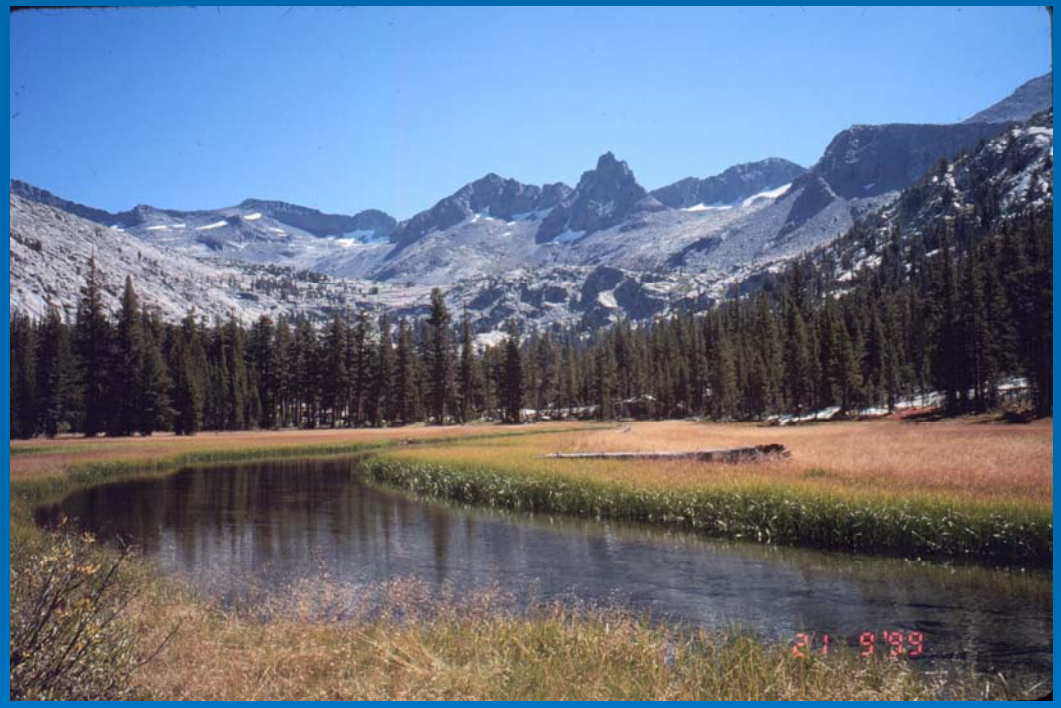
Sensitivity of Mineral Weathering Rates to Annual Variations in Runoff



David Clow[1], Sarah Godsey[2], Jim Kirchner[2]

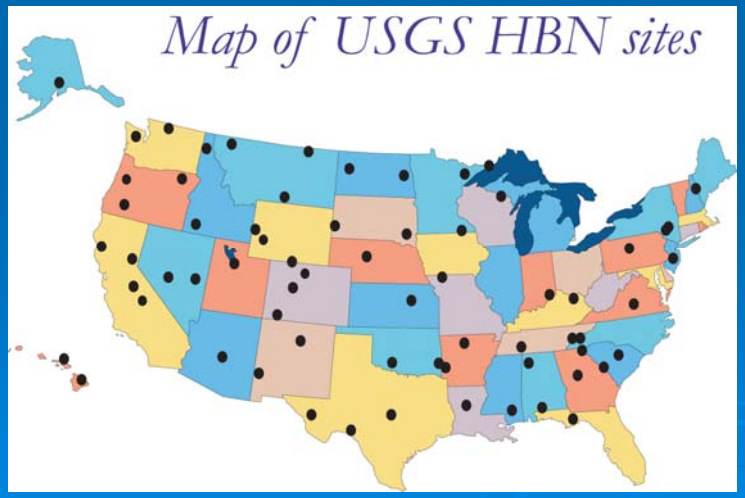
1. U.S. Geological Survey, Denver
2. University of California, Berkeley

