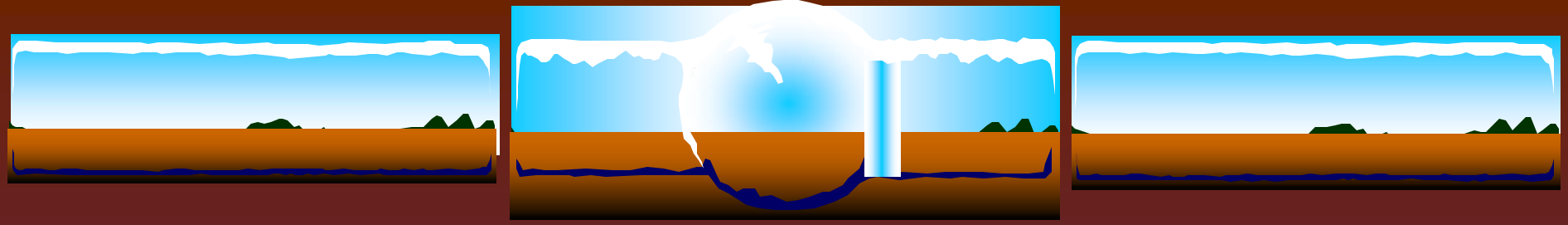

DOE's EGS Program Review

- Models of Subsurface Rock-Water Chemical Processes Affecting Fluid Flow

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- University of California, San Diego
- 858-534-6374; 858-534-3286
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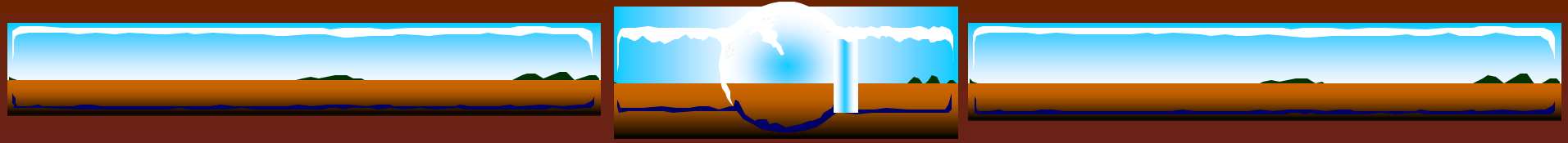
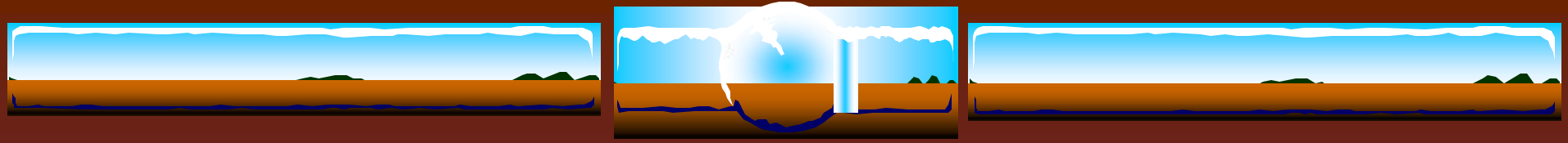


Project Objective

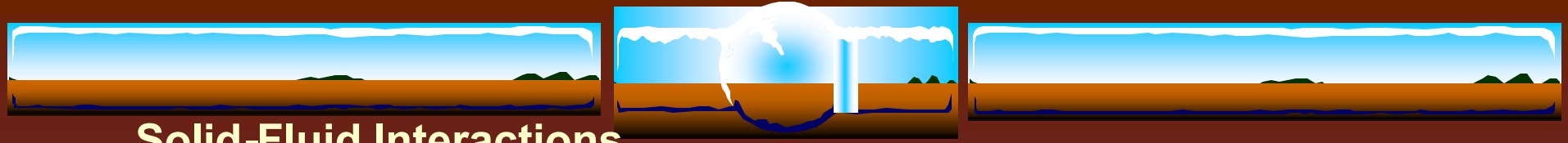
- Expand preliminary Al chemistry H-Na-Al-OH-Cl-H_2O model and extend to 250ºC. Combine with our TEQUIL models that include silica and with mineral properties databases. Begin adding K system within data availability.

