Lecture N_4

RT Modeling

A reactive transport model is a numerical simulation where fluid-flow, heat transfer, mass transport and chemical reactions are simulated. An initial model is created, which specifies the mineralogy in different regions of the model, as well as a temperature and pressure regime. Porosity and permeability across the model are also specified. The first step of the reactive transport modelling process is to chemically equilibrate the initial mineralogy according to thermodynamic principles. Once this initial equilibration has taken place, fluid within the model can be transported. A series of transport steps are undertaken, where fluid is moved around the model according to the inbuilt fluid modelling code. After completing the transport stage, another chemical equilibration step is undertaken, completing the first timestep of the model. The reactive transport model then continues to perform additional timesteps, first transporting fluid and then calculating chemical reactions between the transported fluid, its contained species and and solids within the model. The reactive transport model is halted after a set period of geological time has been simulated, generally in the order of 1 to 10 My (Chopping 2008).

Fluid Flow is driven by gradients in hydraulic potential, which in turn are influenced by

- Deformation (extension/compression)
    - Fluid pressure decreases with dilation, increases with compaction.
        - Fluid moves towards dilatant sites (e.g. dilatant jogs or releasing bends in faults)
        - Downward flow during crustal extension
        - Upward flow during crustal shortening
        - Upward flow during gravitational compaction of sediments

    - Fluid flow rate depends on strain rate
    - Deformation also influences permeability and therefore influences pathways.
- fluid production (magmatic/metamorphic)
    - Converting solid to fluid generally leads to an increase in volume, therefore the fluid flows away from regions that produce fluid
    - If fluid cannot escape as fast as it is produced, fluid pressure will increase, resulting in:
        - Veins, breccias, fault reactivation
        - Rotation of principle stresses as the rock expands
    - Examples of fluid production
        - Production of hydrocarbons
        - Metamorphic devolatilisation
        - Magmatic volatiles
- fluid density (which depends primarily on temperature)
    - Density-driven flow = convection
    - Temperature and salinity are key controls
    - Horizontal variations in fluid density always result in convection
    - e.g. temperature gradient around an intrusion
    - Vertical variations in fluid density drive convection if they are big enough (critical Rayleigh number)
    - Typical geothermal gradients are insufficient to drive convection unless the permeability is above "average" e.g. in faults
- topography
    - Sloping water table
        - Horizontal component to fluid pressure gradient
        - Fluid moves down and out from high ground towards lower ground
    - Fluid source = meteoric water
    - Topographically-driven flow can penetrate to several km

The driving forces for fluid flow can be expressed in Darcy's Law (Figure1). The aforementioned parameters not only influence the fluid pressure gradient and fluid density, but also permeability and viscosity (Sheldon et al 2008).