Observations at various scales

- US Hydrologic Benchmark Network
- Plot Scale

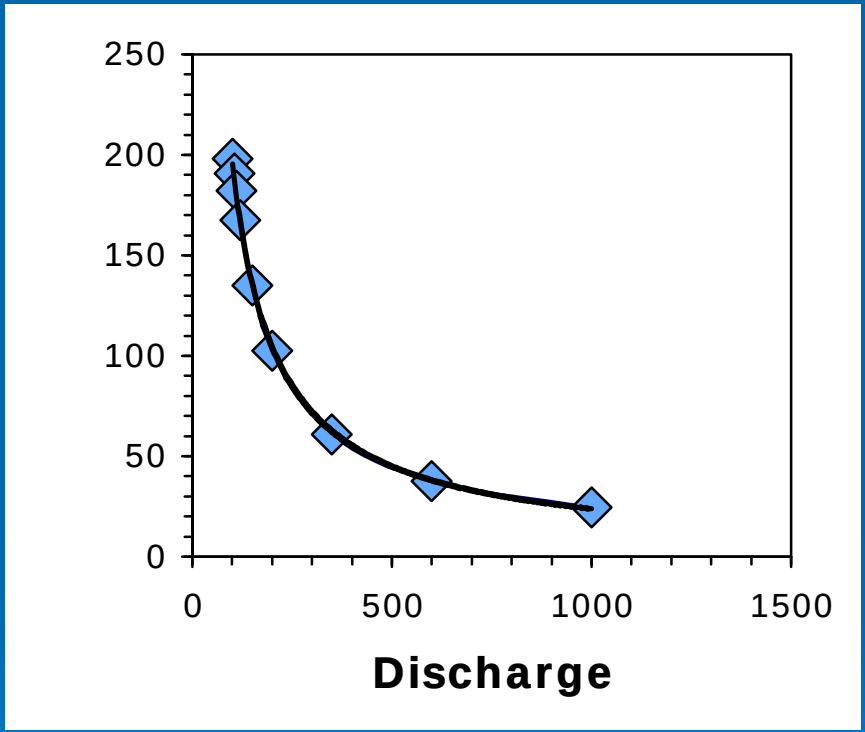
USGS Hydrologic Benchmark Network

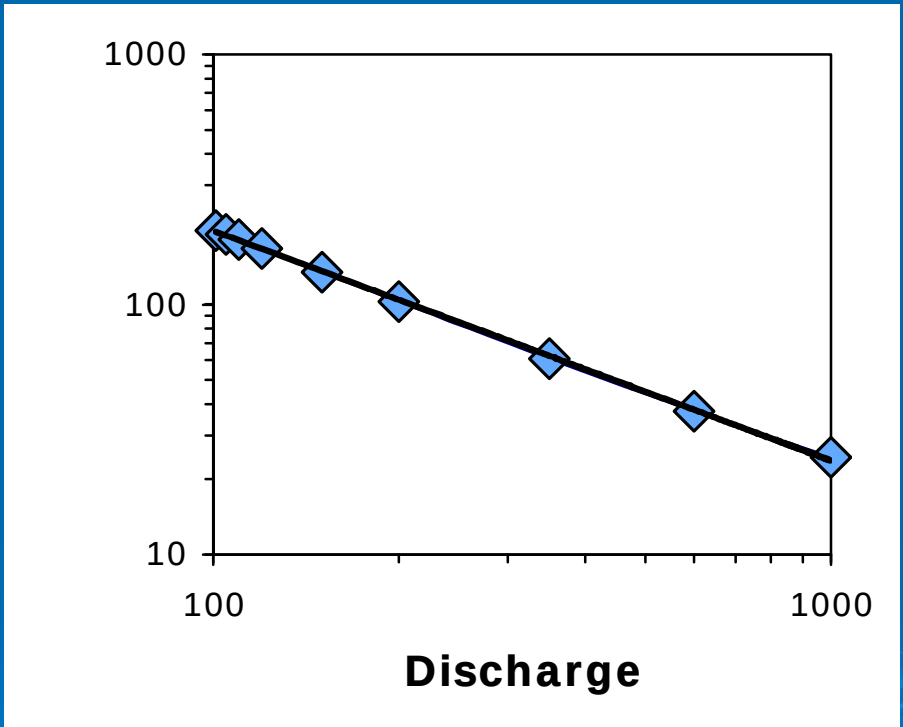
- Range of bedrock types, but mostly granitic
- Undeveloped basins
- N = 59



