Stable isotopes as tracers of reaction kinetics

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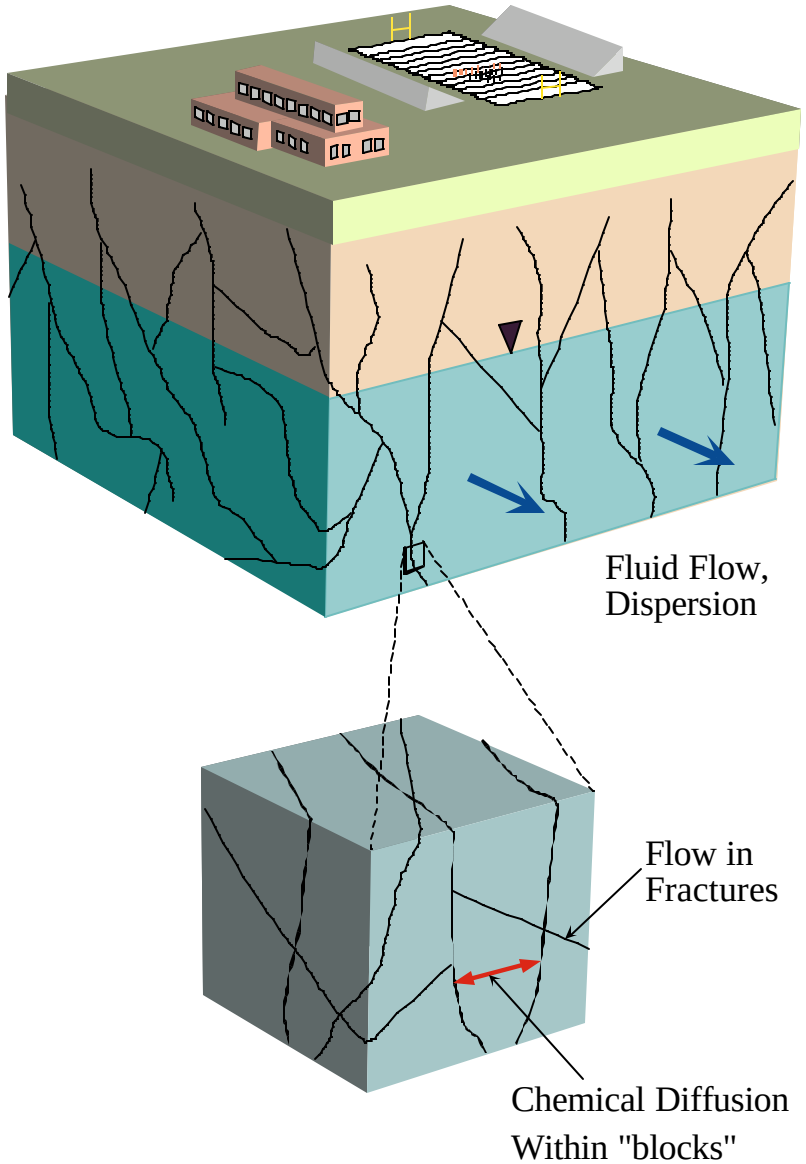
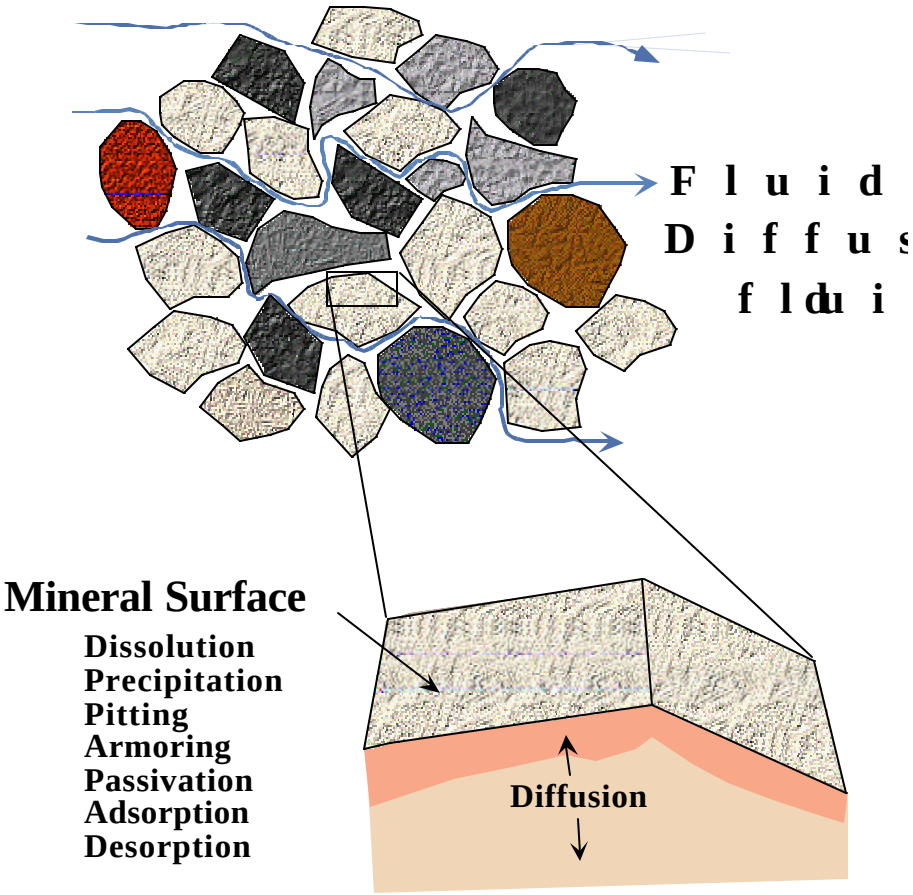
Issues

