Up-Scaling Reaction Rates from Pore-to-Core Scale

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Motivation: Reaction rates developed during porous media flow may be significantly different from rates determined in lab measurements (typically conducted in well mixed batch reactors using pulverized reactive media) due to rock microstructure heterogeneity:

- reactive mineral surfaces are not uniformly accessible to reactive fluids due to random deposition of mineral grains
- variation in reactive species concentrations throughout pore space
- variation in flow rates within a pore network

Goal: Capture accurate pore-to-core scaling of reaction rates to account for the above

Tools: sandstone core samples (Viking formation, Alberta basin)
X-ray computed microtomography (XCMT)
backscattered electron microscopy (BSE)
energy dispersive X-ray spectroscopy (EDX)
reactive network flow models

Medium Characterization

Cores

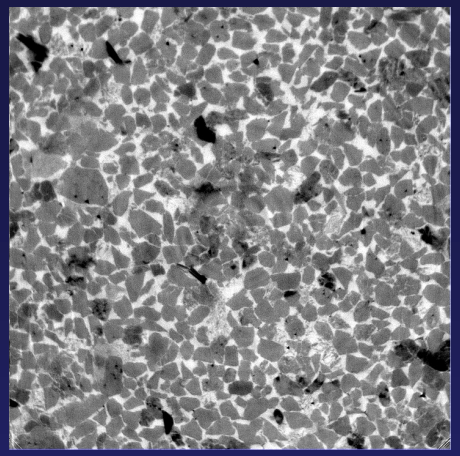
- sandstone (14% porosity)
- shaley sandstone (4%)
- conglomerate sandstone (7%)

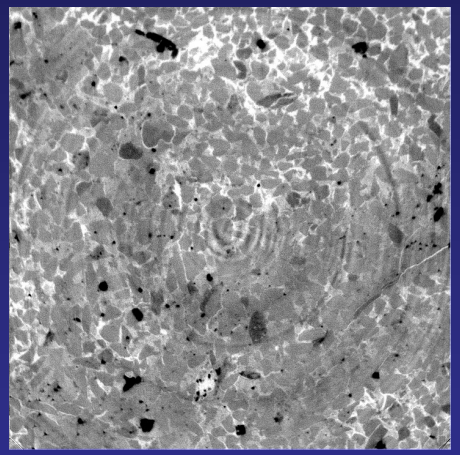
XCMT and Image Analysis

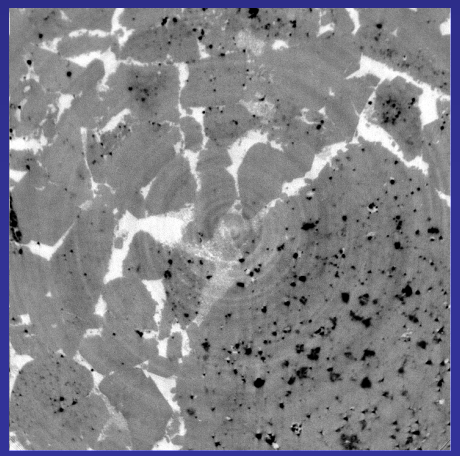
Void space characterization

3.98 μm voxel resolution

- pore position, volume, surface area
- throat position, area, perimeter, shape
- pore network description

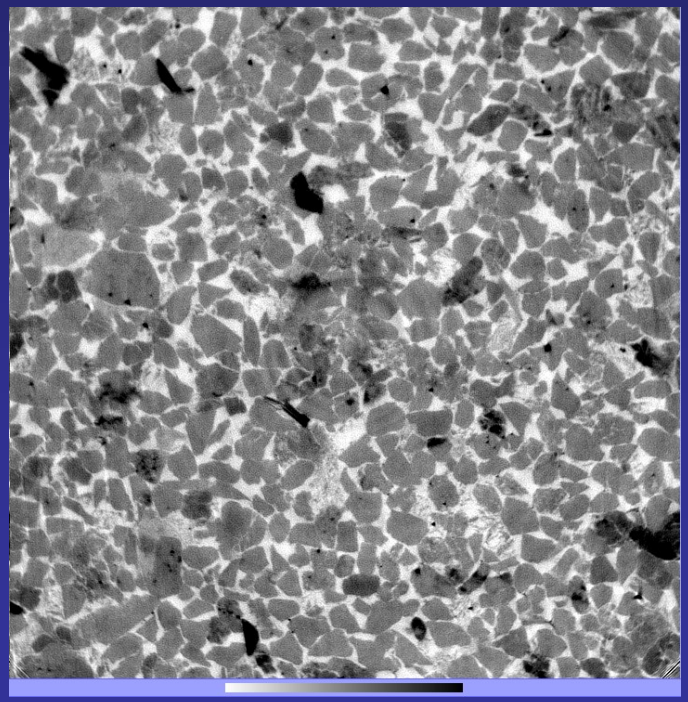




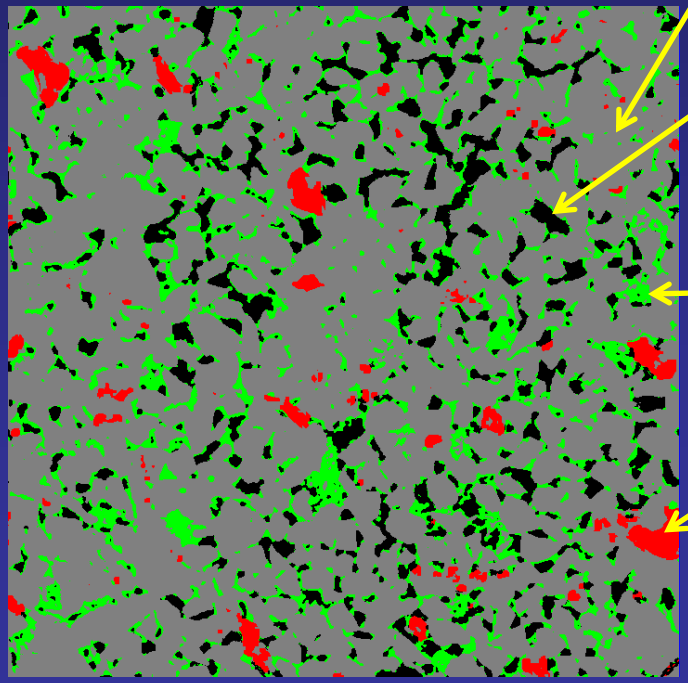


Coarse mineral segmentation

- air (CT ~ 0)
- clays ($0 < CT < CT_{quartz}$)
- quartz
- allogenic grains (AG) ($CT_{quartz} < CT$)
  - benchmarked against BSE and EDX analyses