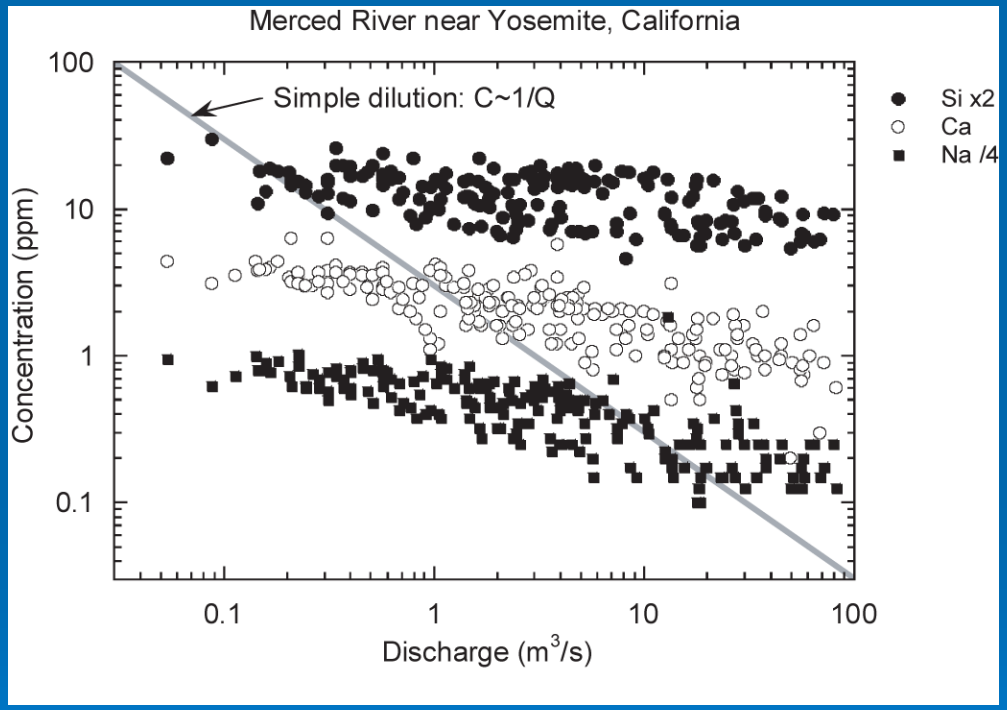
Big Thompson River, Colorado

Simple Mixing
2 Component





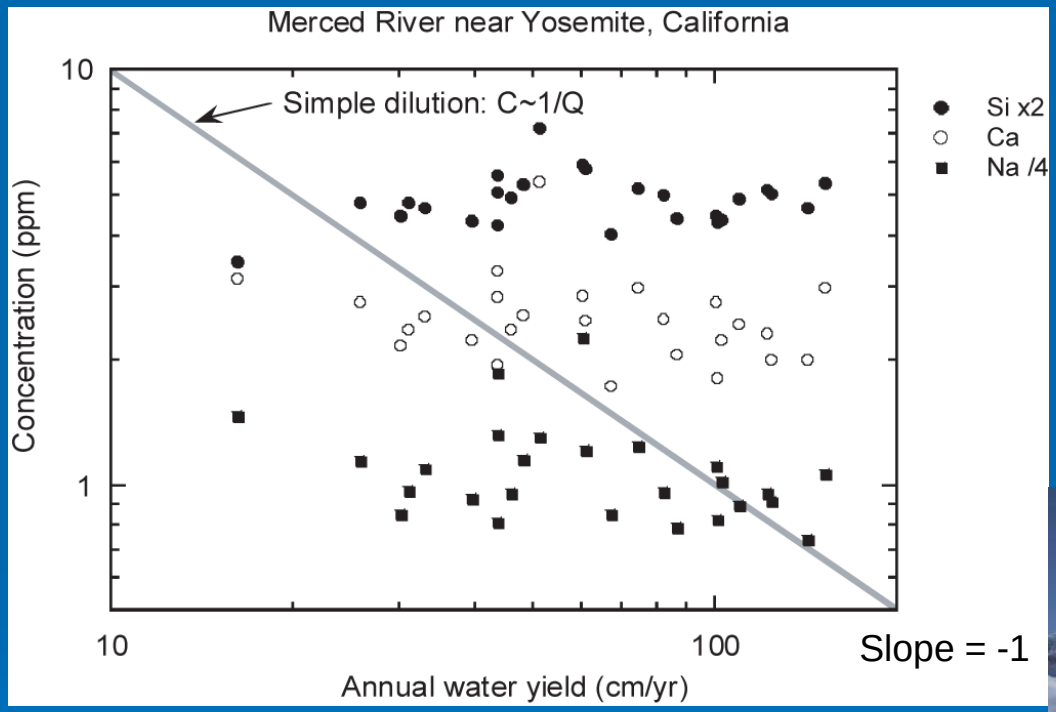
Concentrations vary much less than discharge (streamflow)



- Note log-log scale

From Godsey, Kirchner, and Clow, in prep.
Concentration-discharge relationships reflect chemostatic characteristics of catchments

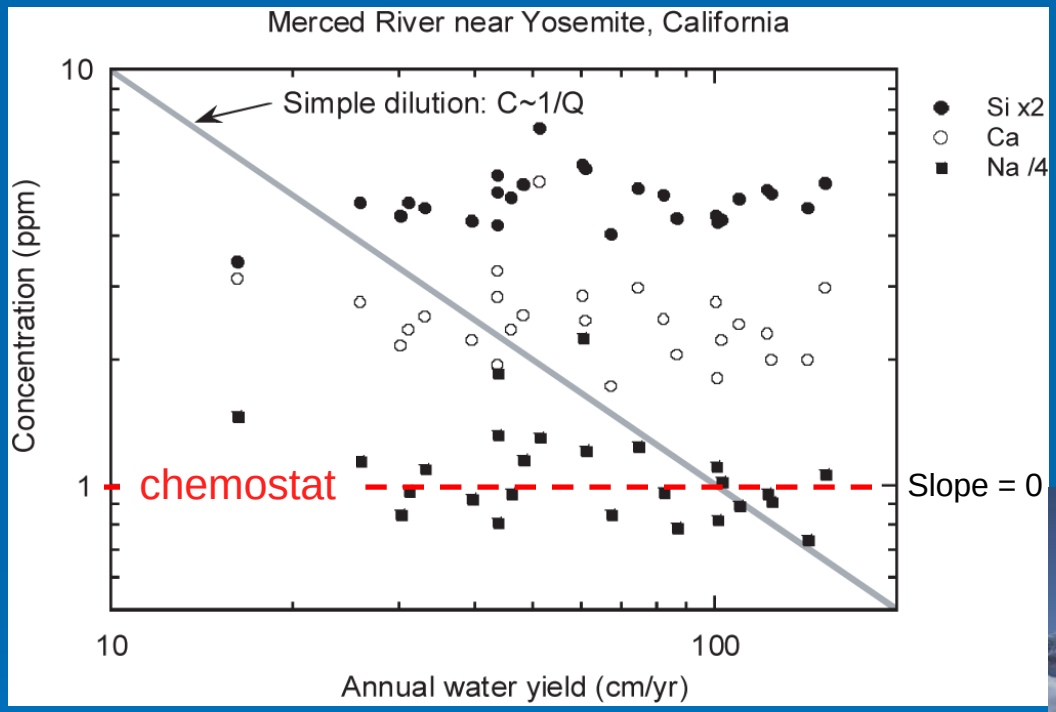
Concentrations Invariant at Annual Scale as well



- Slope of log C:log Runoff provides clues
  - Slope = -1 for simple dilution

From Godsey, Kirchner, and Clow, in prep.