- Modified from original statement of objectives to concentrate on expanding our primary objective (1, see above), which includes T-P conditions most relevant to EGS*, and to eliminate secondary objectives (2-4) dealing with very high TP conditions (250ºC-350ºC and supercritical) and fluid inclusion analyses. *See Peer Review comments.



EGS Problem

- Chemical reactions between formation minerals and hydrothermal fluids and/or injectates can lead to changes in formation permeability. These changes can result in fluid flow problems that limit the economical production of EGS energy sources.
- The chemistry of EGS resources and energy production processes is poorly characterized.
- Our TEQUIL Equation of State (EOS) Pitzer models, which accurately predict gas-solid-liquid equilibria in evaporite, carbonate and silica systems to high solution concentration (I >15 *m*) and temperature (250°C; P˜ 1 atm), did not include the aluminum and aluminum silicate minerals that dominate hydrothermal reservoir mineralogy.
- To add these minerals to our TEQUIL models, we must overcome the difficult technical problem of developing an equation of state model that correctly predicts the highly complex pH dependent aqueous chemistry of aluminum and aluminum solid phase interactions as a function of T.
- This program will produce the first high accuracy model, tailored to the solution mixing properties in the composition-T-P region of interest to EGS, that includes the most common hydrothermal solution and mineral components. In the process we will validate many thermodynamic databases in literature.



Solid-Fluid Interactions

?

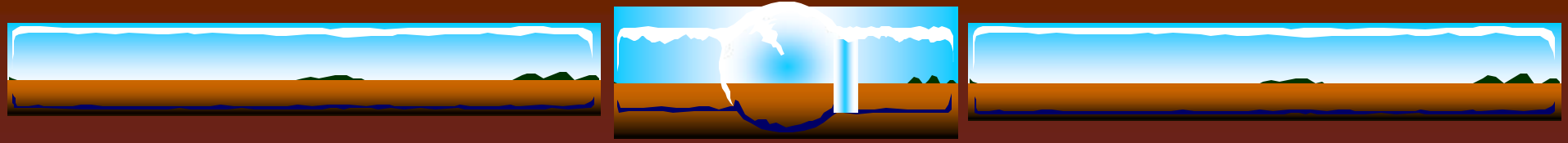
Formation Mineral Dissolution Precipitation

?

Formation Permeability Changes

?