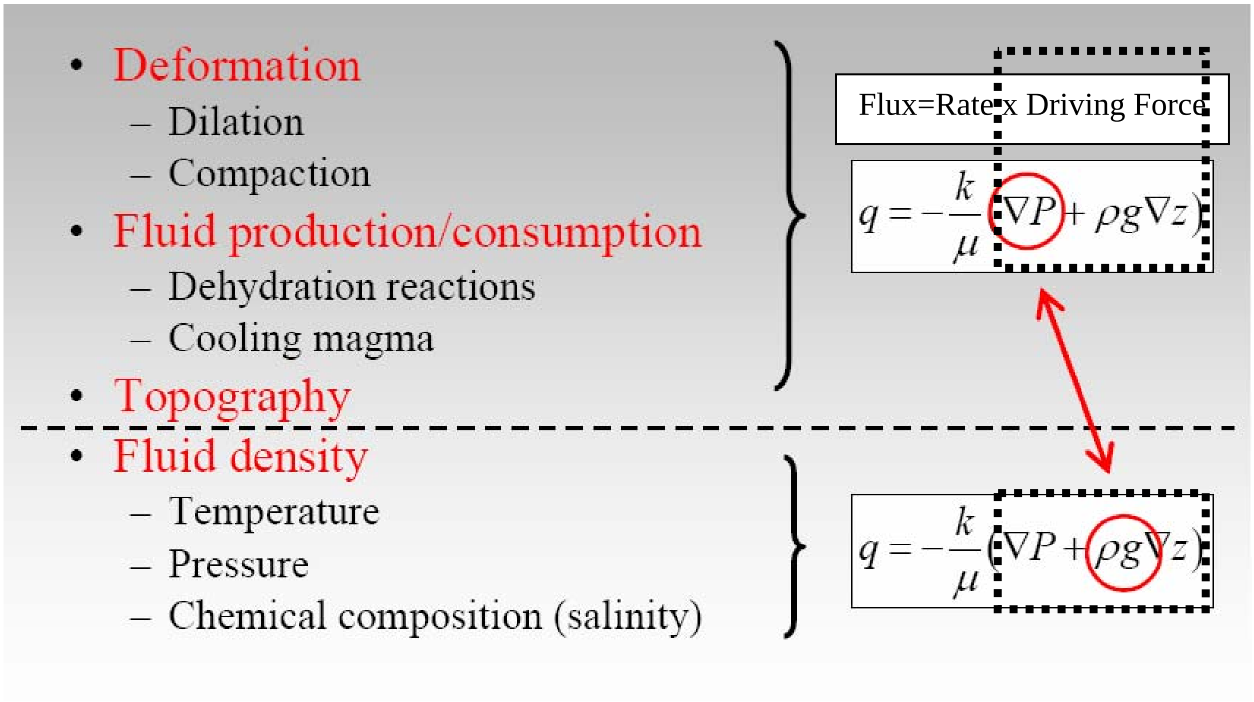

Figure 1: Parameters influencing fluid flow and their relation to Darcy's Law

Heat transfer involves 3 processes:

- Conduction is a diffusive process: 'heat will flow from hot to cold'. Geotherms are conductive. **Fourier's Law** defines specific heat flow q_i (heat flow normalized by area) as the product of the thermal conductivity tensor λ_{ij} and the temperature gradient vector dT/dz:

$$q_i = -\lambda_{ij}\left(\frac{\partial T}{\partial z}\right)$$

- Advection is heat transport by a solid, fluid or gas. Non-Isothermal flow is always associated with advective heat transport. In porous medium flow **Darcy's equation** describes the linear relationship between the specific fluid discharge q and the pressure gradient over a wide range of pressure gradients:

$$q = -\frac{\kappa}{\mu}(\nabla P - \rho_f g)$$

- Convection is density driven flow. Density varies with P, T, and chemistry, so we are looking for gradients in P, T and chemistry. Convection in geological systems occurs when the Rayleigh number > $4\pi^2 \sim 39.5$ (critical value).

$$Ra = \frac{\rho^2{}_f c_p \alpha k H \Delta T g}{\mu K}$$

Mass transport

- Molecular diffusion is solute transport down concentration gradient (i.e. tea-bag in hot water) and results from a gradient in chemical potential or concentration. Solute flux is directly proportional to the concentration gradient. The physical process driving molecular diffusion is the random motion of ions in solution. Ions in a region of higher concentration will eventually mix with ions in a region of lower concentration to create an equal distribution in space.
- Advection describes transport of solutes by movement of medium (e.g. fluid). Advection and diffusion compete as transport processes in hydrothermal solutions. Depending on the diffusive flux and the hydraulic flux, one is more important than the other and they may operate at different scales and directions!
- Dispersion describes the effect of an inhomogeneous flow field. The microscopic heterogeneity of porous media creates groundwater velocity fields, i.e. a variance in the groundwater velocity around the average linear velocity. These variations create an indirect transport process called mechanical dispersion. Because of mechanical dispersion, a concentration front that originally is sharp will spread out or disperse as it is transported by advection with the groundwater. Molecular diffusion depends only on a concentration gradient and is dominant at lower velocities. Mechanical dispersion dominates at higher velocities. At the pore scale, diffusion and mechanical dispersion are interconnected and can only be artificially

separated. The combined effects of mechanical dispersion and molecular diffusion are called hydrodynamic dispersion.

Chemical reactions

- At chemical equilibrium, the potential energy, the Gibbs free energy, G, of the chemical system is minimized. The Gibbs free energy is related to:
  - enthalpy H (representing thermal energy),
  - temperature T (in Kelvin), and
  - entropy S (representing disorder or randomness of a system)

$$\mathbf{G = H\text{-}TS}$$

- Chemical potential μ is the driving force of chemical reactions and in turn depends on the dimensionless activity, a, of the dissolved solution species via the following equation, with the chemical potential at standard conditions (μ°) and the ideal gas constant, R.

$$\mu_i = \mu_i^\circ + RT \ln a$$

- The saturation index, SI, reflects the saturation state of a solution with respect to a mineral phase. Precipitation reactions are essential for development of ore deposits. They can be estimated using saturation indices calculated on the basis of data from chemical analyses.

$$\mathrm{SI} = \log \frac{\text{ion activity product}}{\text{solubility product}}$$

SI = 0 → thermodynamic equilibrium

SI > 0 → solution supersaturated → precipitation

SI < 0 → solution undersaturated → dissolution

- Rates of mineral reactions fall into 3 goups:
  1. reaction rates may be so slow relative to the time period of interest that the reaction can be ignored altogether
  2. reactions can be too fast to maintain equilibrium

3. the remaining reactions. Only those require a kinetic description (Figure 2).