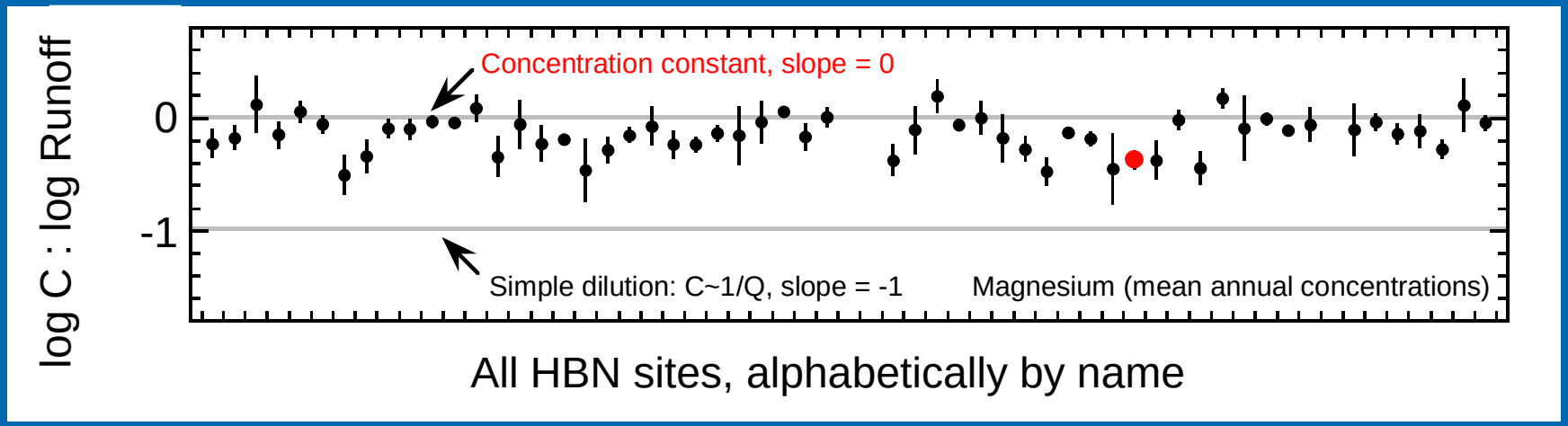
Concentrations Invariant at Annual Scale as well



- Slope of log C:log Runoff provides clues
  - Slope = -1 for simple dilution
  - Slope = 0 for perfect chemostat

From Godsey, Kirchner, and Clow, in prep.

Most HBN basins show chemostatic behavior



- Consistent with transport control on weathering rate
- But, outlet chemistry solutions are far from saturation…

From Godsey, Kirchner, and Clow, in prep.

“Put a grain of feldspar in a beaker of water and stir for 10^5 years”

Tim Drever

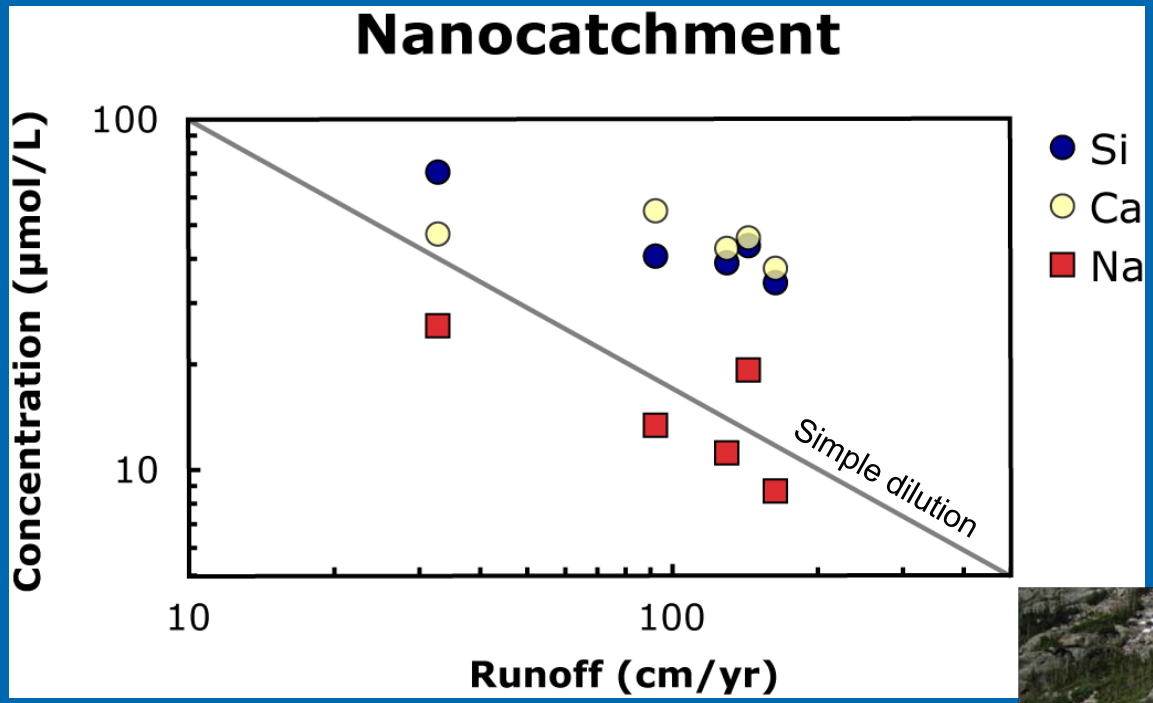
- Weathering reaction will slow down as solution approaches saturation

