

## MARINE BIOLOGICAL AND CHEMICAL PROCESSES

### I. INTRODUCTION

- A. Largest volume of chemical/biol. activity in sed. env. associated with oceanic/marine depositional systems
1. 70% of Earth's surface covered by ocean water: marine deposits comprise a major portion of the sedimentary record
  2. Other significant chemical/biological environments include fresh-water lacustrine and saline/brine evaporite basins.
- B. Chemical composition of surface waters
1. Ocean water abundant in array of dissolved ions; major components include Cl, Na, SO<sub>4</sub>, Mg, Ca, K, HCO<sub>3</sub>, Br, and Sr. (in order of decreasing abundance see attached table)
  2. River water abundant in HCO<sub>3</sub>, Ca, H<sub>4</sub>SiO<sub>4</sub>, SO<sub>4</sub>, Cl, Na, Mg, and K (in order of decreasing abundance, see attached table)
- C. Sources of Dissolved Ionic Species
1. Subaerial chemical weathering of primary silicate bearing rocks, release of dissolved ions for transport in solution (rivers to oceans)
  2. Groundwater dissolution below surface, percolation and discharge to surface water bodies
  3. Corrosion or chemical dissolution by flowing rivers over river channel materials
  4. Volcanic influx at mid-oceanic ridges and spreading centers.
- D. Residence time of ionic species in seawater
1. Residence Time: the average amount of time that a particular chemical element remains in solution in the ocean before precipitating. (average range in 100's of thousands to millions of years: refer to attached table)
- E. Depositional Products Associated with Chemical/Biological Processes
1. Biogenic Calcium Carbonate (skeletal/shell secretion)----"Limestone"
  2. Direct Calcium Carbonate Precipitation from Seawater (biologically influenced)
  3. Evaporite Minerals through high evap./saline process (gypsum, halite, anhydrite---sulfate and chloride minerals)
  4. Siliceous Precipitates and Siliceous Skeletal Tests
  5. Manganese Nodules and Phosphorite Deposits

### II. BIOLOGICAL PROCESSES

#### A. Secretion of Calcium-Carbonate Skeletons by Organisms

Through the metabolic process in the marine ecosystem, dissolved Ca and bicarbonate ions are utilized from seawater to biogenically construct shell and skeletal material... a primary mode of limestone formation in the ancient sedimentary record.

Calcium carbonate in the rock record is largely derived through biogenic processes, however it is theoretically possible to directly precipitate calcium carbonate directly from seawater through purely

inorganic reactions, however, natural occurring oceanic conditions are not conducive to mode of formation.

### 1. Organic secretion of CaCO<sub>3</sub> by living organisms

- a. external protective shells (soft parts inside) (e.g. solitary organisms: molluscs, bivalves)
- b. internal skeletons supporting soft parts (e.g. colonial organisms: corals)
- c. Carbonate mineralogy
  - (1) Calcite: Hexagonal xl structure, high Mg vs. low Mg, calcium carbonate with admixtures of Mg as impurity
  - (2) Aragonite: Orthorhombic xl structure, High Mg vs. low Mg
  - (3) Calcite and aragonite = polymorphs (i.e. same chemical composition, differing crystal form)
  - (4) Dolomite: CaMg(CO<sub>3</sub>)<sub>2</sub>: a variation of calcium carbonate, in which Mg partially substitutes for Ca atom.
    - (a) Dolomitization: process of Mg replacement of Ca to form Ca-Mg carbonate compounds.
- d. Select organisms also construct skeletal material composed of Silica dioxide (e.g. radiolaria/diatoms), or Calcium phosphate (e.g. modern brachiopod "Lingula")

### 2. Favored Environments of Formation

- a. Shallow, well-oxygenated seas, abundant sunlight (photic zone). Calcium carbonate secreting organisms abundant.

### 3. Organic Processes

- a. Coral = carbonate factory, transferring dissolved calcium and carbonate from seawater into skeletal matter through metabolic process.

Direct diffusion of dissolved calcium and carbonate + metabolic processes (food intake) = skeletal secretion.