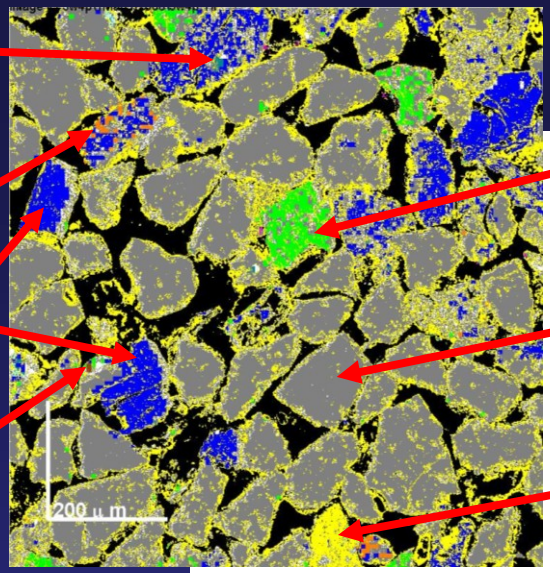


sandstone



BSE/EDX image analysis – 2D

(C.A. Peters)



titanium

annite

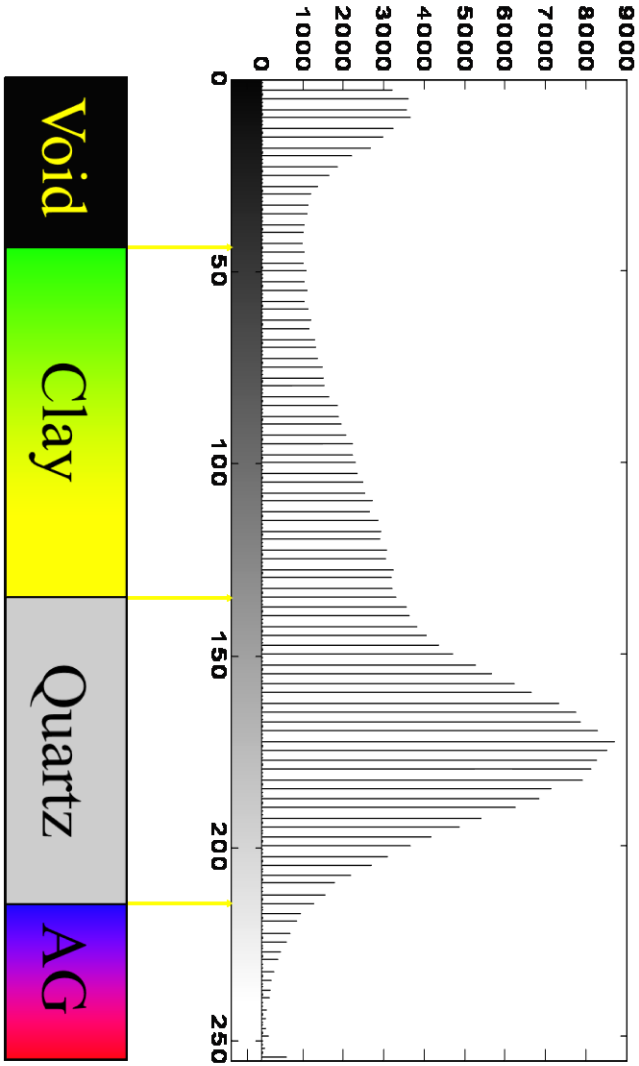
K-feldspar

apatite

anorthite

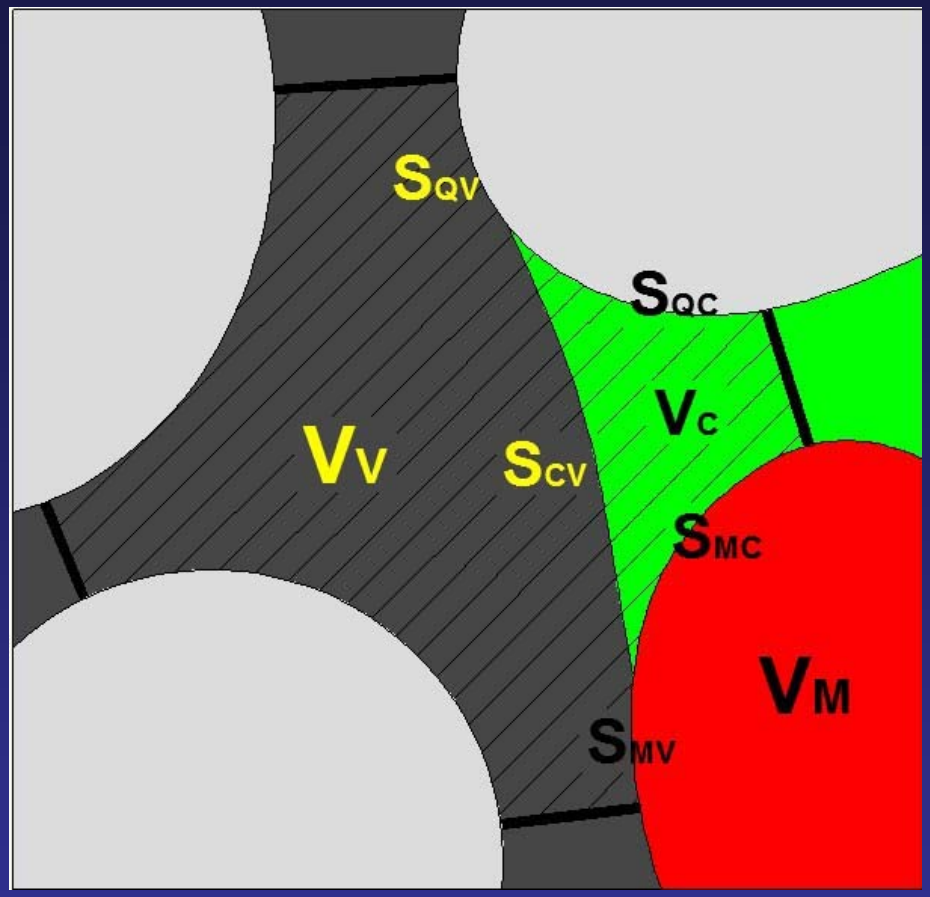
quartz

kaolinite



Mg chlorite
Kaolinite
Montmorillonite
Albite

Dolomite
Illite
K-Feldspar
Anorthite
Calcite
Apatite
Biotite
Fe chlorite
Siderite
Titanium dioxide
Iron oxides
Pyrite



Mineral distribution integrated into pore-network model provides accessible surface areas

Reaction Model

Interaction of the clay kaolinite and the feldspar anorthite with acidic brine as a model for reaction of the dissolved component in CO_2 sequestration

Initial conditions

- saline water, pH 6.6
- dissolved solids as per equilibrium of saline water with quartz and kaolinite

Injected solution

- Acidic saline, pH 3.01
- dissolved CO_2
  [H_2CO_3] from solubility of CO_2 (1.01 M) at 100 bar and 50°C

System of 15 aqueous species and 11 reactions

- 2 involve the solid species - modeled dynamically
- 9 purely aqueous - modeled as instantaneous

Dynamic reactions:

$$Al_2Si_2O_5(OH)_4(s) + 6H^+ \leftrightarrow 2Al^{3+} + 2H_4SiO_4 + H_2O \qquad (1K)$$

$$Ca_2Al_2Si_2O_8(s) + 8H^+ \leftrightarrow Ca^{2+} + 2Al^{3+} + 2H_4SiO_4 \qquad (1A)$$

Instantaneous reactions

$H_2O \leftrightarrow H^+ + OH^-$	$H_4SiO_4 \leftrightarrow H_3SiO_4^- + H^+$	$Al^{3+} + 2OH^- \leftrightarrow Al(OH)_2^+$
$H_2CO_3 \leftrightarrow HCO_3^- + H^+$	$H_3SiO_4^- \leftrightarrow H_2SiO_4^{2-} + H^+$	$Al^{3+} + 3OH^- \leftrightarrow Al(OH)_3$
$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$	$Al^{3+} + OH^- \leftrightarrow Al(OH)^{2+}$	$Al^{3+} + 4OH^- \leftrightarrow Al(OH)_4^-$