- Volume-averaged rates of reaction (ion exchange and solution - precipitation) are difficult to predict because they depend on several parameters
  - Thermodynamic departure from equilibrium
  - Effective surface area of reaction
  - Non-uniformity of flow
- In many cases it is difficult to predict which reactions will be most important
  - Uncertainties in mineralogy
  - Uncertainties in fluid chemistry

Field Scale Effects



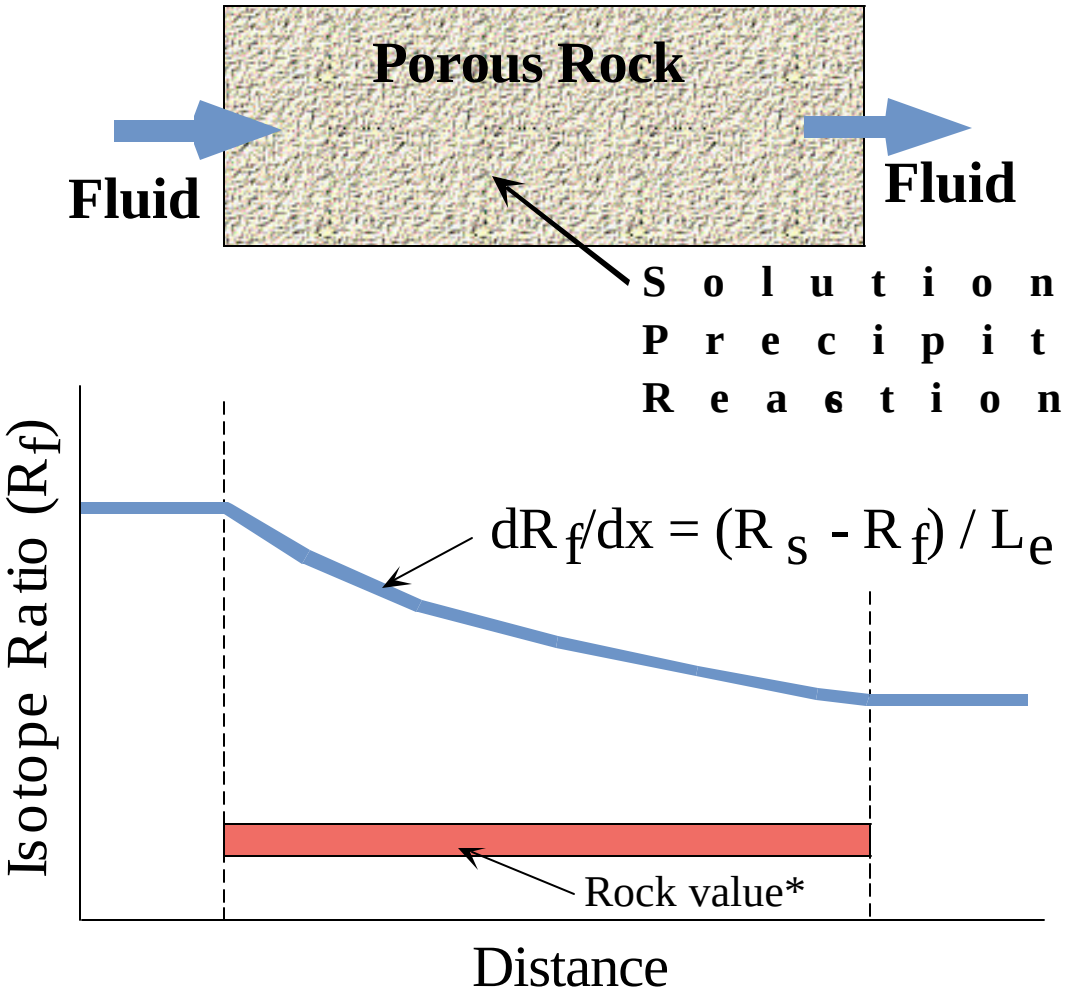
Grain Scale Processes in Rocks



Value of isotopes

- Respond monotonically with reaction progress
- Different elements can be used to monitor different reactions
  - Carbonate dissolution or precipitation
  - Weathering reactions of feldspars
  - Evaporation-condensation
- May be possible to evaluate scale of flow non-uniformity (dual-permeability behavior)