Fluid Flow

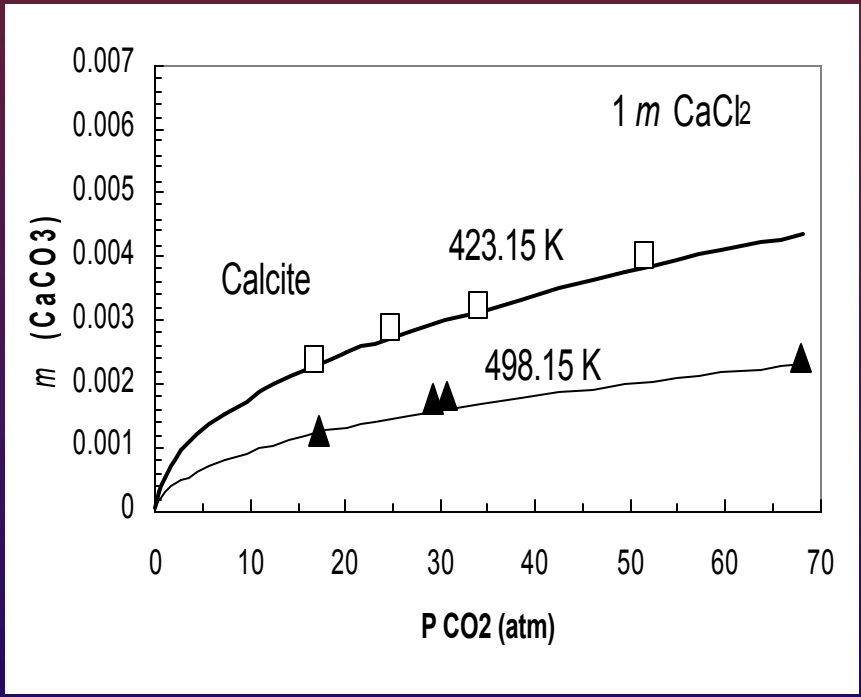


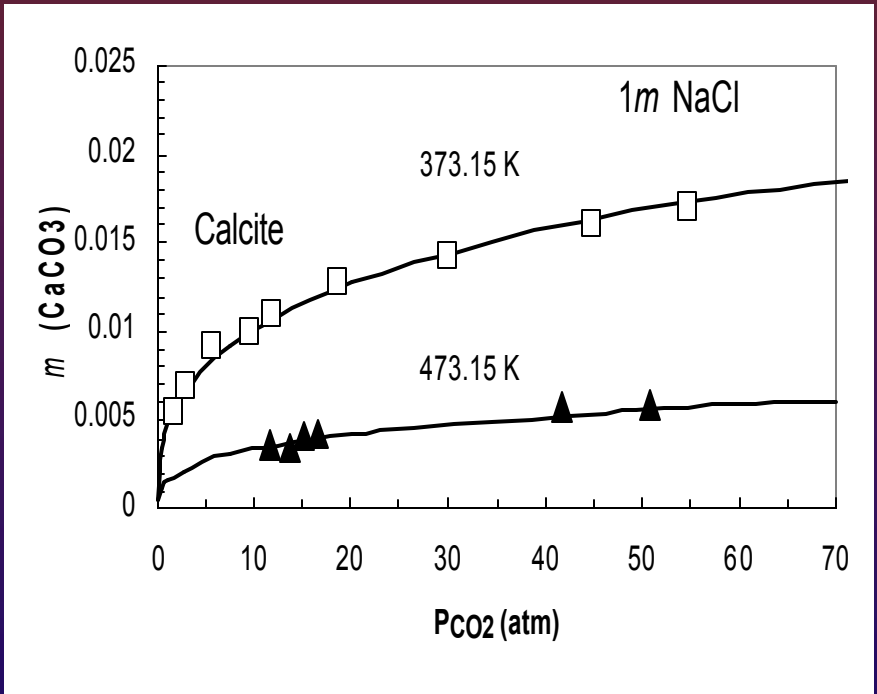
Background/Approach

- **We have Pitzer-based TEQUIL models of solid-liquid equilibria in evaporite, carbonate and silica systems to high solution concentration (I >15 *m*) and temperature (250°C; P˜ 1 atm).**

- **These can predict solute activities, fluid mixing, mineral solubilities, vapor pressure with accuracies near experimental data over wide composition-temperature ranges. Models incorporated in many codes (e.g., EQ3NR, PHRQPITZ).**

Calcite Solubility in Brines at High Temperature
Comparison of Model Predictions and Experimental Data