Laboratory determined rates for the dynamic reactions have form

$$r = r_{pH}\, f(\Omega) \qquad (2)$$

$$r_{pH} = \left(k_H \{H^+\}^{\alpha} + k_{H_2O} \{H_2O\}^{\beta} + k_{OH} \{OH^-\}^{\chi} \right)$$

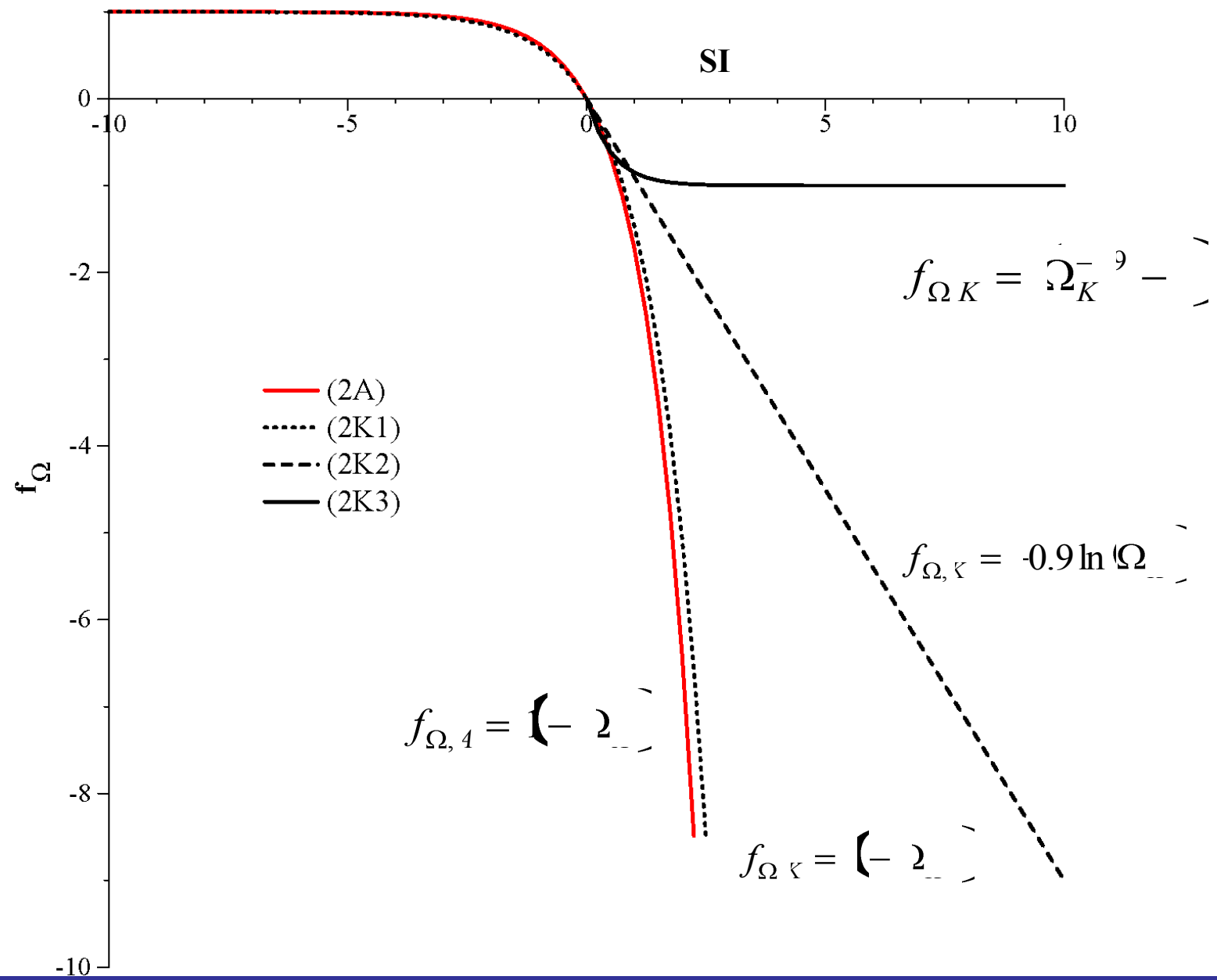
reflects pH dependence of aqueous reaction

f reflects rate dependence on saturation deviation from equilibrium

$$\Omega = \frac{\prod_{\text{product species}\,\alpha} \{\alpha\}^{\alpha}}{\prod_{\text{reaction species}\,\sigma} \{\sigma\}^{\beta}\, K_{eq}}$$

Ω - saturation state ($< 1 \rightarrow$ under saturated $\rightarrow$ dissolution,
$> 1 \rightarrow$ over saturated $\rightarrow$ precipitation)

SI - saturation index = $\log \Omega$
($< 0 \rightarrow$ dissolution, $> 0 \rightarrow$ precipitation)


SI
0
-10
-5
0
5
10
-2
-4
-6
-8
-10
f_Ω
(2A)
(2K1)
(2K2)
(2K3)
$f_{\Omega K} = \Omega_K^{-9} -$
$f_{\Omega,K} = -0.9 \ln(\Omega$
$f_{\Omega,4} = (-\Omega$
$f_{\Omega K} = (-\Omega$

Reactive Network Flow Model

- one network, incl. mineral dist'n, built for each sandstone core
- each simulated volume 20.14 (2.9×2.9×2.4) mm^3
- clay phase assumed kaolinite
- AG phase assumed anorthite
- Single phase flow (Patzek model)
- 7 seepage rates considered – 0.1, 0.5, 1, 5, 10, 20, 58 ($\cdot 10^{-4}$ cm/s)
- Rate laws (2A, 2K, $2K_1$, $2K_2$, $2K_3$) assumed to hold at the sub-micron scale

  used for reactions occurring within a single pore

  2K, $2K_1$ always used for kaolinite dissolution.

  2K, $2K_1$, $2K_2$, $2K_3$ investigated for kaolinite precipitation

Computation of species concentrations in pore *i*:

15 aqueous species

9 aqueous reactions (2 dynamic reactions serve as source terms)

→ 6 independent species

chose H_2O, H^+, H_2CO_3, H_4SiO_4, Al^{3+}, Ca^{2+}

total concentrations of the independent species conserved

In pore *i*,

- update the ***total concentrations*** of each of the independent species via ADR ODE
- compute equilibrium concentration of each of the 15 individual species.

Scale up

Reactive network model yields mass changes $M_{K,i}$ [mol/s] of kaolinite and $M_{A,i}$ of anorthite for each pore i.

Effective reaction rates, R_N [mol/m^{2}s]

$$R_{N,K} = \frac{\sum_i M_{K,i}}{\sum_i A_{K,i}}, \qquad R_{N,A} = \frac{\sum_i M_{A,i}}{\sum_i A_{A,i}}$$

for entire pore-network (core) are correctly up-scaled for flow and mineral heterogeneities captured in the network.