Isotopic Reaction Length

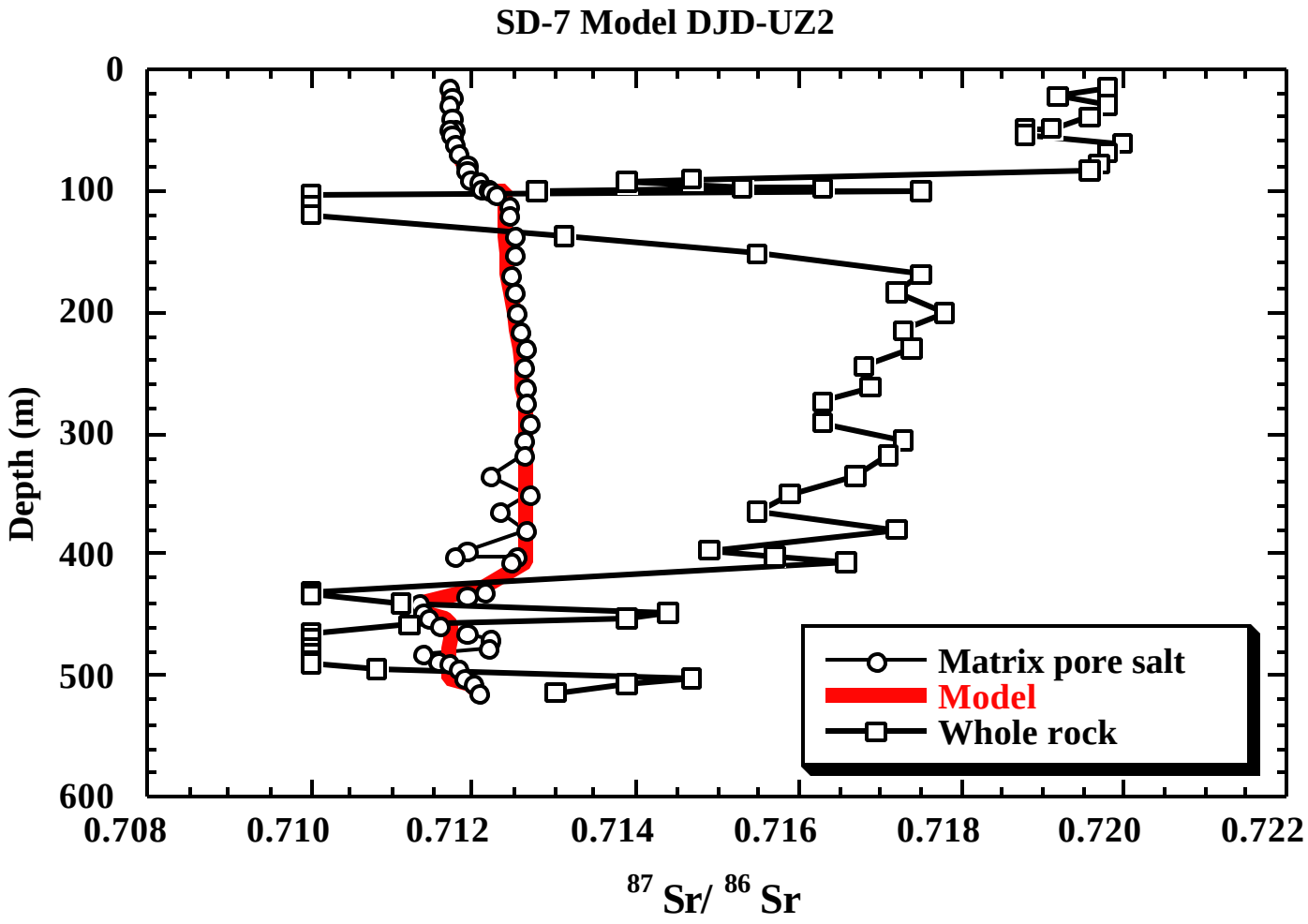


$$L_e = \frac{v_f \, ? \, ?