# Introducing New Statistical Methods in Geochemical Kinetics Modeling for Better Estimations of $CO_2$–Water–Rock Interactions

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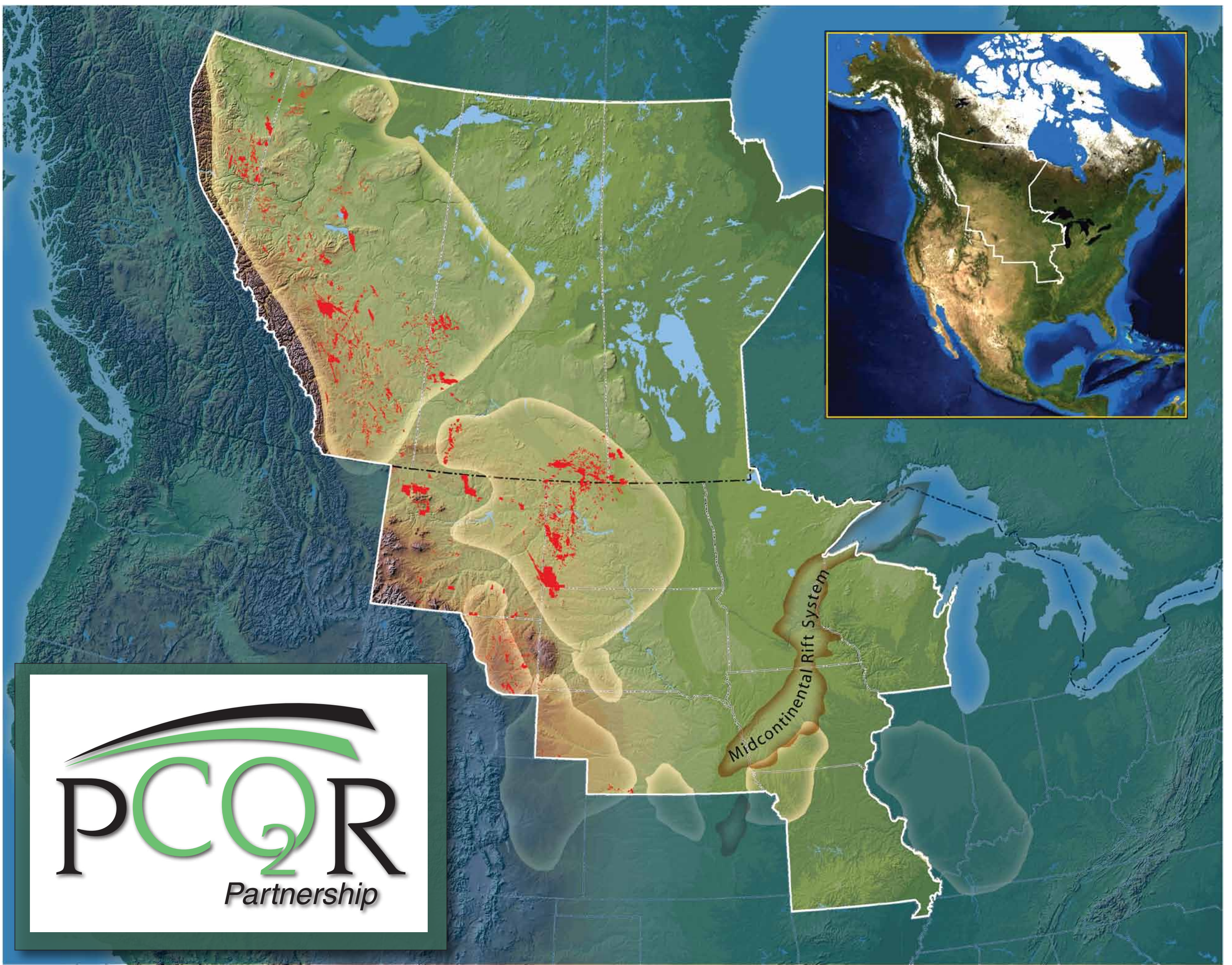
## ABSTRACT

With global interest in geological storage to mitigate the current practice of venting $CO_2$ emissions to the atmosphere, the need to validate sites with regard to a detailed accounting of stored volumes of injectate becomes increasingly important. Specifically, effective measurement, verification, and accounting (MVA) of carbon capture and storage (CCS) projects will depend upon a thorough understanding of what has been injected and the percentages that reside in the gas phase, that are dissolved within formation waters, or that are physically trapped within the rock matrix as new mineral precipitate. Thus a thorough understanding of geochemical interactions is required to advance our understanding of CCS and develop effective MVA protocols.