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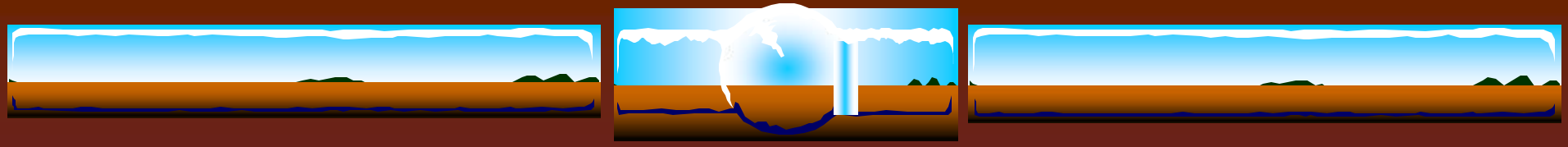
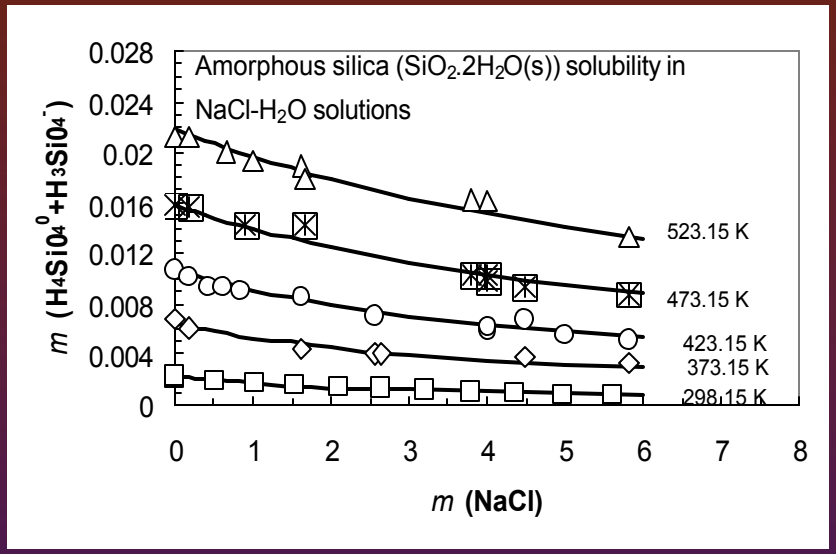
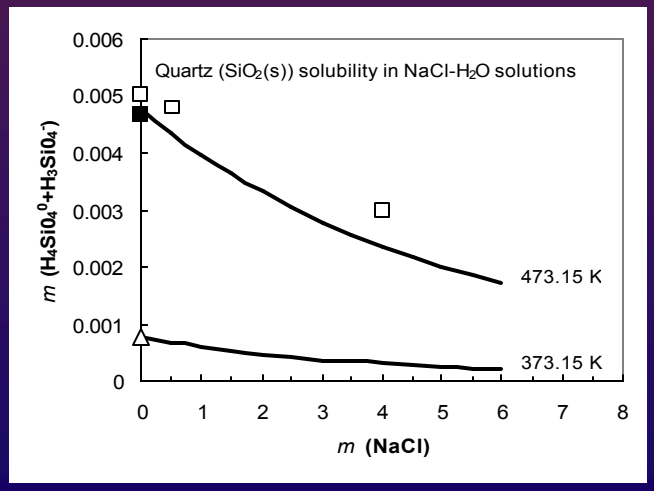
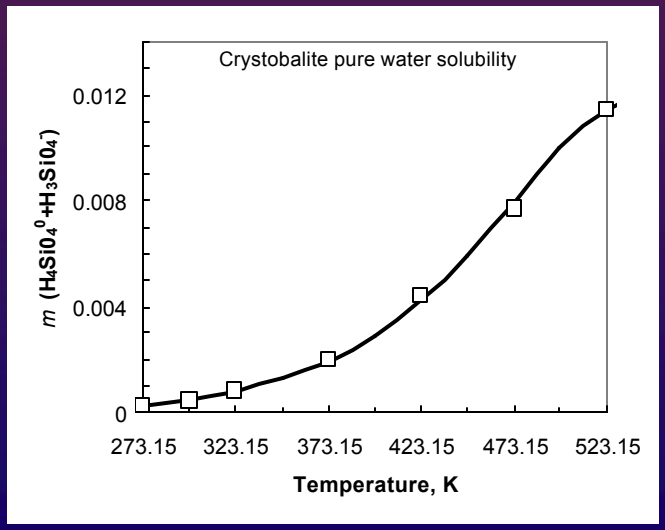


Solubility of SiO_2 Minerals







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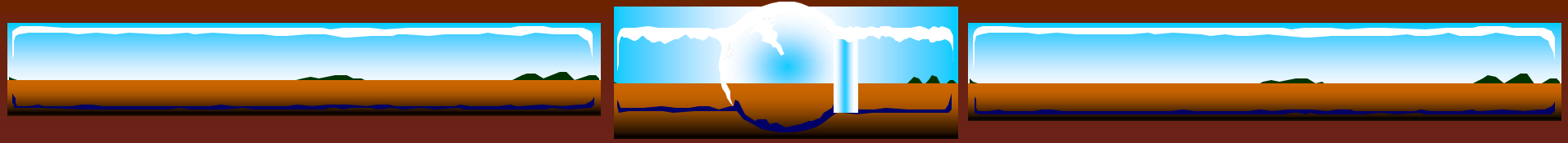