Compare network up-scaled rates against a ***continuum model***

- spatially averaged system properties
- uniform concentrations
- constrained to same physical conditions as network model
- continuum total concentrations $[\alpha_T]$ satisfy

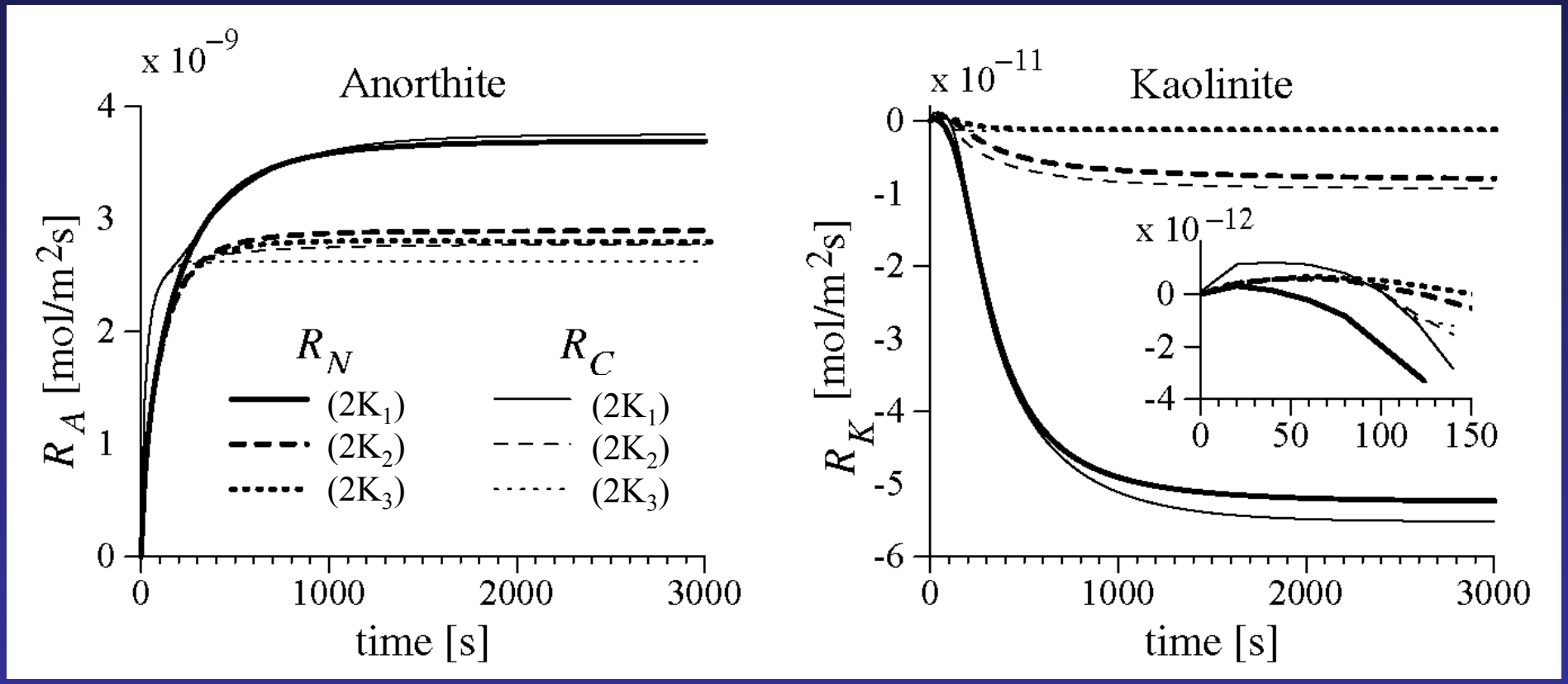
$$V_T \frac{d[\alpha_T]_C}{dt} = Q_T[\alpha_T]_{in} - Q_T[\alpha_T]_C + S_{\alpha_T},$$

- V_T, Q_T, $[\alpha_T]$ total pore volume, volumetric flow rate, inflow concentration of the network model
- S_{α_T} has same form as in network model but with continuum areas and concentrations.
- continuum up-scaled rate laws $R_{C,A}$, $R_{C,K}$ evaluated from lab-based rate laws (2A) – ($2K_3$) evaluated using continuum concentrations.

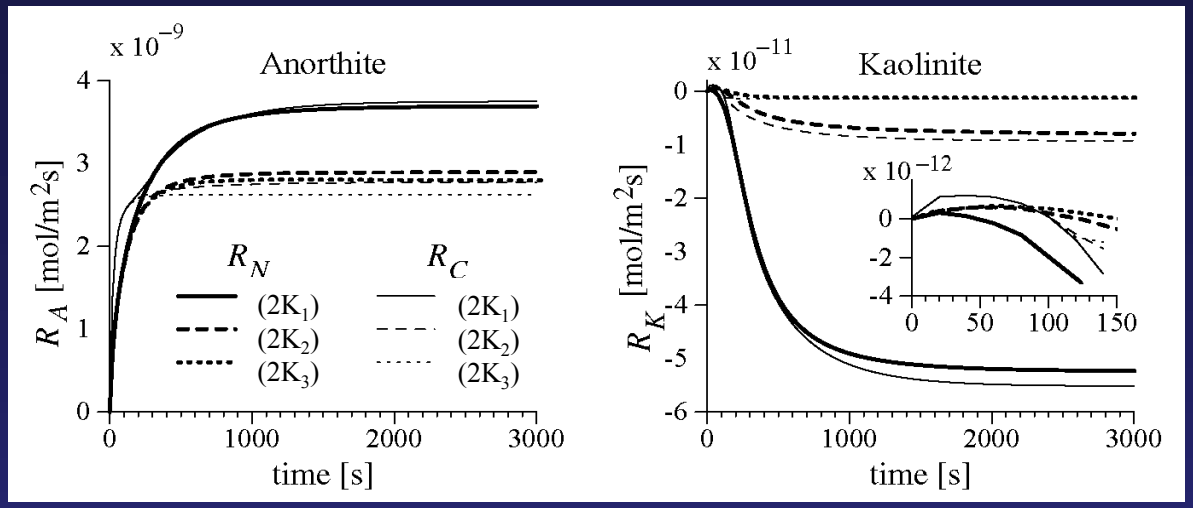
Results

Behavior of up-scaled (core-scale, bulk) rate with time

network: sandstone (3W4) flow rate: $5 \cdot 10^{-4}$ cm/s



- $R_{N,A}$ increased monotonically to steady state dissolution rate
- $R_{N,K}$ initially increased (dissolution), subsequently decreased to steady state precipitation.



Kaolinite rate law affects:

- time to reach steady state
- value at steady state
- strength of coupling between the two reactions.