_f \, C_f}{R \, ?_s \, (1-?) \, C_s}$$

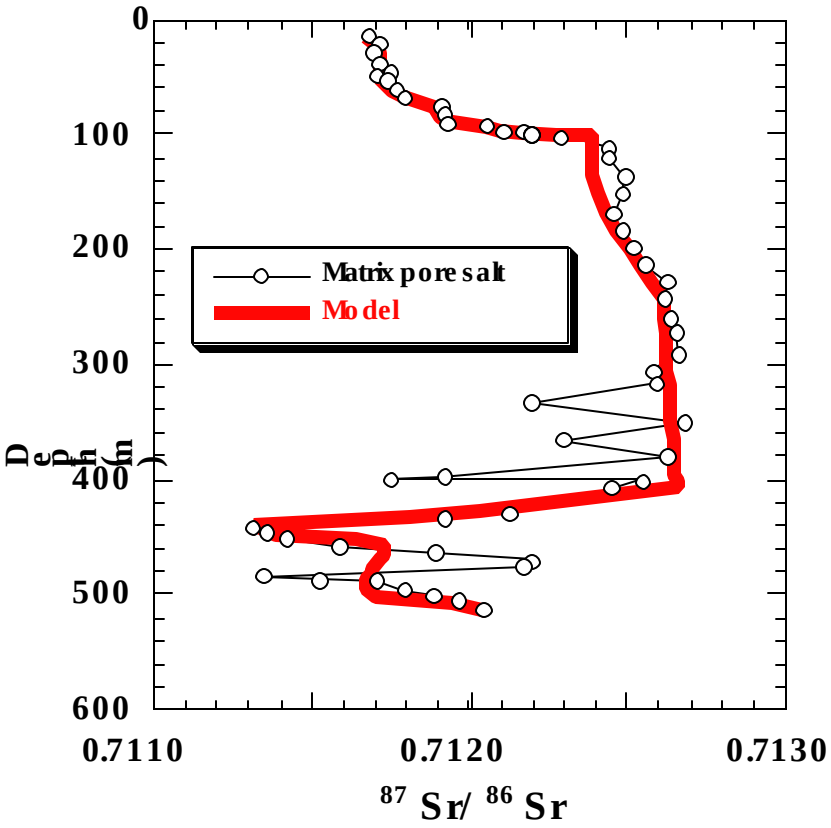
What can be measured?