At present, many uncertainties exist in the numerical modeling of geochemical kinetics, such as the determination of reactive surface area, quantification of $CO_2$ reacting with water, the dynamic nature of the process, and many others. As such, this work introduces a range of estimated uncertainty in an effort to provide a numerical estimation for possible outcomes of geochemical interactions among $CO_2$, water, and reservoir rock. In this work, the conceptual approach for a kinetic modeling analysis is reviewed, and a methodology based on the Fokker–Planck statistical equation is proposed. According to these preliminary considerations, critical variables are identified and determined. Results of this modeling provide a range from the least reactivity to the best reactivity for examined minerals and predict the range of uncertainty that exists in the kinetic modeling based on provided data. This work was performed by the Energy & Environmental Research Center through the Plains $CO_2$ Reduction Partnership, one of the U.S. Department of Energy National Energy Technology Laboratory's Regional Carbon Sequestration Partnerships.



## GEOCHEMICAL KINETICS

$$k_M = k_{25}\exp\left[-\frac{E_a}{R}\left(\frac{1}{T}-\frac{1}{298.15}\right)\right]$$

$$rate_M = \pm k_M A_M a_{H^+}^n\left[\left(\frac{Q_M}{K_M}\right)^{\mu}-1\right]^{\nu}$$

**Where,**

$k$ – the temperature-dependent rate constant
$A$ – the reactive surface area m per kg of water
$a$ – the proton activity
$Q$ – the ion activity product
$K$ – the equilibrium constant
$M$ – the mineral index
$k_{25}$ – the rate constant measured at 25°C
$R$ – the gas constant
$E_a$ – the activation energy of the reaction
$T$ – the absolute gas temperature
$\mu$ & $\upsilon$ – correcting coefficients

## PROBLEM

Modeling inputs are hard to estimate:

- High variability of input parameters
- High heterogeneity of natural systems
- Difficulties with fundamental constants estimation

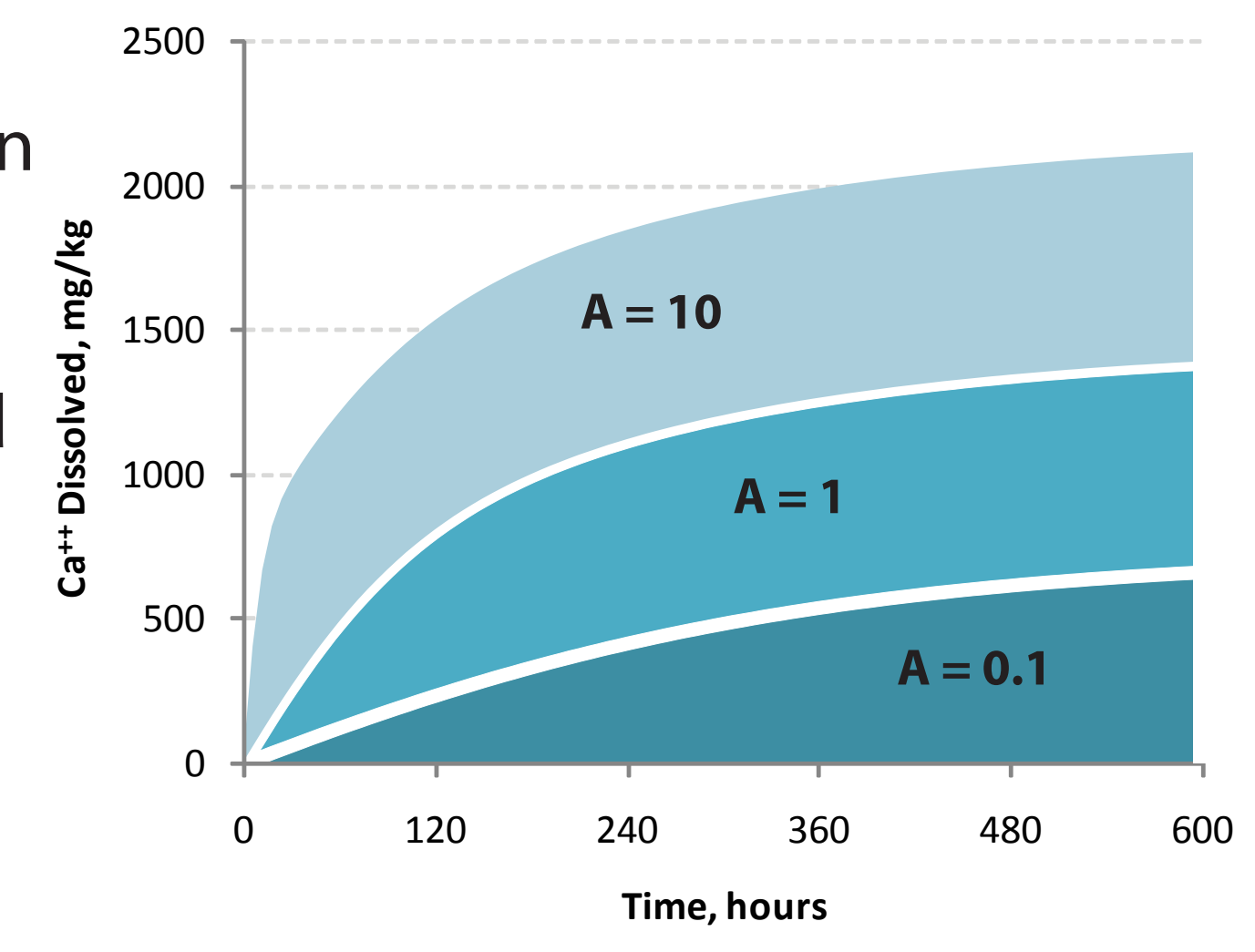
As a result:

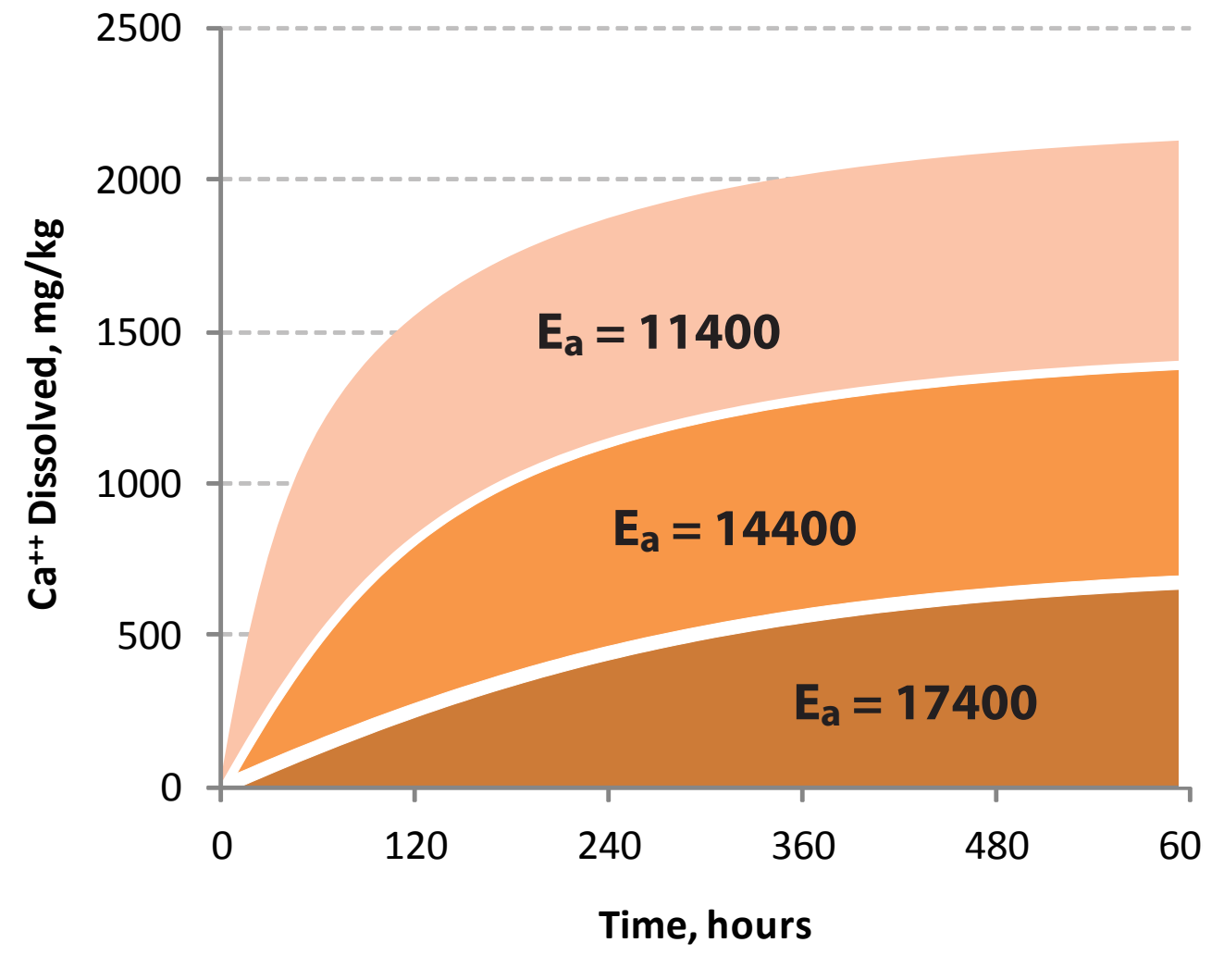
- High level of uncertainty for kinetic rate estimation
- Low capabilities for predictions and risk estimations