- (1) Reef building corals: live symbiotically with algae, triggering calcium carbonate precipitation through photosynthetic removal of carbon dioxide (see below under item (b)).

High rates of carbonate secretion in well oxygenated, photic zone

- (2) Non-reef building corals: found as solitary dwellers, in non-photoc zones, do not live symbiotically with algae

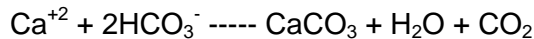
Much slower rates of carbonate secretion

- b. Green and Red algae: very important catalysts for carbonate sedimentation

- (a) Process: algae thrive in calcium carbonate supersaturated waters, during photosynthesis:

algae consume carbon dioxide---reduces capacity of water to hold dissolved calcium and bicarbonate---triggers  $\text{CaCO}_3$  precipitation

Removal of  $\text{CO}_2$  drives following reaction to right:



Solubility of calcium carbonate is strongly controlled by  $\text{CO}_2$  content of seawater, as  $\text{CO}_2$  content increases, solubility of calcium carbonate increases. As carbon dioxide content decreases, solubility of calcium carbonate decreases (hence precipitation)

- c. Solitary Organisms: e.g. molluscs, bivalves

- (1) remove calcium and carbonate ions from seawater, through metabolic process, incorporate ions in soft tissue circulatory system.

Critter blood saturated with respect to calcium, used to secrete protective shell.

- (2) Shell secretion: incremental secretions and shell buildup with age of organism.

4. Factors affecting biochemical reaction and carbonate mineralogy

- a. organic growth rate of organism  
b. accessory inorganic compounds (e.g. Strontium, Mg)

- (1) E.g. calcium and strontium are very similar with respect to ionic ratios, hence, strontium can substitute as an accessory element for calcium in skeletal tests.

- (2) Corals can not chemically discriminate the difference between strontium and calcium, hence incorporate Strontium into shell test at same ratio as that found in seawater

- (a) forms basis of Strontium-Strontium isotope dating of skeletal tests (strontium comprises an unstable radionuclide).  
(b) forms basis of strontium isotope stratigraphy in marine deposits, based on the correlation of strontium ratios.

- c. temperature of water and sunlight available for algal photosynthesis.

B. Degradation of Skeletal Matter into Skeletal Debris: Lime Sand and Mud

1. \*\* Almost all calcium carbonate produced in the ocean is related to metabolic secretion by organisms. Hence, most calcium carbonate forming limestones, is composed of skeletal debris.
2. Predators crush hard shells of organisms, eating soft tissue, thus in large part account for considerable creation of carbonate skeletal debris.
3. E.g. Modern coral reefs, associated with large volumes of sand-sized carbonate skeletal debris.
  - a. Attacked by predatory fish and boring predators, broken skeletal matter, in concert with high energy wave action-----net result: carbonate sediment production.
4. Predatory sediment factories: e.g. sponges, algae, fungi, worms, pelecypods: all act as borers and crush & chewers,
  - a. To digest soft tissue, must crush carbonate skeleton, swallow and excrete lime fecal pellets.

C. Biolamination of Lime Mud by Baffling Organisms

1. Algae comprised of filamentous physiological components, coated in a sticky mucilage for subsequent trapping of food and nutrients on shallow sea floor
  - a. Algae is photosynthetic, hence abundant in shallow photic zones, forming extensive mucilagenic sticky mats.
2. Algal mats trap fine-grained suspended lime mud, once mat is coated with mud, a second layer of mucilagenic material is secreted, and mud is bound between the organic layers.
  - a. Algal stromatolites: a finely laminated lithified deposit of alternating layers of lime mud and algal mucilagins. Comprising a marine "cabbage" like structure.
    - (1) Organic matter decomposes, leaving behind fine carbonate laminae.
    - (2) Stromatolites date back to Precambrian, and are found through present.

D. Pelletization of Lime Mud

1. Bottom lime mud feeders, eat mud, digest organic material, and pass calcium carbonate as compacted, rounded fecal pellets.