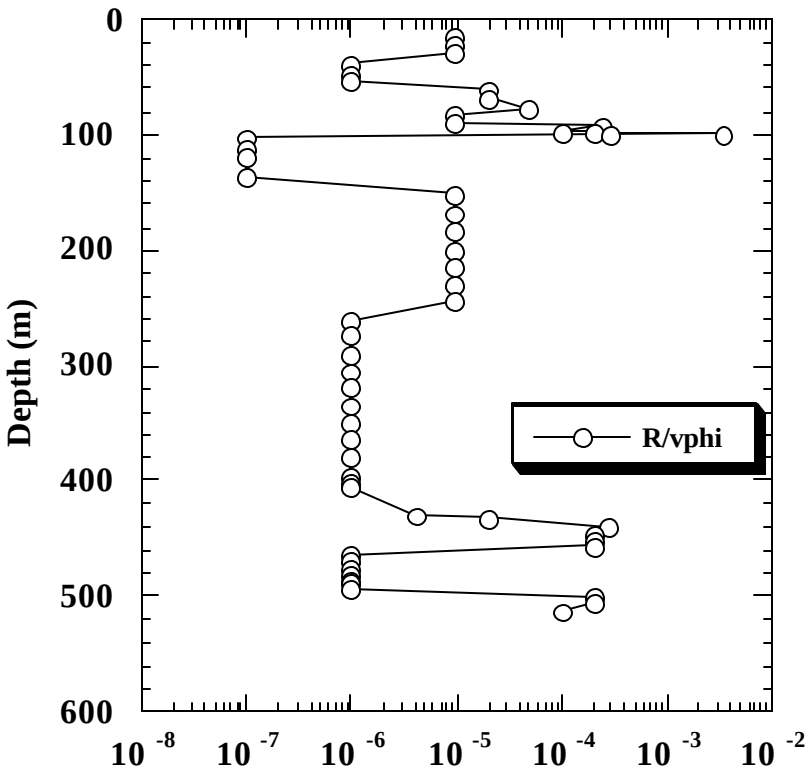
- Changes in fluid composition versus distance or time
- Lengthscale of change gives R/v_f
  (volume averaged: reaction rate / fluid velocity)
- Timescale of change gives vol. ave. reaction rate
- Isotopes of potential interest:
  (O, D, ^{13}C, ^{14}C, ^{15}N, Sr, Ca, U, others)
- In some cases tracers need to be added, in others natrual variations may be useful
- Requires fluid (or vapor) sampling