R_N and R_C agreement

- $R_{C,A}$ cannot distinguish rate law models when $R_{C,K}$ is positive
- R_C either larger or smaller than R_N at steady state – depending on governing rate law

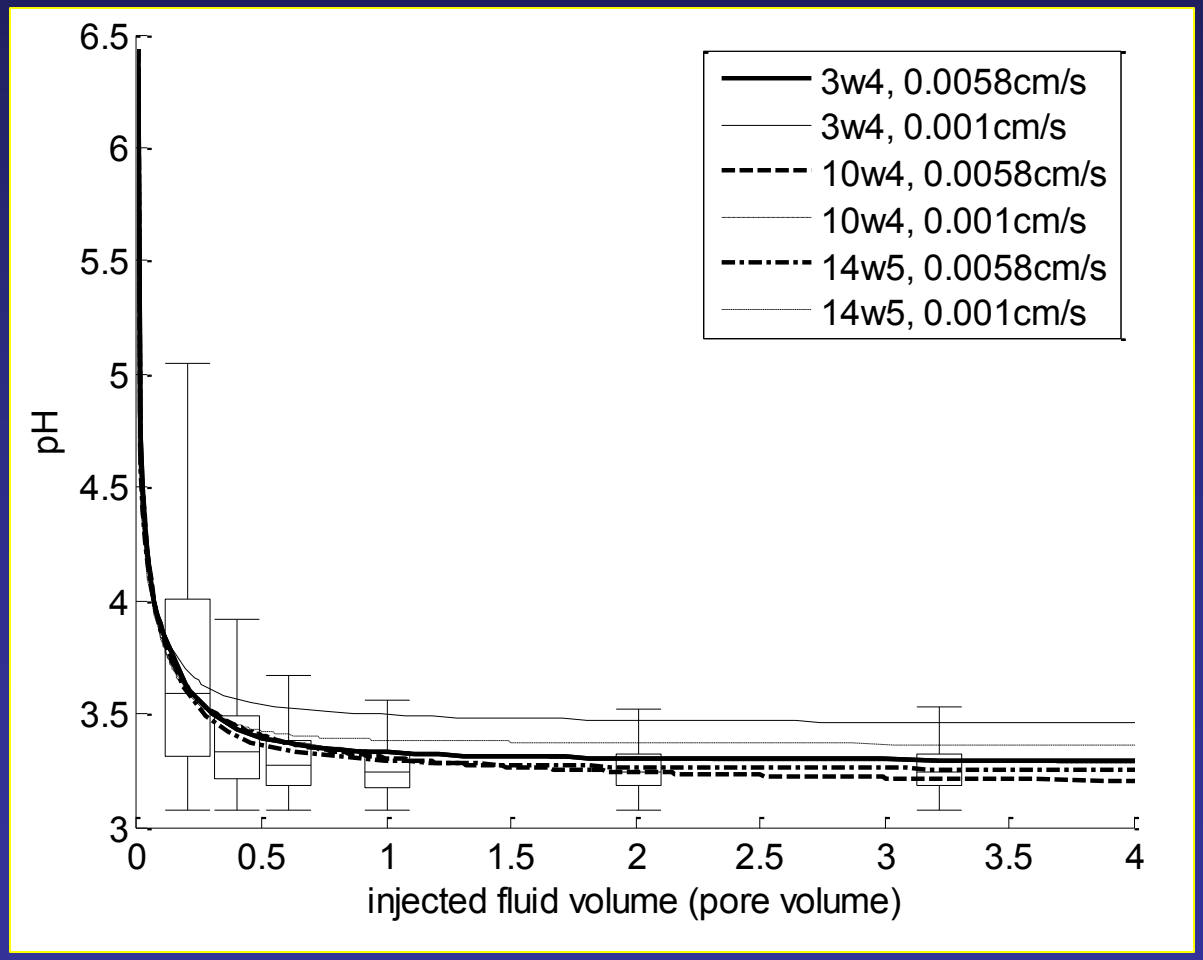
Anorthite reaction far from equilibrium - up-scaled rate $R_{N,A}$ dominated by pH for all time.

- $K_{eq.A}$ large, inflow solution acidic $\rightarrow \Omega_A \leq 10^{-10}$ and $f_{\Omega,A} \sim 1$ everywhere in network
- $R_{N,A}$ determined by $r_{\mathrm{pH},A}$ term
- $r_{\mathrm{pH},A} \sim k_{\mathrm{H}^+,A}\{\mathrm{H}^+\}$

pH equilibrates rapidly

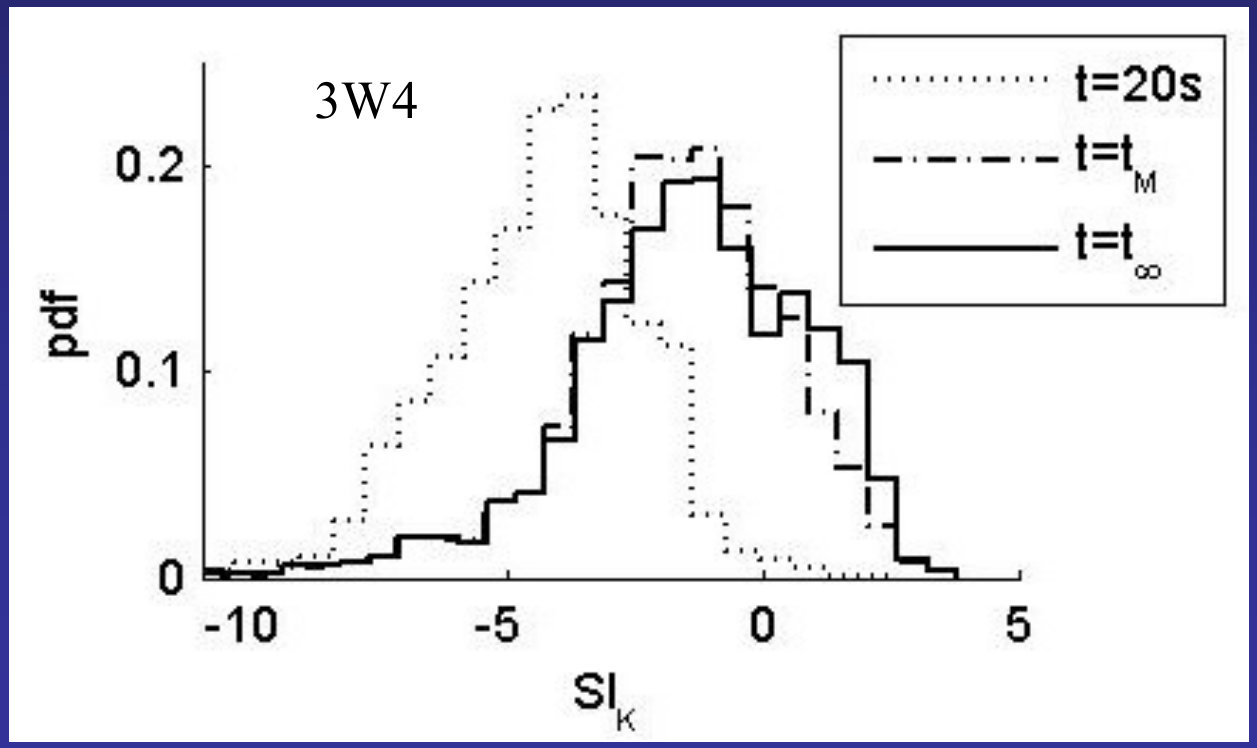
Time for pH to equilibrate and steady state value of pH depend on

- flow rate
- strength of koalinite rate law



Kaolinite reaction is close to equilibrium - up-scaled rate $R_{N,K}$ affected by $f_{\Omega,K}$ as well (i.e. by $SI_K \equiv \log(\Omega_K)$)

- $R_{N,K}$ depends on the full distribution of positive and negative parts of SI_K and the relative weighting the micro-scale rate law gives to pos. and neg. SI_K values.
- SI_K distribution moves in time toward positive values.
- steady state reached when net kaolinite precipitation rate balances species production by the anorthite dissolution rate