- a. Pellets may accumulate as bedded deposits, with subsequent pore-water cementing by calcium carbonate, thus preserving the pellet.

E. Bioturbation by Burrowing Organisms

- 1. Bioturbation: mixing of sediment by burrowing organisms (e.g. worms, molluscs, crustaceans, insects)
  - a. Net result of bioturbation: homogenization of sediment, creating massive, featureless deposit of lime mud/limestone.

F. Biochemical-Mineral Reactions: Effects of Microorganisms

- 1. Includes organisms such as bacteria, fungi, algae, lichen.
- 2. Microorganisms very important in the biochemical-mineralogical alteration process (e.g. soil formation, organic weathering)
  - a. Heterotrophic Bacteria: bacteria that obtain energy through the oxidation of organic matter---net byproduct --- organic acids, important weathering agent.
  - b. Autotrophic Bacteria: bacteria that obtain energy through oxidation of inorganic matter --- net byproduct --- inorganic acids (silicic, nitric), effective weathering agent.
    - (1) Sulfate reducing bacteria: through bacterial action, critters reduce sulfate to form hydrogen sulfide, and in presence of iron, pyrite (FeS) (source of acid mine drainage in Pennsylvanian coal deposits)... "rotten egg" smell associated with some limestones.
      - (a) also responsible for sulfate reduction above Gulf Coast salt domes, and formation of native sulfur deposits.
      - (b) Remember:  $\text{SO}_4^{-2}$  ion a somewhat major component of seawater.

III. CHEMICAL PROCESSES

The role of water in the sedimentary environment is obvious, not only provides medium of transport, and ecological environment, also provides physical medium for physicochemical reactions within pore fluids (water contained within pore spaces of sediment), as well as primary geochemical reactions resulting in the direct precipitation of mineral matter (e.g. evaporites).

A. Eh and pH Defined

- 1. pH Defined: the "activity" of hydrogen ions in a solution; defines the concepts of acidity and alkalinity.
  - a. "activity" = essentially equivalent to the effective concentration of a given ion in solution.

- (1) By definition, a pure substance such as water, or a solid mineral, has an activity = 1.0.
- (2) The lower the overall concentration of ions in solution, the closer activity = concentration.
  - (a) As concentration of dissolved ions increases, e.g. seawater, activity of a given ion is generally < than its concentration.
  - (b) activity accounts for resistive interference of given ions to reaction, by other electrostatically charged ions in solution.

$$\text{Activity Coefficient} = \frac{\text{effective concentration}}{\text{total concentration}}$$

- (3) Common activity coefficients of common ions found in "average" seawater:

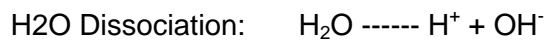
$$\text{Cl}^- = 0.63, \text{Mg}^{+2} = 0.25, \text{SO}_4^{-2} = 0.068, \text{CO}_3^{-2} = 0.021$$

- b. Hence pH = negative log base 10 of hydrogen ion activity of a solution:

$$\text{H activity} = 0.0001 = 10^{-4} \quad \text{pH} = -\text{Log}_{10} (10^{-4}) = 4 \text{ (acidic)}$$

$$\text{H activity} = 10^{-14} \quad \text{pH} = -\text{Log}_{10} (10^{-14}) = 14 \text{ (basic)}$$

#### Important reactions involving pH



Law of Mass Action:  $\frac{\text{Activity Products}}{\text{Activity Reactants}} = \text{constant}; \quad \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = K_w = 10^{-14}$

By Definition  $[\text{H}_2\text{O}] = 1.0$ ; hence  $\frac{[\text{H}^+][\text{OH}^-]}{1} = 10^{-14}$

At Neutral:  $[\text{H}^+] = [\text{OH}^-] = 10^{-7}$ ; hence  $[\text{H}^+] = 10^{-7}$ ;

therefore  $\text{pH} = -\log_{10}(10^{-7}) = -(-7) = 7.0$  standard pH units

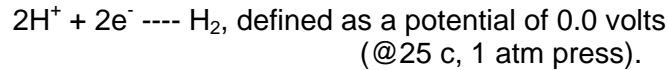
2. Eh Defined = "Redox" potential = Oxidation-Reduction Potential. A measure of the ability of a geochemical system to sustain oxidation and/or reduction reactions respectively.