“Put a grain of feldspar in a beaker of water and stir for 10^5 years”

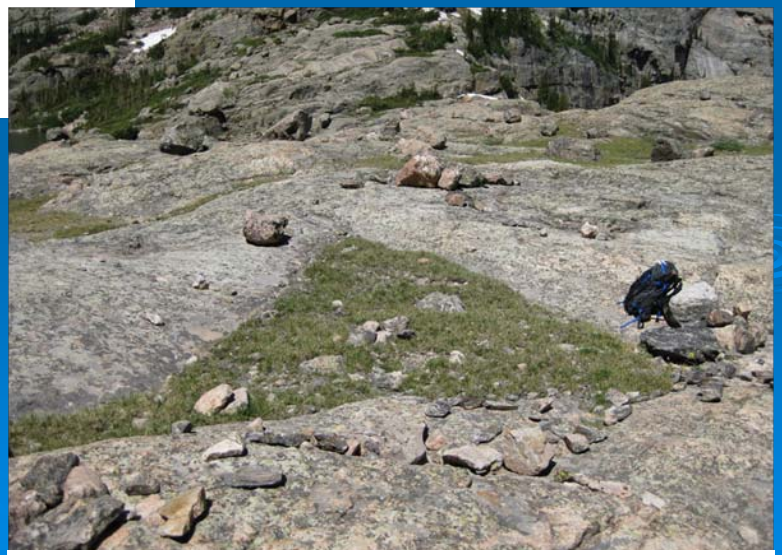
Tim Drever

- Weathering reaction will slow down as solution approaches saturation
- How long does it take?

Flowpath length matters



- Equilibrium length (E_l) is length required to achieve saturation
- If flowpath > E_l, weathering reactions will be transport controlled
- Equilibrium length varies by mineral
  - $E_{l\text{-calcite}} < E_{l\text{-albite}}$

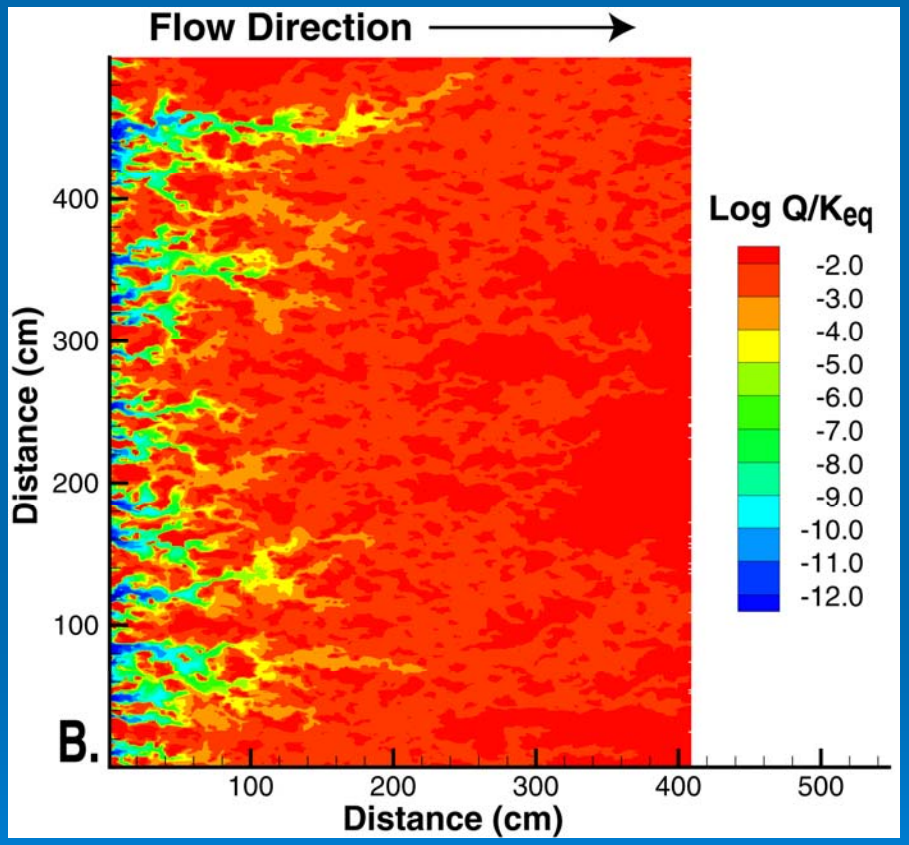


Nanocatchment (3m x 3m)

There is a distribution of residence times and saturation indices in natural systems

- Advection dominates in macropores
- Diffusion dominates at internal sites
- Mechanism may switch at intermediate sites depending on flow rate

