

## Mineral-Fluid Interactions

- All Global-scale phenomena begin with atomic scale dissolution reactions!
- Mineral-fluid reactions control the dissolved load
- which also control:
  - quality of fresh water
  - development of soil
  - distribution of plant and nutrients
  - integrity of underground waste repositories
  - genesis of some ore and HC deposits
  - geochemical cycling of elements

- Minerals react with cells and fluids; implicated in cytotoxicity studies
- Derives influence from surface properties:

Chemical and Electrical  
Mechanical and Dimensional

- Mineral Surfaces are Complex
- Properties of surface dependent on:
  1. composition
  2. atomic structure
  3. surface charge
  4. microtopography
- Mineral surfaces are complex: structurally, chemically and topographically. As a result, reactivity can vary dramatically from one surface to another.

- Mineral surfaces are not static nor inert, they are dynamic and highly interactive with their environment.
- Foundation of surface interactions can be reduced to two fundamental mechanisms:
  - chemical species attachment to
  - chemical species detachment from
 mineral surfaces.
- All geochemical processes at mineral-fluid interfaces involve interactions at the atomic scale. This leads us to **Atomistic** approaches.
- Mineral reactivity depends on surface properties  
(distinctly different than those of the bulk properties):
  - composition
  - atomic structure
  - surface charge
  - microtopography

Reactions take place on scale of few - tenths nm.

## 1. Surface Composition

- Fresh surfaces are highly reactive due to under-coordinated surface atoms and "dangling" bonds
- Results in surfaces covered with a layer of foreign material which passivates the surface.

This process is instantaneous and ubiquitous.

Two other surface compositional modifiers:

- (a) sorption of other species besides adventitious contaminants
- (b) desorption of components

Lateral compositional heterogeneity also affects surface reactivity.

**ergo. surface compositions are essentially never representative of the bulk**

## 2. Surface atomic structure

- Surface atomic structure is different from the bulk structure,... it is a **defect!**
- Relaxation of atoms occurs at the surface which results in changes of bond angles, length; Varies with symmetry of xl.  
Surface atoms may also change position to better accomodate sorbed species.  
**ergo. surfaces dynamic and interactive**

## 3. Surface microtopography

- Most surfaces are **rough** on a molecular scale
- Surface roughness provides reaction flexibility not apparent on flat surfaces
- Models of surface shape contain:
  - terraces: flat areas
  - steps: separate terraces. 1-many atomic layers high
  - kink sites: where step changes direction twice in short distance
  - adatom: an atom added to step or terrace, or admolecule.
  - vacancy: atomic or molecular-sized hole in terrace
- Importance of surface shape

Atoms that compose terraces are common; have higher coordination than other surface sites.

- at top edge of step, nearest neighbors is reduced
- atoms at outer corners of kink sites have even fewer neighbors.

- terrace adatoms have fewest nearest neighbors

**surfaces with lower coordination are more reactive**

#### 4. Surface Charge

- All surfaces are electrically charged
- Surface reactions proceed through a series of steps that are pH dependent.
- exact speciation, popln depends on specific material
- EDL = electronic double layer  
consists of static charge on mineral surface and diffuse later of counter ions adjacent to this in soln
- Zeta potential = charge is related to charge at slipping plane
- Theory on sorption phenomena  
non-specific adsorption = species in soln sorb to any surface with opp. chg.

sorption densities decrease with increasing ionic strength due to competition effects.

specific adsorption = species in soln do not adsorb according to surface charge.

### Mineral Surfaces and Biological Activity

- Activity dependence on surface composition  
Some elements are selectively leached from minerals. ex. Mg from chrysotile fibers  
amount of leaching varies from fiber to fiber and along length of single fiber  
Sorption of certain chemicals inhibits reactivity and toxic nature. e.g. chrysotile, erionite
- Activity dependence of surface atomic structure  
studies of quartz polymorphs have different cytotoxicity; perhaps due to different atomic packing densities.

- Activity dependence of surface microtopography  
surface topo controls surface chemistry.  
no studies available for biolo. activities.
- Activity dependence on surface charge  
S.C. originates from chemical interactions between surface and its surroundings.  
perhaps due to their acid/base characteristics and ability to release H
- Cf Chrysotile and Croco.  
chry: OH on back of sheet. rolling produces edges of Si tetr and Mg octa.  
si-O immediately coordn with H. ergo surface site carries weak acid character.

## SUMMARY

- Mineral surfaces are dynamic and tailor themselves to the surroundings. They are complex and heterogeneous.
- Same minerals from different localities may be very different biological activities due to minor and trace element chemistry and physical properties. ergo. differences in cytotoxicities and carcinogenicities.
- Toxicity and pathogenicity depend on
  - mechanical/dimensional properties: shape, stiffness, flexibility, fracture characteristics
  - Chemical properties: dissoln mechanisms and kinetics,
  - surface properties: composn, atomic structure, microtopo, charge and dependence on Ph, durability, trace leements and phases.
- note that many of these features change with time.
- reason that glass fibers are not dangerous, is they have little mechanical integrity, adn their rate of dissolution if very high!

## Methods of Modeling Surface Reactions

- Transition State Theory:

Permits calc of kinetic rate constants based on ID of activated complexes whose formation and destruction control reaction rates.

Only correct where elementary reactions can be defined, and partition coefficients and vibrational properties deduced.

- Ab initio calculation:

Evaluate interatomic forces within molecular clusters based on first principal assumptions in quantum mechanics.

Can also be applied to determine of the energetics associated with chemisorption processes and dissolution and ppt kinetics.

- Molecular dynamics and Monte Carlo calculations

Complimentary approaches permitting dynamic modeling of the physical and chemical characteristics of surfaces for given time steps.

MD calc. the posn and vel of individual particles or atoms; calculated as function of time based on equilibrium and non-equilibrium interatomic potentials within a set of initial and boundary conds.

Monte Carlo calc. are a stochastic approach which simulates the dynamic rate of ion attachment, detachment, and diffusion at the surface. Based on the probability of interaction determined by potential energy involved.

These theories have the ability to link atomistic or microscopic simulations with the macroscopic thermodynamics of mineral-water interfaces. e.g. soly.