- a. Oxidation: chemical reactions in which participating elements lose orbital electrons, hence valence numbers increase.

- b. Reduction: chemical reactions in which the participating elements gain orbital electrons, hence valence numbers are "reduced".

- c. Eh is measured as the electron concentration of a solution, hence Eh is measured as the "potential" (i.e. volts) of a solution across a standard hydrogen electrode.

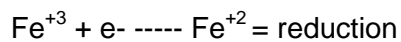
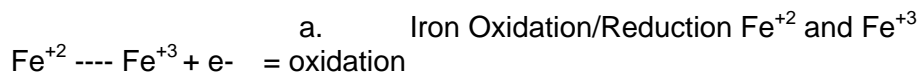
Standard reference reaction:



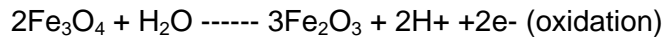
Eh > 0.0 volts, indicates an oxidizing condition (loss of electrons, oxides tend to form)

Eh < 0.0 volts, indicates a reducing condition (gain of electrons) (e.g. oxygen deficient compounds, eg. sulfides tend to form)

### 3. Common Oxidation-Reduction Reactions



- b. Magnetite oxidation to hematite:



- c. High Eh values (i.e. oxidizing conditions) are commonly associated with low pH (i.e. acidic conditions), and vice versa: low Eh values are commonly associated with high pH values.

- (1) Eh is measure of free electrons in solution, high Eh = higher tendency for loss of electrons, hence higher voltage
- (2) pH is measure of free protons in solution, in form of  $\text{H}^+$  protons, lower pH = higher no. of protons in solution

Hence: high Eh = high electron content, low pH = high proton content; solution maintains balance of electrostatic charge in that high Eh and low pH are naturally occurring tendencies in aqueous solutions.

## B. Calcium Carbonate Stability as Function of pH

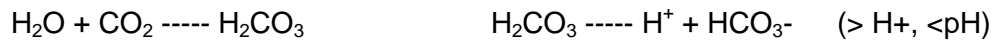
### 1. Definitions:

- a. Ion Solubility: the relative ability of ionic/elemental species to dissolve into solution. High Solubility = very dissolvable
- b. Mineral Precipitation: the crystallization of solid compounds from ionic species in a solution.
- c. Solution Equilibria

- (1) "Saturated" Solution: a condition in which the rate of precipitation = rate of dissolution for a given set of ionic species.
- (2) "Undersaturated" Solution: a condition in which a solid mineral species or compound will readily dissolve into solution, if soluble.
- (3) "Supersaturated" Solution: a condition in which a ionic species will readily combine to precipitate out of solution.

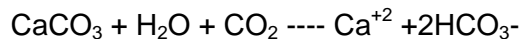
## 2. Important reactions involving CO<sub>2</sub>, H<sub>2</sub>O, CaCO<sub>3</sub>, and pH.

- a. Dissolution of Carbon Dioxide (gas) in water results in production of Carbonic Acid, which subsequently dissociates into free H<sup>+</sup> ions and the bicarbonate anion (HCO<sub>3</sub><sup>-</sup>), hence increasing hydrogen ion activity, and by definition decreasing pH (becoming more acidic).



- b. As Calcium Carbonate (solid) reacts with water in presence of free hydrogen ions, the solid Calcium Carbonate dissolves forming free Ca<sup>+2</sup> ions and free bicarbonate ions, hence consuming free hydrogen ions, decreasing hydrogen ion activity, and by definition increasing pH (becoming more basic). i.e. Calcium Carbonate acts to neutralize or buffer the solution by consuming hydrogen ions.