2-dimensional Model of Saturation State for Plagioclase

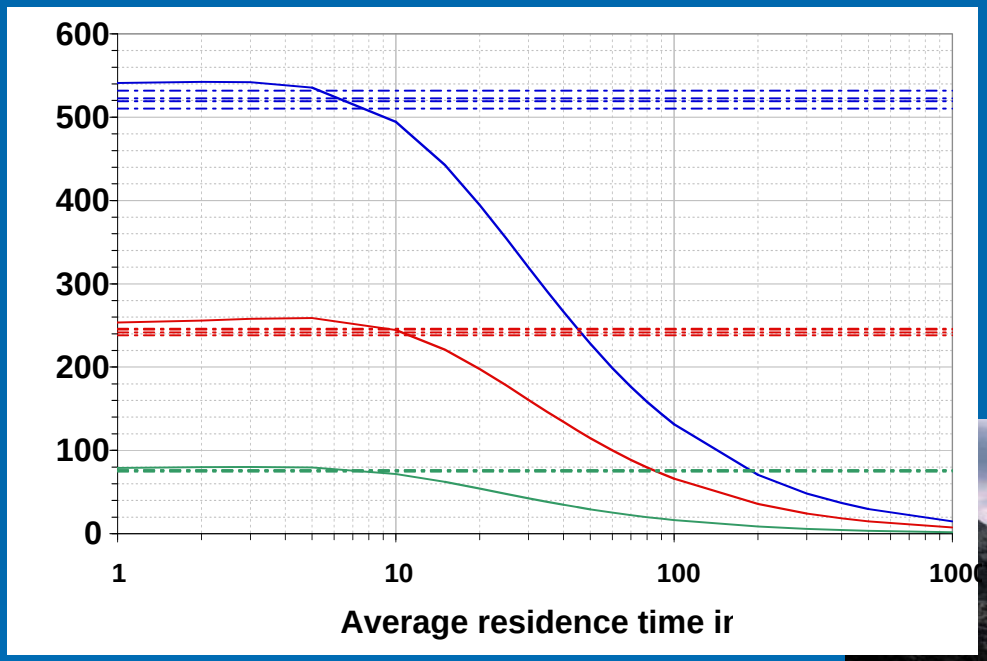


- Heterogenous permeability causes spatial variations in saturation state
- Leading to transport-control of reaction rates in areas close to saturation
- Residence time is key

From Steefel, 2008

Geochemical Kinetics and Transport, Ch. 11 *in* Kinetics of Water-Rock Interaction, Brantley, Kubicki, White. eds.

Some Water is Surprisingly Old



Blue – CFC12
Red – CFC11
Green – CFC113

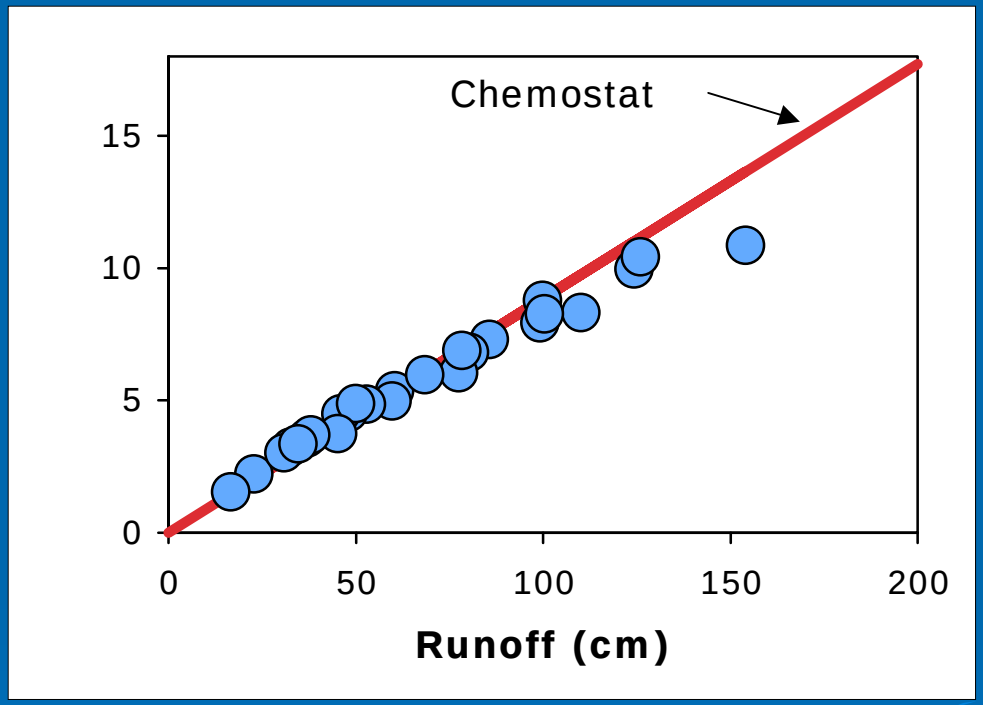
- There are a range of water ages
- And a range of solute concentrations and saturation indices

Other Chemostatic Processes

- Variable reactive surface area
  - Water table variations
- Fast reactions
  - Amorphous aluminosilicates
  - Cation exchange
- Flushing of pore water