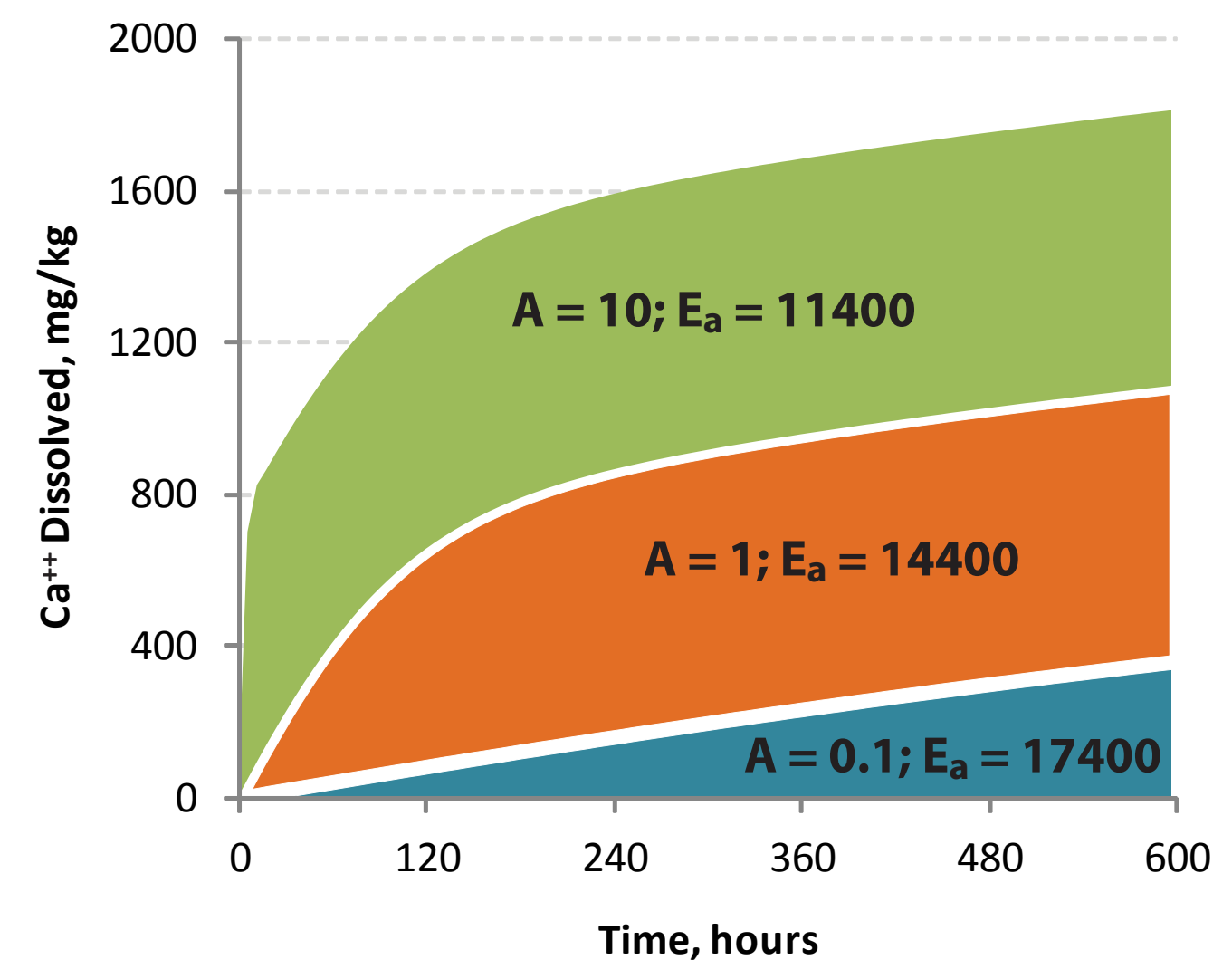
## CALCITE DISSOLUTION EXAMPLES

In this simple example, two parameters for kinetic rate estimation are manipulated: reaction surface area and activation energy. As a result, several scenarios are provided for calcite dissolution problem. Obtained solutions vary by order of magnitude.

**Question:** How to estimate uncertainty under such conditions?







## ORIGINAL FOKKER–PLANCK EQUATION

$$\frac{\partial\psi}{\partial t} = \frac{1}{2}\frac{\partial^2}{\partial C^2}[D(C)\psi] - \frac{\partial}{\partial C}[M(C)\psi]$$

Where,

ψ(X, t) – the function of distribution for probability of concentration of gas C at the time t
C – gas concentration in liquid phase
M(C) – the function characterizing average tendency in evolution of statistical process, gas concentration in liquid phase
D(C) – the function characterizing mean quadratic deviation of the process from its average value, concentration C in time t.

This equation represents the most general classic version of Fokker–Planck form combining deterministic M(C) and statistical D(C) components of the analyzed process. These components (functions) have to be defined and determined independently for every specific process.