Dissolution of Calcite:



- c. A second reaction that may raise the pH involves the direct dissociation of water in presence of Calcium Carbonate as follows:



## 3. Calcium Carbonate-Seawater Systems

- a. pH of river waters ranges from slightly acidic (~6.0) to slightly alkaline (~8.0)
- b. pH of seawater is nearly constant, weakly alkaline at 8.3.
- c. Carbonate sedimentation is most significant in warm, well oxygenated, relatively shallow seawater: those conditions most conducive to marine organic activity.
  - (1) Near-surface tropical waters are supersaturated with respect to calcium carbonate, yet at pH of 8.3, direct inorganic precipitation calcium carbonate does not occur.
    - (a) Difficult for calcium carbonate to directly precipitate from solution due to:



- i) ionic blocking by presence of Mg ions
- ii) the strong buffering capacity of seawater: i.e. the ability of seawater to chemically maintain a steady range of pH (7.4-8.3).
- iii) organic coatings about precipitation "seeds" that prevents inorganic precipitation

#### 4. Dissolution of Calcium Carbonate as a Function of pH

- a. General relationship: as Carbon Dioxide content of water increases, hydrogen ion activity increases, pH decreases-----solid Calcium Carbonate undergoes dissolution
  - (1) Dissolved Carbon Dioxide content is temperature dependent, as T >, Carbon Dioxide content <, hence hydrogen ion activity decreases, pH increases (conducive to calcium carbonate precipitation)

As T <, Carbon Dioxide content >, hence hydrogen ion activity increases, pH decreases (conducive to calcium carbonate dissolution)

- b. At pH = 8.3, dissolution of aragonite and calcite particles by inorganic processes is for all practical purposes non-existent.
- c. However, results from the deep sea drilling project reveal: The porportion of calcium carbonate bearing sediments proportionately decrease with increasing depth as follows: (dramatic reduction at 4000-6000 m depth)
  - (1) Results suggest: dissolved Carbon Dioxide concentration increases with depth in seawater, hence hydrogen ion activity increases, pH descreases ----- Calcium Carbonate Dissolution
    - (a) Cold bottom waters related to oceanic circulation from polar regions, able to carry higher concentration of dissolved carbon dioxide (<T, >solubility of CO<sub>2</sub>).
    - (b) Submarine pressures may also be a factor in that higher pressures may effectively increase the efficiency of carbonic acid dissociation, hence lowering pH and calcium carbonate dissolution.

Hence >T, <P, <CO<sub>2</sub>, >pH, Calcium Carbonate Precipitation  
<T, >P, >CO<sub>2</sub>, <pH, Calcium Carbonated Dissolution

- (c) Carbonate-Compensation Depth (CCD): the depth at which the rate of dissolution of solid calcium carbonate equals the rate of supply: net effect is an effective depth at which calcium carbonate production is not possible through any process (organic or inorganic)

- i) Below the CCD, organisms are primarily soft bodied, and/or comprised of siliceous skeletal tests (Hence deposits of siliceous deposits, either organic, or inorganic (e.g. primary chert) are often interpreted as the product of deep marine sedimentation below the CCD.

## 5. Calcium Carbonate/Silica Stability as a Function of pH

- a. Although seawater is saturated with respect to calcium carbonate at "normal" pH of 8.3 (i.e. under saturated conditions, dissolved ions in solution should precipitate directly out of solution), however calcium carbonate does not precipitate directly from seawater (i.e. inorganically)
  - (1) It is thought that organic compounds prevent the nucleation of calcium carbonate crystals directly from seawater under normal pH conditions. Only at higher pH conditions will calcium carbonate directly precipitate from seawater (as the organic inhibitors are broken down at high pH).
  - (2) Experimentally determined that direct precipitation of calcium carbonate from seawater is only possible at a pH ranging from 9.0 to 10.0, i.e. moderately high alkaline conditions.
  - (3) High pH conditions of 9-10 in the marine environment commonly develop in association with photosynthetic organic activity, for e.g. associated with algal communities
    - (a) Algae + photosynthesis ----- effectively remove CO<sub>2</sub> from the seawater system, decreasing hydrogen ion activity, effectively raising pH, triggering inorganic chemical precipitation of calcium carbonate.

