Modeling of geochemical processes

Linear systems

J. Faimon

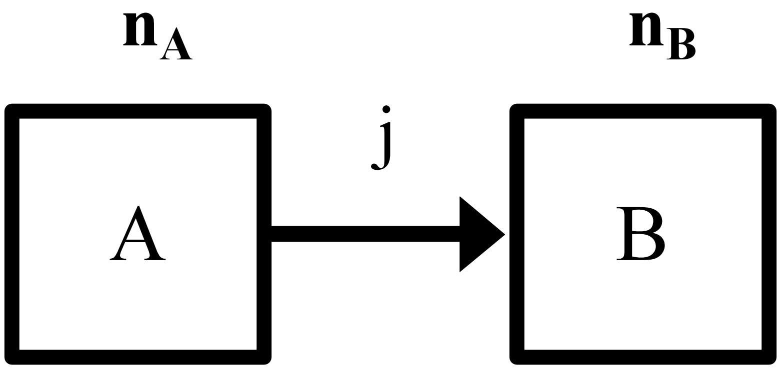
Modeling of geochemical processes

Dynamic simple linear systems

System: individual mass reservoirs

Process: the change (increment, decrement) of reservoir content

the content changes: mass fluxes



$$j = -\frac{dn_A}{dt} = +\frac{dn_B}{dt}$$

$$-\frac{dn_A}{dt} = +\frac{dn_B}{dt} = k\, n_A$$

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Reaction (exchange) mechanisms

$$2A + B \xrightarrow{k} 3C$$

$$-\frac{dn_B}{dt} = k A^2 B$$

$$j = -\frac{dn_B}{dt} - \frac{1}{2}\frac{dn_A}{dt} = +\frac{1}{3}\frac{dn_C}{dt} = k A^2 B$$

$$+\frac{dn_C}{dt} = 3k A^2 B$$

$$-\frac{dn_A}{dt} = 2k A^2 B$$

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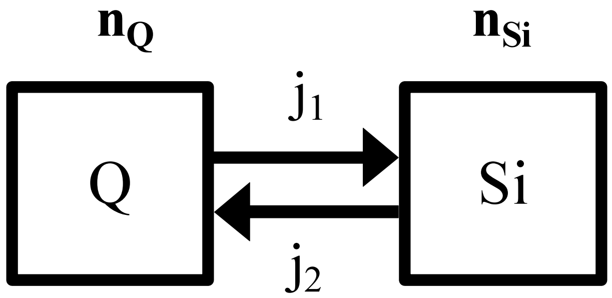
Mineral dissolution

Quartz

$$SiO_{2(Q)} + 2H_2O \underset{k_2}{\overset{k_1}{\rightleftarrows}} H_4SiO_4$$



Rate Law

total Si-flux into solution: $$j = +\frac{dn_{Si}}{dt} = j_1 + j_2$$

$$j_1 = k_1\{Q\} \qquad j_2 = -k_2\{Q\}a_{Si}$$

$$+\frac{dn_{Si}}{dt} = k_1\{Q\} - k_2\{Q\}a_{Si}$$

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Mathematical solution

substitution: $n_{Si} = V[Si]$

$a_{Si} = [Si]\gamma_{Si}$

$$+\frac{V\,d[Si]}{dt} = k_1\{Q\} - k_2\{Q\}\,[Si]\gamma_{Si}$$

rewriting:

$$+\frac{d[Si]}{dt} = \frac{\{Q\}}{V}\left(k_1 - k_2[Si]\gamma_{Si}\right)$$

Integration

variable separation:

$$\frac{d[Si]}{\left(k_1 - k_2[Si]\gamma_{Si}\right)} = \frac{\{Q\}}{V}\,dt$$

substitution:

$$k_1 - k_2[Si]\gamma_{Si} = x \qquad dx = -k_2\gamma_{Si}\,d[Si] \qquad d[Si] = -\frac{dx}{k_2\gamma_{Si}}$$

$$-\frac{1}{k_2\gamma_{Si}}\frac{dx}{x} = \frac{\{Q\}}{V}\,dt \qquad \frac{dx}{x} = -k_2\gamma_{Si}\frac{\{Q\}}{V}\,dt$$

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$$\ln x = -k_2 \gamma_{Si} \frac{\{Q\}}{V} t + C$$

C is integration constant

re-substituting $$\ln\left(k_1 - k_2 [Si] \gamma_{Si}\right) = -k_2 \gamma_{Si} \frac{\{Q\}}{V} t + C$$

finding of the integration constant from initial conditions

$$t = 0 \qquad \ln\left(k_1 - k_2 [Si]^0 \gamma_{Si}\right) = C$$

$$\ln\left(k_1 - k_2 [Si] \gamma_{Si}\right) = -k_2 \gamma_{Si} \frac{\{Q\}}{V} t + \ln\left(k_1 - k_2 [Si]^0 \gamma_{Si}\right)$$

$$\ln\left(k_1 - k_2 [Si] \gamma_{Si}\right) = \ln e^{-k_2 \gamma_{Si} \frac{\{Q\}}{V} t} + \ln\left(k_1 - k_2 [Si]^0 \gamma_{Si}\right)$$

$$\left(k_1 - k_2 [Si] \gamma_{Si}\right) = \left(k_1 - k_2 [Si]^0 \gamma_{Si}\right) e^{-k_2 \gamma_{Si} \frac{\{Q\}}{V} t}$$

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$$k_1 - k_2 [Si]\gamma_{Si} = k_1\, e^{-k_2 \gamma_{Si} \frac{\{Q\}}{V} t} - k_2 [Si]^0 \gamma_{Si}\, e^{-k_2 \gamma_{Si} \frac{\{Q\}}{V} t}$$

$$-k_1 + k_2 [Si]\gamma_{Si} = -k_1\, e^{-k_2 \gamma_{Si} \frac{\{Q\}}{V} t} + k_2 [Si]^0 \gamma_{Si}\, e^{-k_2 \gamma_{Si} \frac{\{Q\}}{V} t}$$

$$[Si] = \frac{k_1}{k_2 \gamma_{Si}} \left[1 - e^{-k_2 \gamma_{Si} \frac{\{Q\}}{V} t} \right] + [Si]^0\, e^{-k_2 \gamma_{Si} \frac{\{Q\}}{V} t}$$