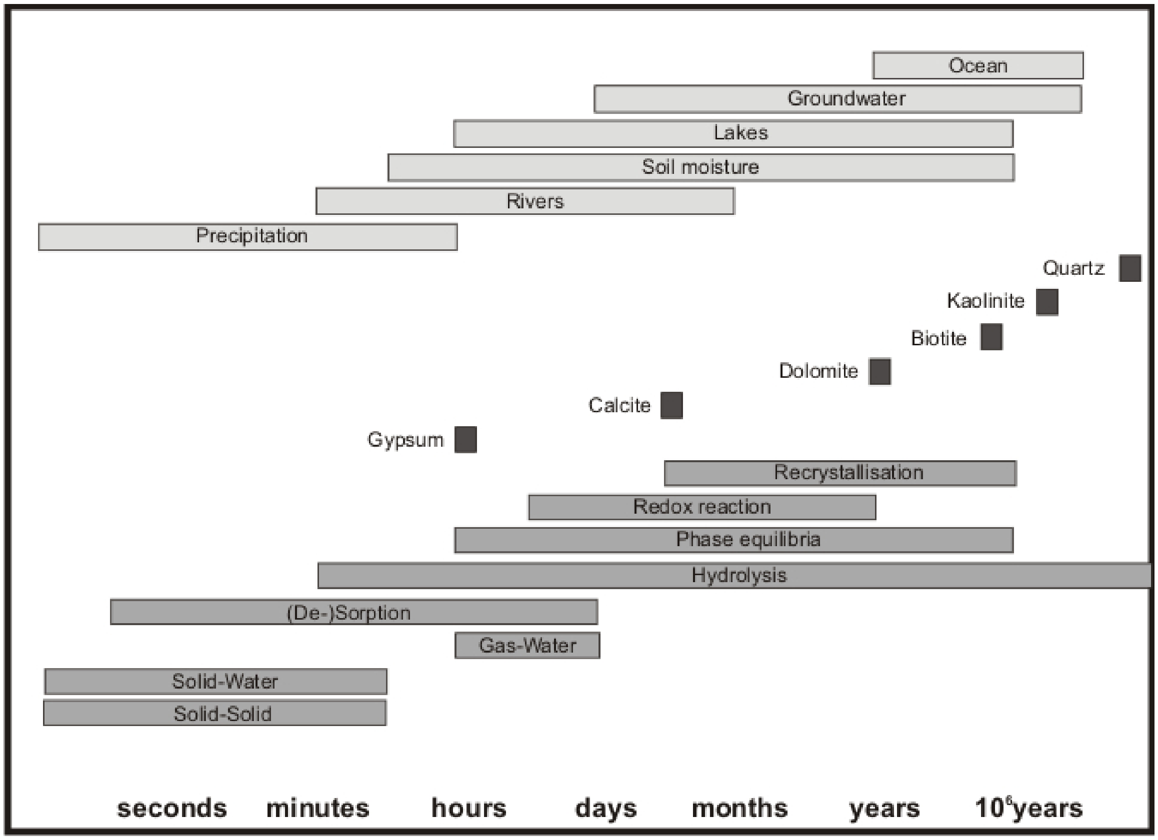

Figure 2: Reaction rates (after Merkel and Planer-Friedrich 2005)

Five fundamental end-member types of reactive transport environments

- Flow across mineralogical boundaries
- Moving reaction fronts
- Reactions within thermal gradients
- Mixing zone environments
- Local flow enhancement due to faults

References:

Chopping, R., Cleverley, J.S., Henson, P.A., and Roy, I.G. (2008). Reactive transport models: from geochemistry to geophysics to exploration targets. pmd*CRC Final Report: Project Y4 PART III.

Merkel, B. J., and Planer-Friedrich, B. (2005). Groundwater Geochemistry: A Practical Guide to Modeling of Natural and Contaminated Aquatic Systems, Springer.

Sheldon, H. A., Zhang, Y., and Ord, A. (2008). Archaean gold mineralisation in the Eastern Yilgarn: Insights from numerical models. pmd*CRC Y4 Project Contribution to section III of the final report**:** 17p.