### b. Silica Solubility

- (1) Silica and silica dioxide are relative stable under acidic through moderately alkaline conditions (pH 1-9.0), however at pH of 9 and above, silica becomes soluble and readily dissolves to form Silicic Acid.

Hence, under high pH (alkaline) conditions of 9.0 and above: silica simultaneously dissolves as calcium carbonate precipitates inorganically.

Refer to attached figure...

## C. Inorganic Chemical Mineral Formation

### 1. Evaporite Minerals

- a. E.g. Gypsum (CaSO<sub>4</sub>·H<sub>2</sub>O), Anhydrite (CaSO<sub>4</sub>), and Halite (NaCl)

- b. Form through hyperconcentration of dissolved ions in saline brine waters, upon evaporation, evaporite minerals precipitate directly from solution (supersaturated solution) to form "salt" beds.
  - (1) Evaporite sequence as water is removed via evaporation
    - (a) Gypsum----- Anhydrite ----- Halite ----- MgCl-----KCl  
50% Evap-----80% evap-----95% evap
- c. Type of evaporite deposits a function of brine ionic composition and concentration of dissolved ions in solution.
  - (1) Water budget of basin influx vs. evaporation loss becomes a critical determining factor in the evaporite formation process
    - (a) Seasonal climatic perturbations are readily preserved in laminated/varved evaporite deposits

## 2. Authigenic Minerals

- a. Authigenesis: process of mineral formation that takes place within the pore spaces of sediment or rock body, subsequent to the deposition of that body (i.e. secondary mineral growth within previously deposited sediments/rock)
- b. Chemical reactions take place within the confine of interstitial pore solutions
  - (1) Interstitial = "between grains"
  - (2) Formation waters: waters contained in the primary pore spaces of sedimentary strata.
    - (a) Meteoric water: that water which has percolated into formation pore spaces from external, meteoric sources.
    - (b) Connate water: "fossil water" trapped in pores spaces of sediment and subsequently, sedimentary rock at the time of deposition.
- c. Authigenic Silicate Minerals (i.e. sedimentary silicates)
  - (1) Authigenic zeolites: a family or variable composition clay minerals: hydrous aluminosilicates containing calcium, sodium and potassium in varying proportions (varieties include clinoptilolite, phillipsite, laumontite, and analcite)
    - (a) Zeolite mode of origin
      - i) formed from pore-water reaction with volcanic glass/pyroclastics
      - ii) may also form in sediments associated with saline lakes

- (2) Authigenic feldspar: commonly occurring as K-spar ( $\text{KAlSi}_3\text{O}_8$ ) and albite plagioclase ( $\text{NaAlSi}_3\text{O}_8$ )
  - (a) Zeolitic alteration of volcanic glass can ultimately result in authigenic feldspar as a final end product.
- (3) Other Authigenic silicates include: quartz, zircon, Tourmaline, Muscovite

#### D. **Miscellaneous Chemical Reactions and Mineral Formation**

- 1. Marine Chemical Products of Uncertain Origins
  - a. Phosphorite (Calcium carbonate-phosphate: i.e. apatite) and Manganese Nodules (Manganese Oxides)
    - (1) Associated with quiet water conditions, and periods of very slow terrigenous sedimentation. Clastic sediments generally shut down chemical precipitation process.
      - (a) Phosphorites thought to be associated with oceanic circulation patterns and "upwelling" of cold, nutrient rich bottom waters rich in phosphate ions ( $\text{PO}_4^{-2}$ )
      - (b) Manganese nodules found in both marine and lacustrine conditions. Origin possibly related to submarine bacterial activity or volcanic activity
        - i) Precipitation process involves oxidation of  $\text{Mn}^{+2}$  to  $\text{Mn}^{+4}$
        - ii) Mn-Fe oxides precipitate about a grain nucleus, accumulating into a nodule shape with concentric internal "growth" structures.