Differences between R_N and R_C values

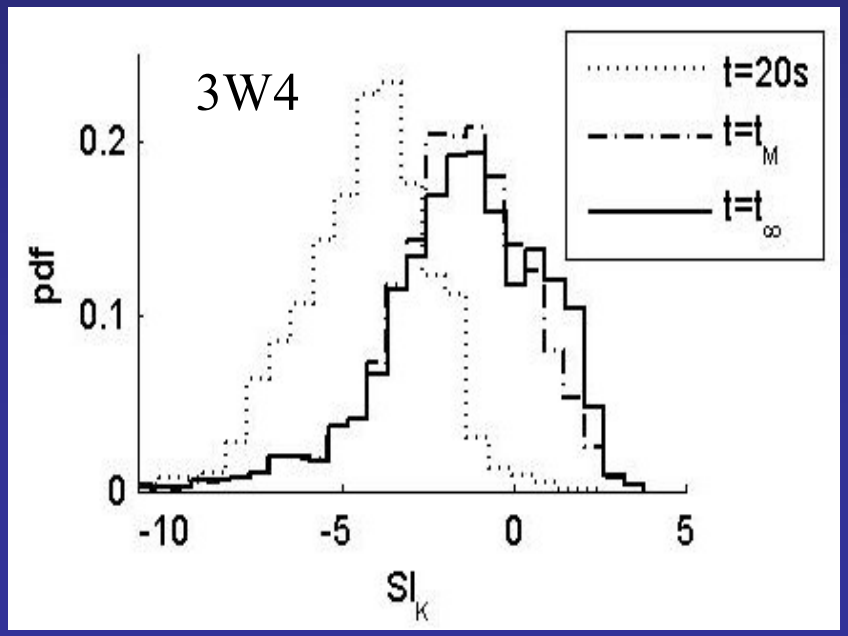
$R_{N,A}$ depends on the details of the pH distribution in the network

$R_{C,A}$ depends on a single pH value

In addition:

$R_{N,K}$ depends on the details of the entire distribution of SI_K

$R_{C,K}$ depends on a single SI_K value



Applicability of core-scale up-scaled reaction rates

Utilize, in condensed form, as local (e.g. by grid block) data in larger scale numerical computations.

Concentrate on:

- Is the reaction in the local region in steady state?

  - *time to reach steady state* (t_{99})

- In steady state, apply appropriate local up-scaled rates

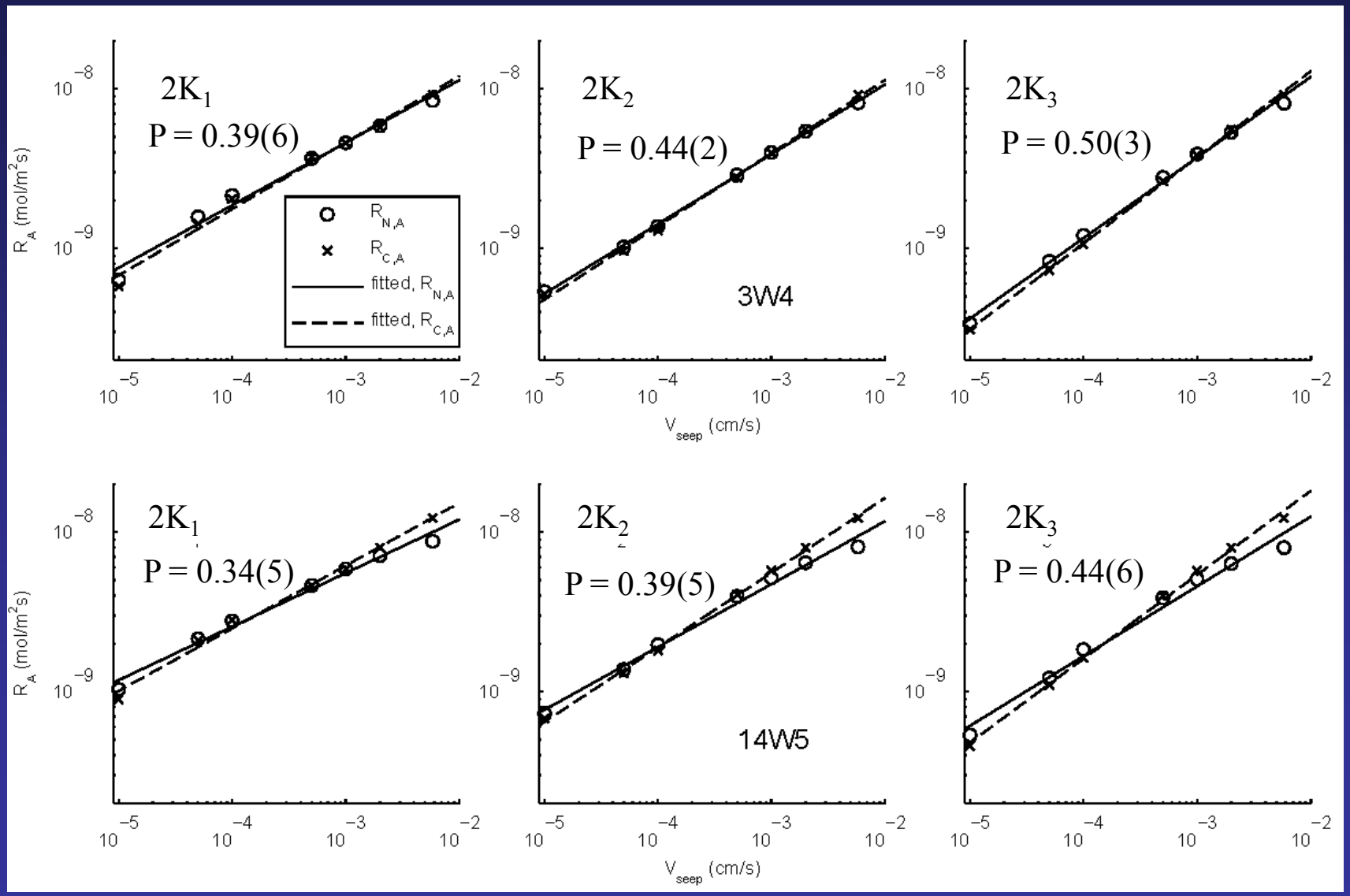
  - *steady state value of the up-scaled reaction rate*