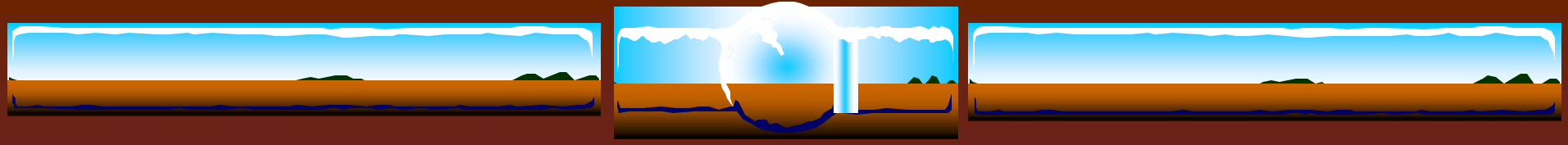
Modeling Approach

Condition for chemical equilibrium; e.g., K-feldspars

$KAlSi_3O_8(s)+8H_2O = Al(OH)_4^-(aq)+K^+(aq)+3H_4SiO_4(aq)$

$$\Delta G_f(K-spar) = \mu_{Al(OH)_4^-} + \mu_{K^+} + 3\,\mu_{H_4SiO_4} - 8\,\mu_{H_2O}$$

$$\mu_i = \mu_i^o + RT \ln \gamma_i m_i$$



Cation (M) Activity Coefficient Expression

$$\ln\gamma_i = z^2 F + \sum_a m_a(2B_{Ma} + ZC_{Ma}) + \sum_c m_c(2\Phi_{Mc} + \sum_a m_a\psi_{Mca}) +$$

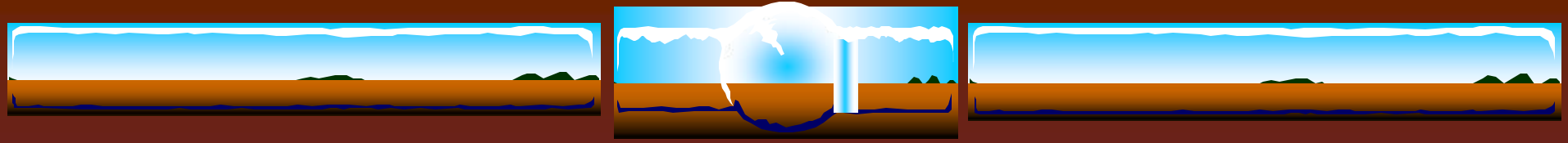
$$\sum_{a\ a<a'} m_a m_{a'}\psi_{Maa'} + |z_M| \sum_c \sum_a m_c m_a C_{ca} + \sum_n m_n(2\lambda_{nM}) + \sum_n \sum_a m_n m_a \varsigma_{naM}$$

$$F = -A^{\phi}\{I^{0.5}/(1+1.2I^{0.5}) + (2/1.2)\ln(1+1.2I^{0.5})\} + \sum_c \sum_a m_c m_a B'_{ca} +$$

$$\sum_c \sum_{c'} m_c m_{c'}\Phi'_{cc'} + \sum_a \sum_{a'<a} m_a m_{a'}\Phi'_{aa'}$$

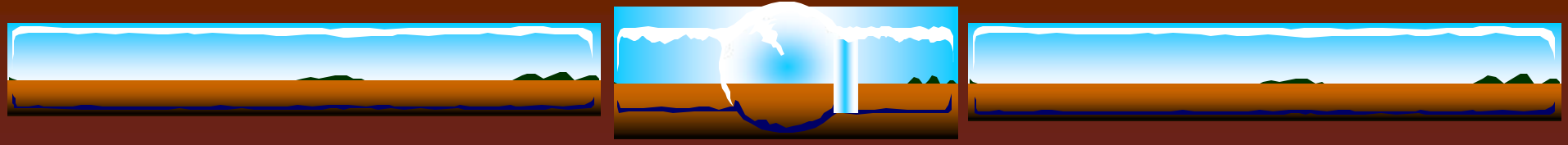
$$B_{ma} = \beta^0_{Ma} + \beta^1_{Ma} g(\alpha, I^{0.5}) + \beta^2_{Ma} g(12 I^{0.5})$$

$$g(x) = 2(1-(1+x)e^{-x})/x^2,\ \Phi_{ij} = \Theta_{ij} + {}^E\Theta_{ij}(I),\ Z = \sum_i |z_i| m_i$$



Unique Aspects of Approach

- **All experimental data are evaluated.**
- **Consistent thermodynamic description for the activities of the solvent and the charged and neutral solutes.**
- **Both ion associated and specific interactions consistently included in free energy description.**
- **A free energy representation so all other properties may be obtained by differentiation.**



Results/Accomplishments

Complete Yrs 1, 2 Work Plan in 4/05 Peer Review

Task 1:

? Use activity data & mononuclear Al speciation constants in NaCl solutions to make aqueous Al model (to 250ºC).

