  and of  $\text{Cl}^-$  (charge balance is satisfied)
    - iii. For  $\text{Ca}^{2+}$ , eq/L = (3 mol/L)\*(2 eq/mol) = (+) 6 eq/L
    - iv. For  $\text{Cl}^-$ , eq/L = (6 mol/L)\*(-1 eq/mol) = (-) 6 eq/L
2. Water chemistry in the environment
  - a. Water chemistry includes pH, redox state, and dissolved and (nano)particulate constituents
  - b. pH is a measure of acidity; in natural systems pH is usually buffered by  $\text{HCO}_3^-$ 
    - i.  $\text{pH} = -\log([\text{H}^+])$
    - ii. acidic waters:  $\text{pH} < 7$        $[\text{H}^+] > [\text{OH}^-]$
    - iii. alkaline/basic waters:  $\text{pH} > 7$        $[\text{H}^+] < [\text{OH}^-]$
    - iv. Chemical reactions that produce or consume  $\text{H}^+$  can change pH
      1. Produce  $\text{H}^+$  - acid rain/point sources, organic acids, hydrolysis reactions
      2. Consume  $\text{H}^+$  - weathering of carbonate rock
  - c. Redox conditions
    - i. Set by the relative abundance of e- acceptors, notably oxygen gas
    - ii. Oxic, suboxic, and anoxic describe different oxygen gas levels
    - iii. Oxidizing and reducing describe redox state
  - d. Dissolved ions
    - i. Base Cations
      - $\text{Na}^+, \text{K}^+, \text{Ca}^{2+}, \text{Mg}^{2+}$
      - Do not participate in redox reactions; limited acid-base reactions
      - Particularly dominant cations in *basic* environments
      - Rock-derived, some atmospheric
    - ii. Bicarbonate anion
      - $\text{HCO}_3^-$
      - important acid-base chemistry (readily gives and receives protons)
      - major component of *alkalinity* (acid-neutralizing capacity of waters)
      - Atmospheric and rock-derived
$$\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3^0 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$$
    - iii. Sulfate anion
      - $\text{SO}_4^{2-}$
      - undergoes redox reactions to form different sulfur species (e.g.,  $\text{H}_2\text{S}$ )
      - Rock-derived; atmospheric inputs are important
    - iv. Chloride anion
      - $\text{Cl}^-$

- Non-reactive in the environment, hence a “conservative” ion
  - Mostly input to surface waters from precipitation
- v. Dissolved silica (aka silicic acid)
- $\text{Si(OH)}_4^0$
  - the silica tetrahedron that is released during weathering of silicate rocks (rock-derived)
  - Uncharged species (not an ion)
- vi. Metals ( $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ , and  $\text{Mn}^{2+}$  or maybe  $\text{Mn}^{3+}$ )
- Abundant in rocks; poorly-soluble in water
  - Typically insoluble in high pH and/or oxic environments (form oxide minerals)
  - Solubility increases in anoxic and acidic environments
- vii. Dissolved organic matter (DOM)
- Dissolved organic carbon (DOC) – the fraction of DOM consisting of C
- viii. Dissolved gases
- $\text{O}_2$  (DO = dissolved oxygen),  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_4$
- ix. Nutrient ions
- $\text{NH}_4^+$  and  $\text{NH}_3$  (ammonium and ammonia)
  - $\text{NO}_3^-$  and  $\text{NO}_2^-$  (nitrate and nitrite)
  - Inorganic phosphorus (phosphate)
  - Organic N and organic P
- e. Chemistry of major reservoirs