Punch Line

- Fluxes proportional to runoff
- Wetter climate = higher weathering fluxes
- Higher weathering fluxes = greater CO_2 consumption

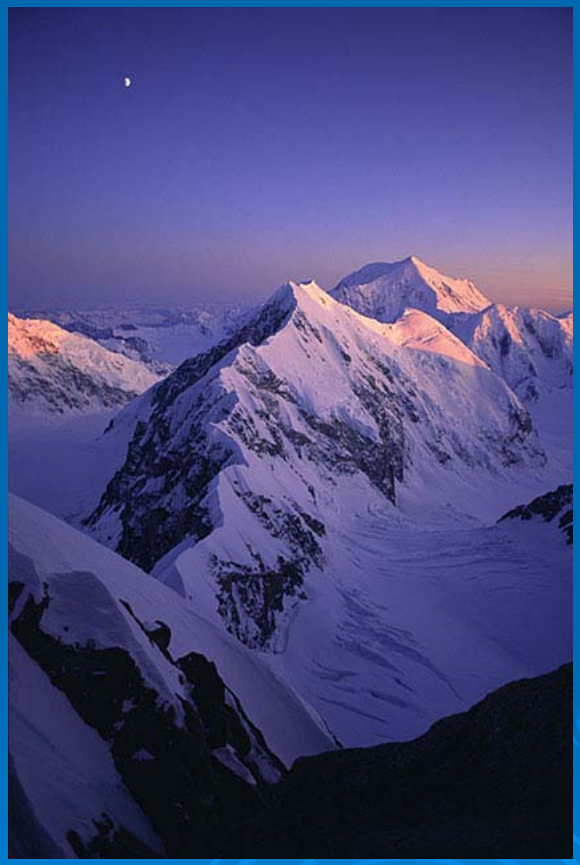


$$2NaAlSi_3O_8 + 11H_2O + 2CO_2 = 2Na^+ + 2HCO_3^- + 4H_4SiO_4 + Al_2Si_2O_5(OH)_4$$

Albite kaolinite

Conclusions

- Watersheds exhibit Chemostatic behavior
- Processes may include:
  - Chemical Affinity effect
  - Variable reactive surface area
  - Cation exchange
  - Seasonal precipitation/dissolution of amorphous aluminosilicates
- CO_2 consumption proportional to runoff



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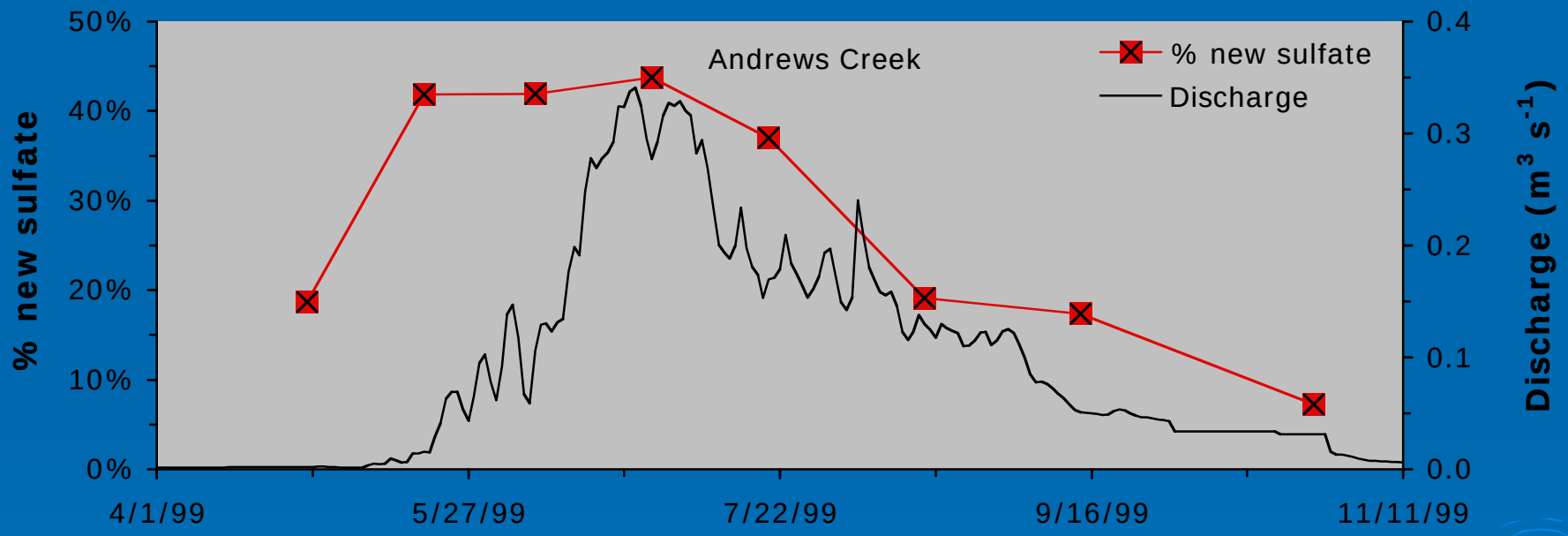
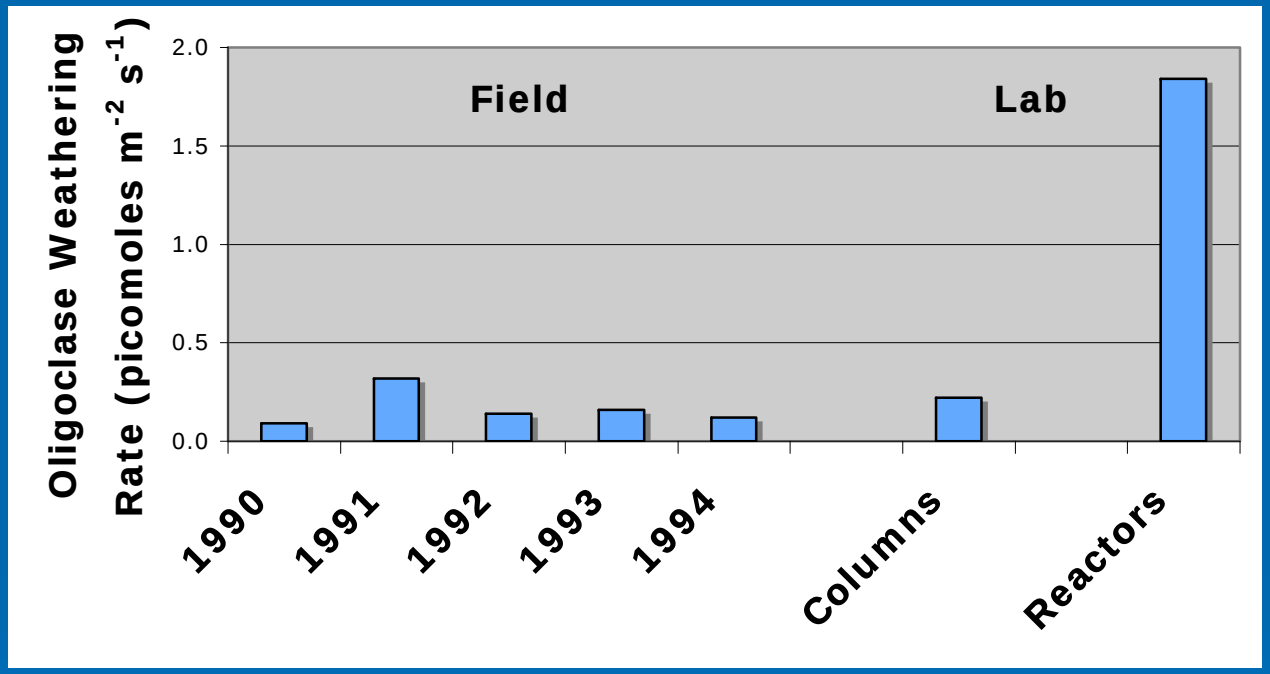
^{35}S indicates up to 40% of water is <1 year old