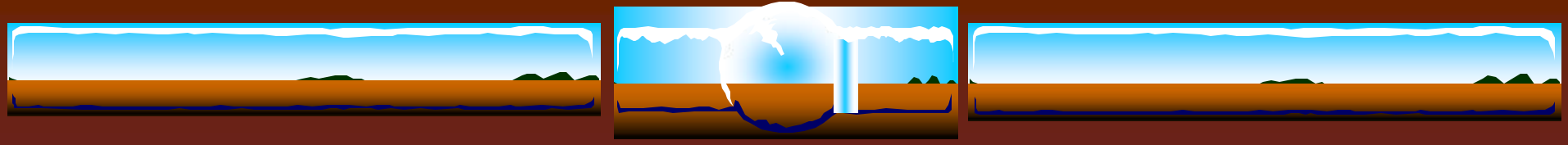
? Test if polynuclear Al species can be neglected.

? Combine model with our TEQUIL solution models including silicic acid chemistry.

Task 2:

? Begin developing a TD data base for hydrothermal minerals that is compatible with our solution models.

? Add aluminum hydroxide & aluminosilicate minerals (including feldspars). Use data bases in literature to add minerals without solubility data.



Problems Addressed

Problem: Limited data to model complicated Al aqueous speciation at intermediate pH. New solution data are available for mononuclear (MN, e.g., $Al(OH)_4^-$) Al species. Poor data base for polynuclear (PN, e.g., $Al_{13}O_4(OH)_{24}^{7+}$) Al species.

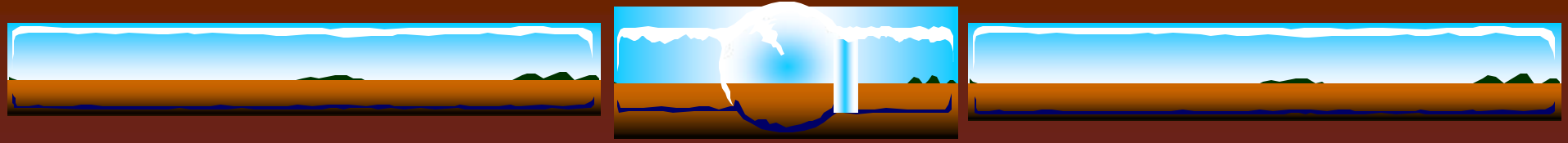
Problem: Availability of sufficient activity data to uncouple evaluation of interrelated aluminum speciation parameters.

Problem: Compatibility of activity (solubility) data and equilibrium constant measurements as a function of pH, solution concentration and temperaure .

Problem: Compatibility of our previous TEQUIL models (e.g., silica) with new aluminum solution model.

Problem: Availability of solubility data for aluminum minerals.

Problem: Compatibility of our solution model and thermodynamic databases in literature.



Results/Accomplishments, Yrs 1, 2

- **<u>Conclusion:</u> A mononuclear aluminum species model is sufficient for the compositions needed for most hydrothermal applications.**