Velocity variation in large scale computations is important

Effect of flow rate on up-scaled reaction rate

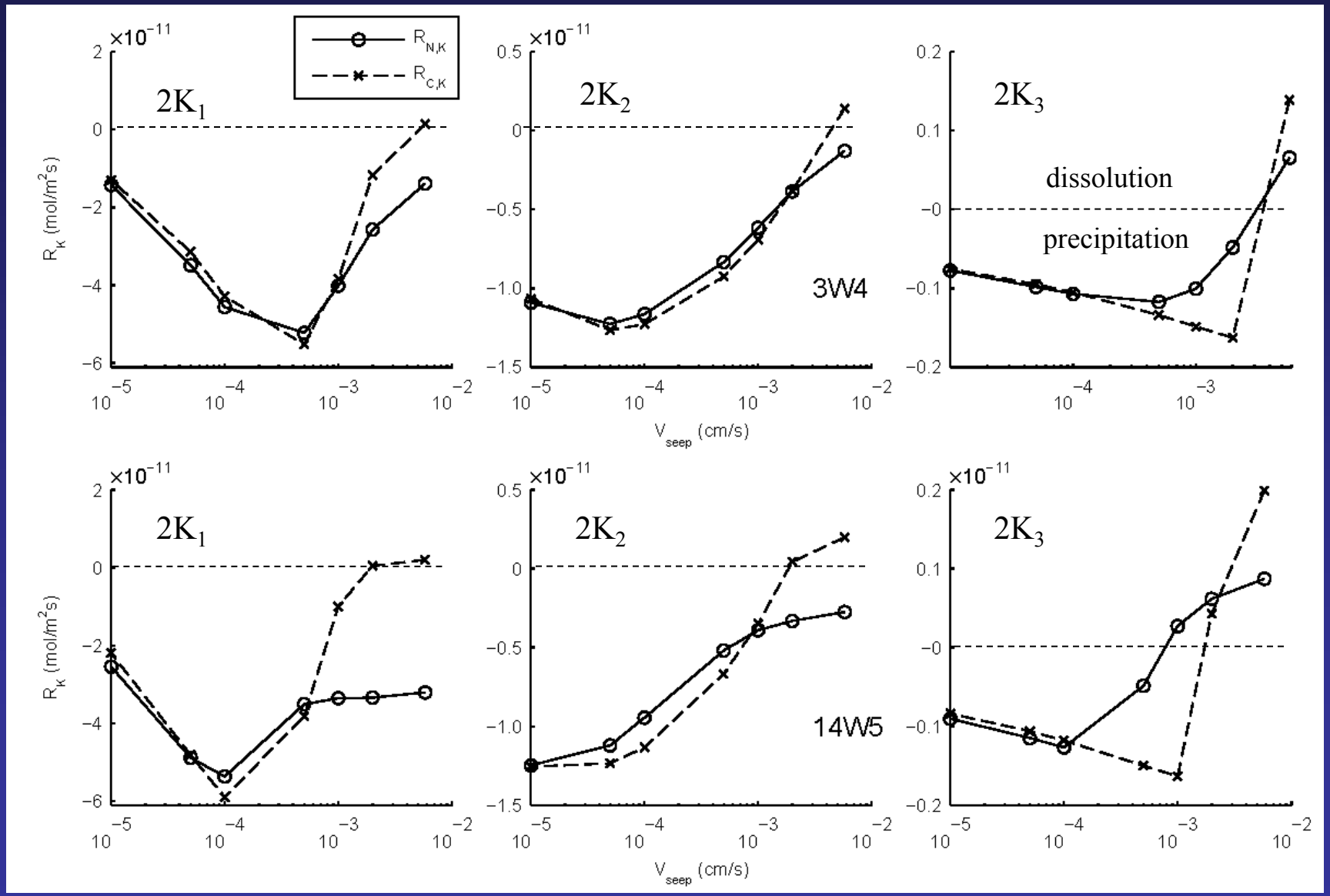
Anorthite: linear dependence of log(ss rate) on log(flow rate)
reflects linear dependence of pH on log(flow rate)

$$R_{N,A} = C v_{seep}^{P}$$



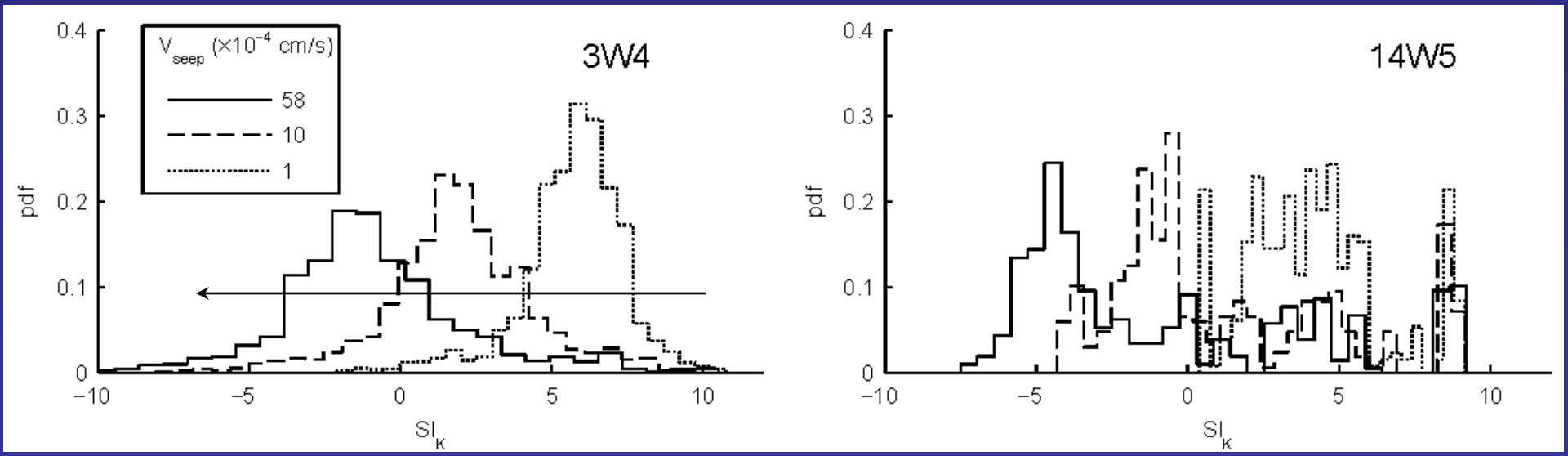
Effect of flow rate on up-scaled reaction rate

Kaolinite: non-linear dependence, trend to increased bulk precipitation at intermediate flow rates, bulk dissolution at high flow rates