Yucca Mountain example:
Data from USGS, modelling At LBNL

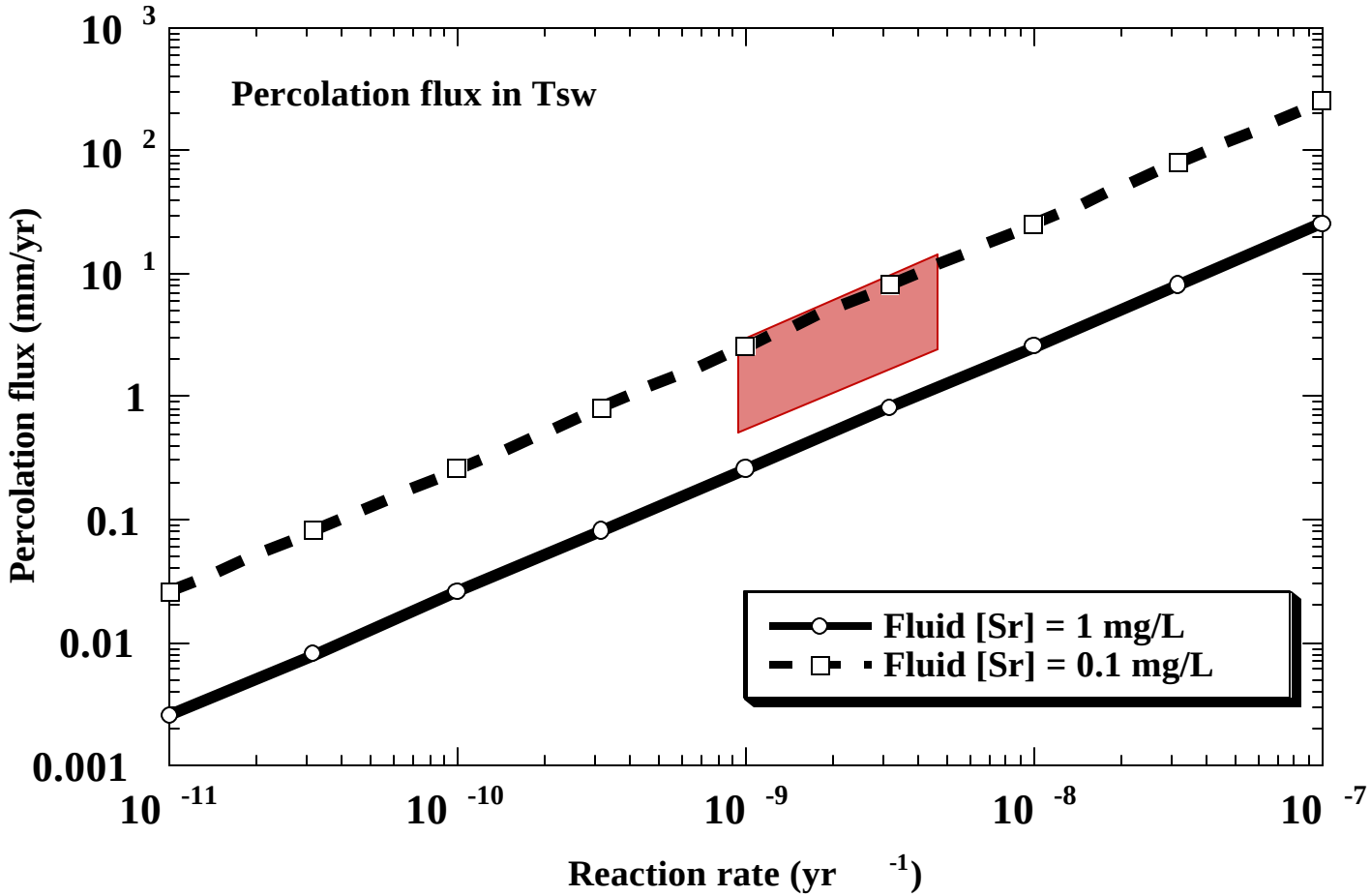


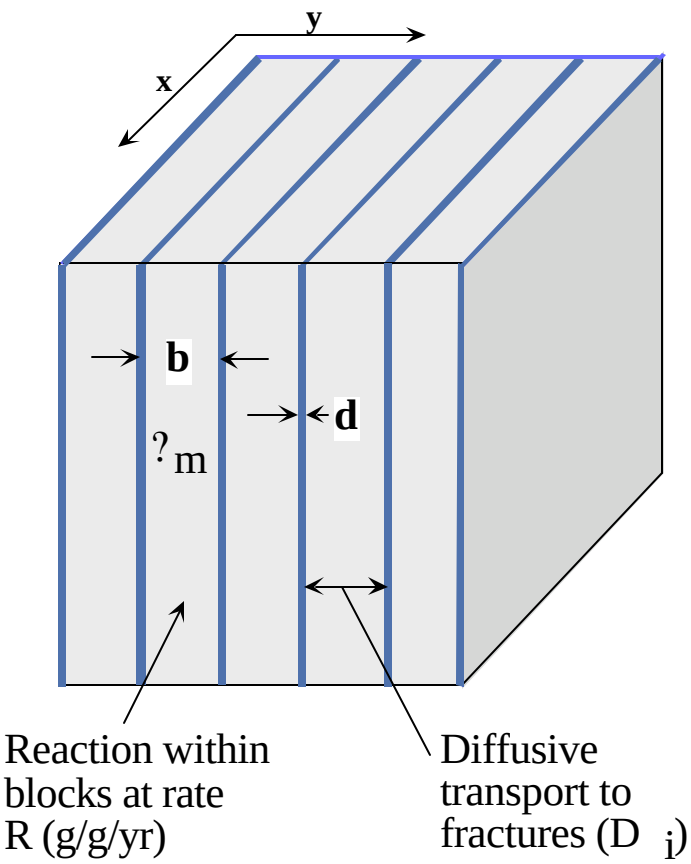
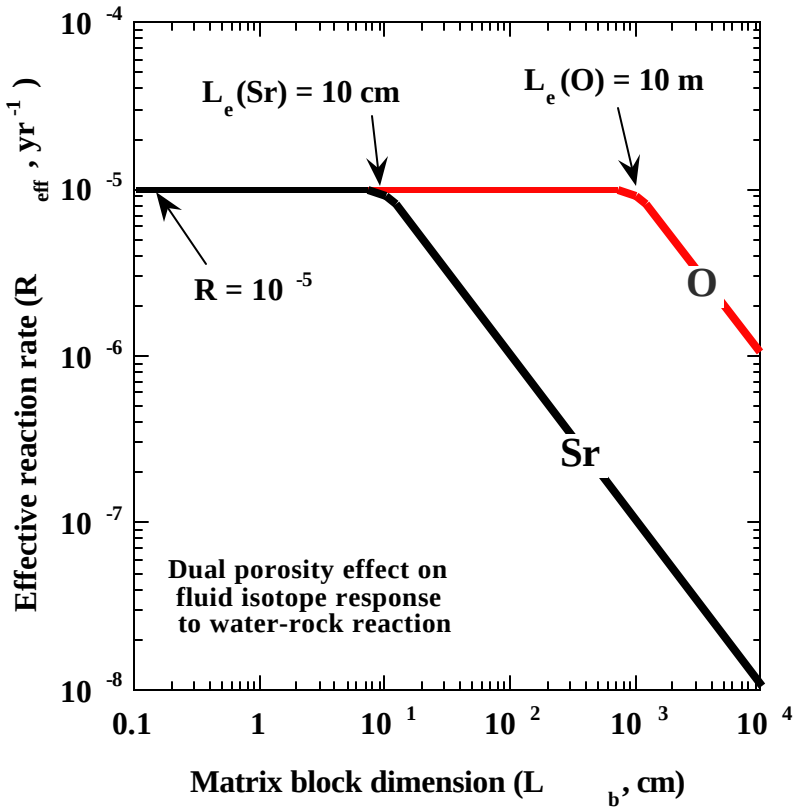
Variations in Sr exchange rate with depth and lithology At Yucca Mountain





The relationship between percolation flux and Sr exchange rate can be constrained (~ weathering rates of glass and feldspars)



Effects of focussed flow may be discernable

Dual Porosity Model