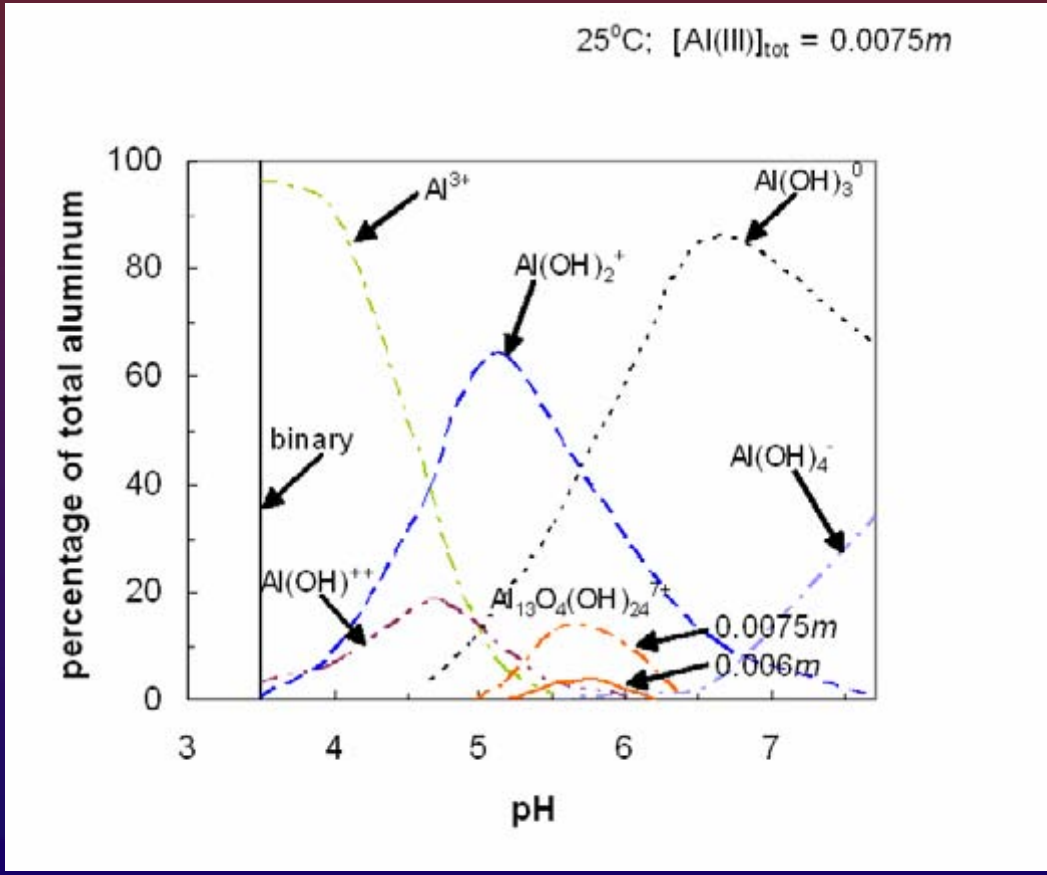
? **In the low and high pH range, the concentration of polynuclear Al species is very low relative to the concentration of Al mononuclear species. Therefore, their neglect in data analyses is justified.**

? **Polynuclear species are high only in aluminum concentration ranges outside that of reservoir waters in near equilibrium with formation minerals ($Al<10^{-5}$ *m*).**

Conclusion: **A mononuclear aluminum species model is sufficient for the compositions needed for most hydrothermal applications.**

? In the low and high pH range, the concentration of polynuclear species is very low relative to that of mono-nuclear species. Therefore, their neglect in data analyses is justified.

? Polynuclear species are high only in aluminum concentration ranges outside that of reservoir waters in near equilibrium with formation minerals ($Al < 10^{-5}$ *m*).



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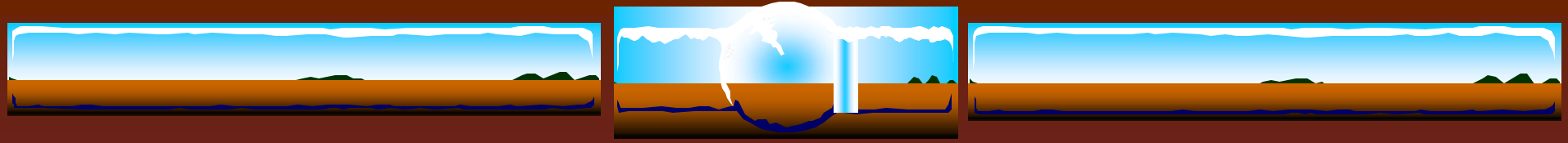
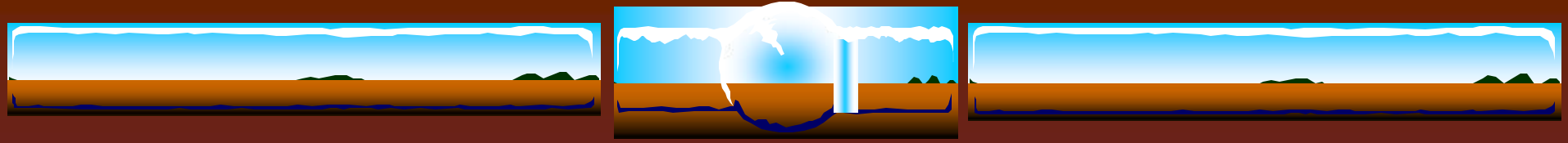