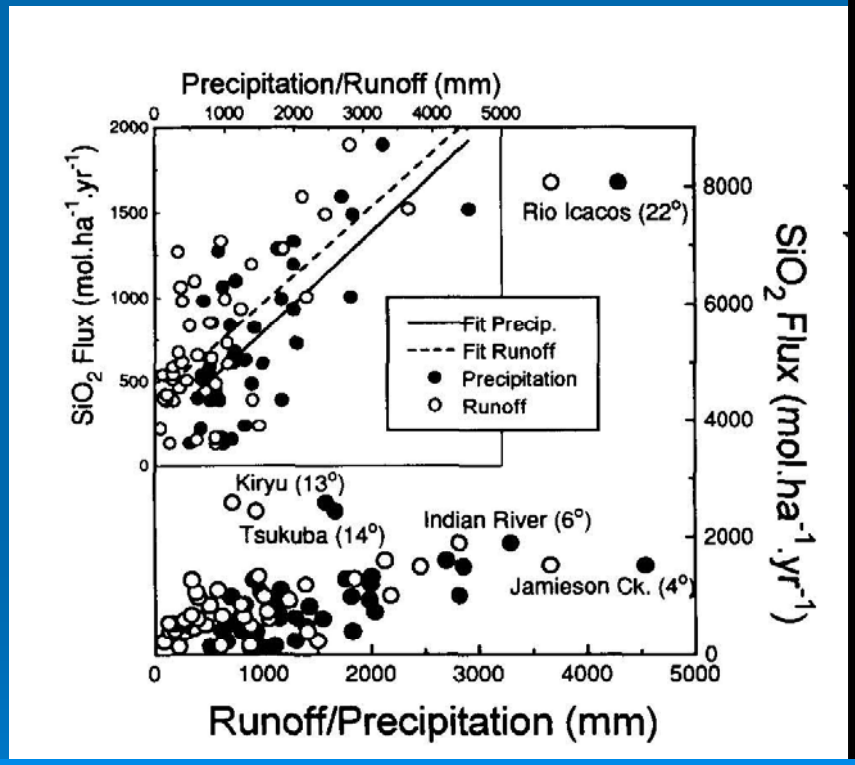
- Water isotopes also indicate lots of young water

Rates are slower in field and in saturated columns than in fluidized-bed reactors



- Probably reflecting transport control in columns
  - Chemical affinity effect

Si Fluxes are Proportional to Runoff



- Fig 6 from White and Blum, 1995