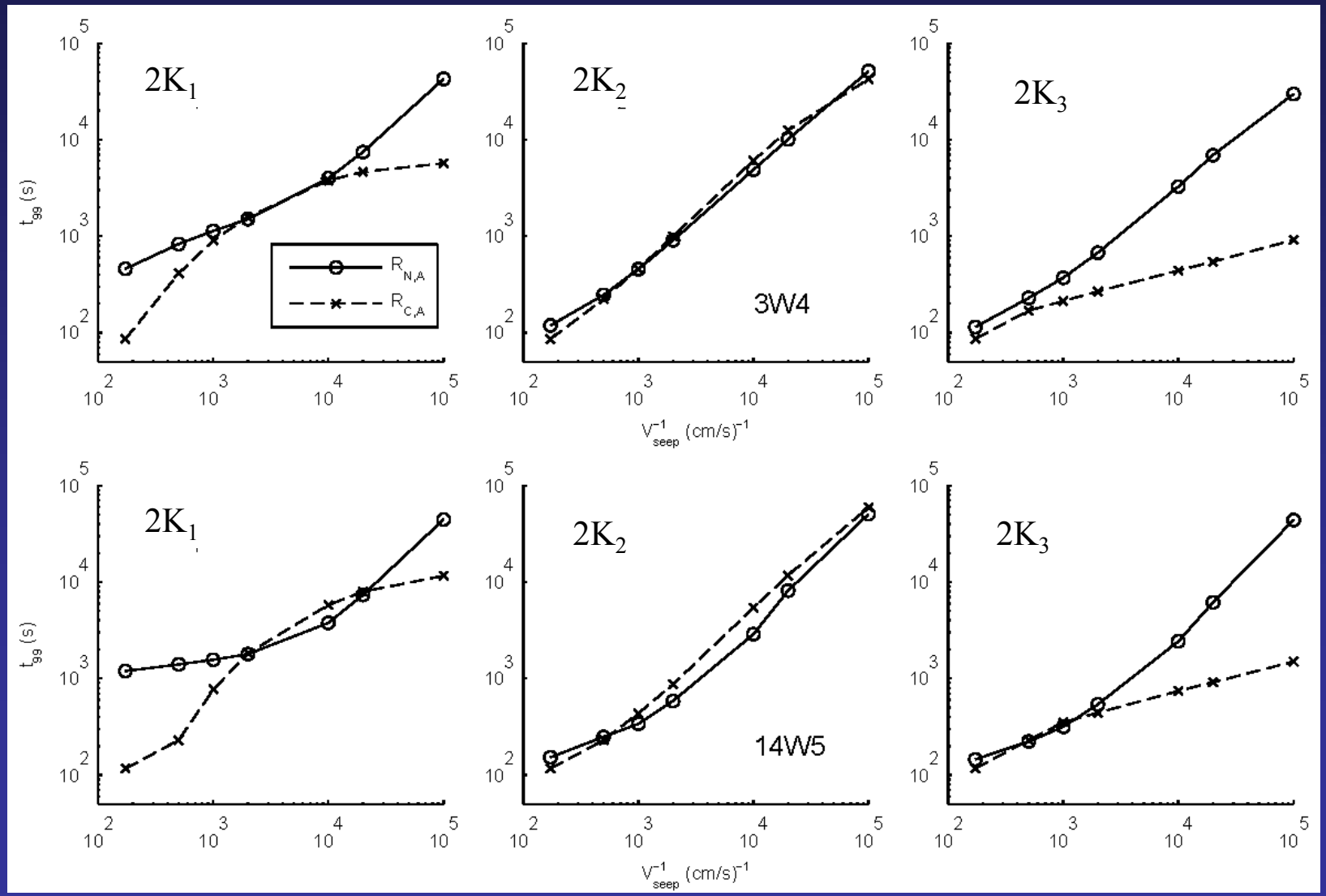


$R_{N,K}$ ss bulk rate behavior reflects competition between pH dominated $r_{pH,K}$ and Ω_K dominated $f_{\Omega,K}$ terms.

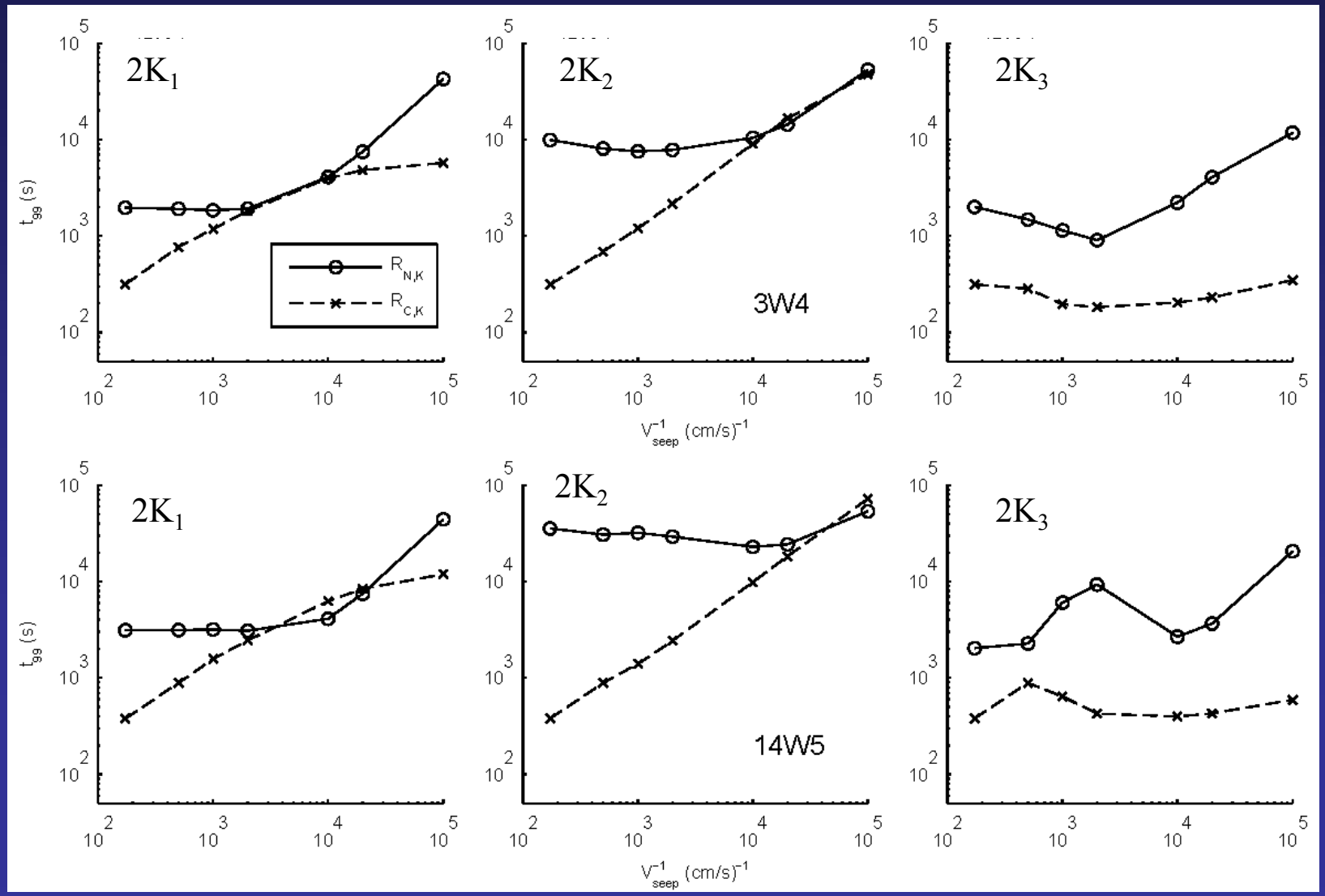
- $r_{pH,K}$ increased with flow rate similarly to (the pH dominated) $R_{N,A}$
- SI_K distribution shifted in the negative SI_K direction with increased flow rate.
- At slower acidic inflow rates, $R_{N,K}$ was enhanced by the shift of SI_K distribution to predominantly positive values while it was reduced by smaller (positive) values of $r_{pH,K}$.
- At higher flow rates, $R_{N,K}$ was decreased by the shift of SI_K distribution to increasing negative values while it was enhanced by larger (positive) values of $r_{pH,K}$.



Anorthite: t_{99} essentially determined by time for pH to equilibrate, i.e. ~ injection of 1 PV.
Therefore t_{99} varies inversely with flow rate.



Kaolinite: t_{99} behavior more complex.



Critique

- No physical change in porosity is implemented in the model. Model does not capture the geometrical or topological changes that reactions produce – with expected impact on R_N.
  In work with PNNL we have demonstrated that a 4% porosity reduction (35% to 31%) due to secondary precipitation can lead to a 40% reduction in flow rate.

- REV to capture microscale reactive flow effects

Thank you

and thanks to the organizers.