The solution for this equation is probability distribution Φ(C) for concentration C in a steady-state process of gas dissolution.

$$\frac{1}{2}\frac{\partial^2}{\partial C^2}[D(C)\Phi(C)] = \frac{\partial}{\partial C}[M(C)\Phi(C)]$$

## STEADY-STATE SOLUTION

From earlier works of Svirezhev et al. (1978) and Haken (1978), and confirmed by direct integration, this equation has a solution:

$$\Phi(C) = \{Const/D(C)\}\times e^{2\int\frac{M(C)dC}{D(C)}dC}$$

Where,

$$\mathrm{M(C)} = \mathrm{rate}\times \mathrm{C_0}\left(1-\frac{\mathrm{C}}{\mathrm{C_\infty}}\right)$$

And,

rate – reaction rate
$C_0$ – initial gas concentration in water
C – current gas concentration in water
$C_\infty$ – equilibrium gas concentration in water

$$\mathrm{rate} = \overline{\mathrm{rate}} \mp \sigma^2_{\mathrm{rate}}$$

Where,

σ – uncertainty factor

$$\mathrm{D(C)} = \sigma^2_{\mathrm{rate}}\mathrm{C}_0^2\left(1-\frac{\mathrm{C}}{\mathrm{C_\infty}}\right)^2$$

$$\Phi(C) = \frac{Const}{\sigma^2_{\mathrm{rate}}\mathrm{C}_0^2\left(1-\frac{\mathrm{C}}{\mathrm{C_\infty}}\right)^2}\times e^{2\int\frac{M(C)dC}{D(C)}dC}$$

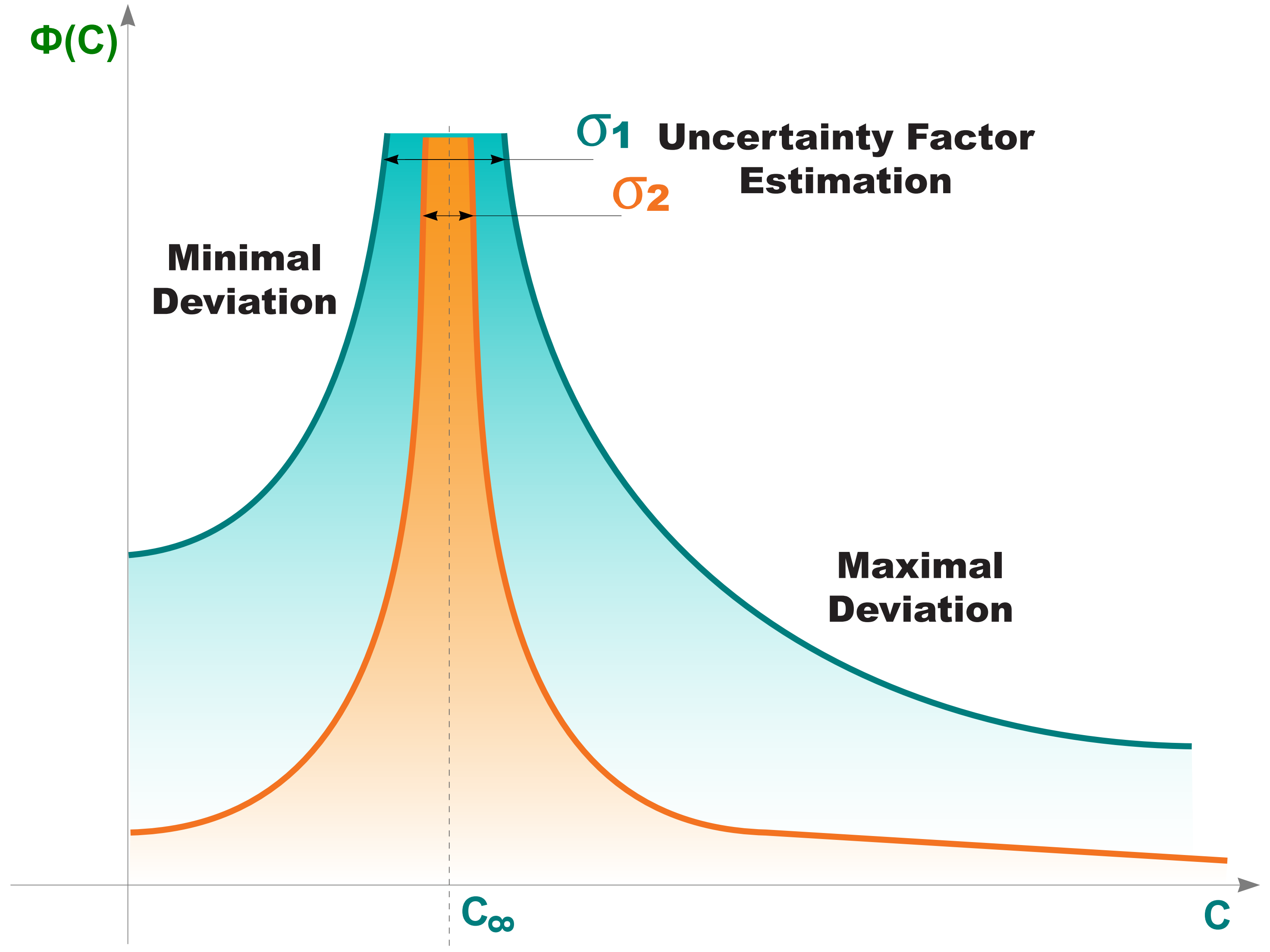
## SOLUTION

$$\Phi(C) = \frac{Const}{\sigma^2_{\mathrm{rate}}\mathrm{C}_0^2\left(1-\frac{\mathrm{C}}{\mathrm{C_\infty}}\right)^{2\times \mathrm{CP}}}$$

Where,

CP – convertability parameter
Φ(C) – probability distribution for gas concentration (C) in water

$$\mathrm{CP} = 1+\frac{\mathrm{rate}}{\sigma^2_{\mathrm{rate}}}\times\frac{\mathrm{C}}{\mathrm{C_\infty}}$$



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