Mononuclear Aluminum Hydrolysis Species

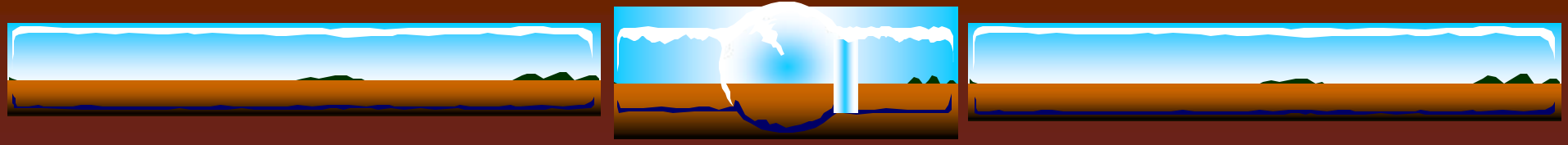
- $Al^{3+} + H_2O = Al(OH)^{2+} + H^+$ KH,1 (1)
- $Al(OH)^{2+} + H_2O = Al(OH)^+ + H^+$ KH,2 (2)
- $Al(OH)^+ + H_2O = Al(OH)_3^0 + H^+$ KH,3 (3)
- $Al(OH)_3^0 + H_2O = Al(OH)_4^- + H^+$ KH,4 (4)



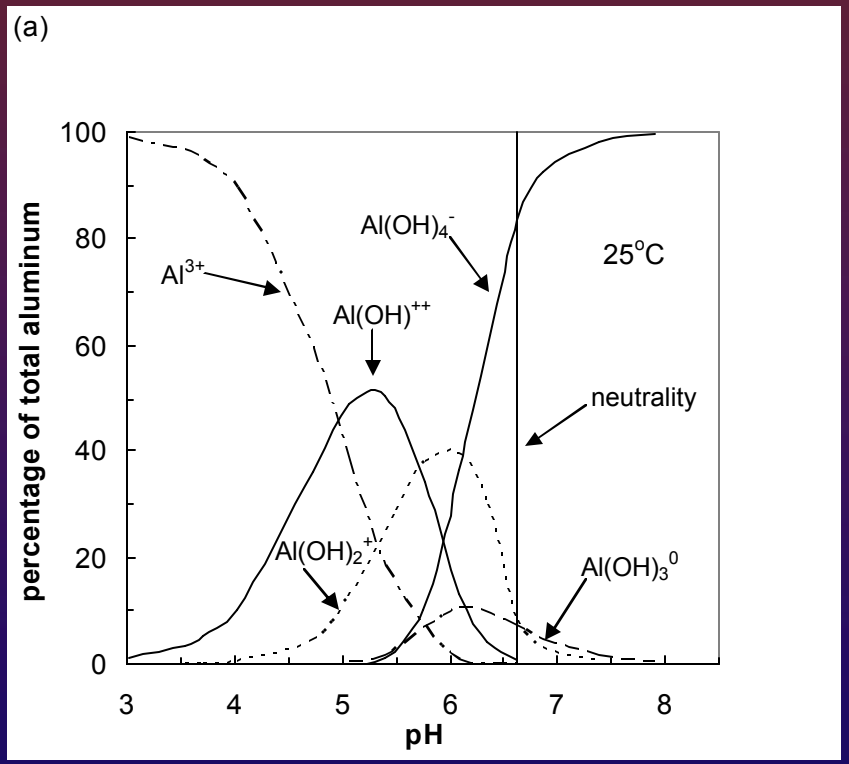
Conclusion: Solution model parameterization yields good agreement with Al speciation data in the literature

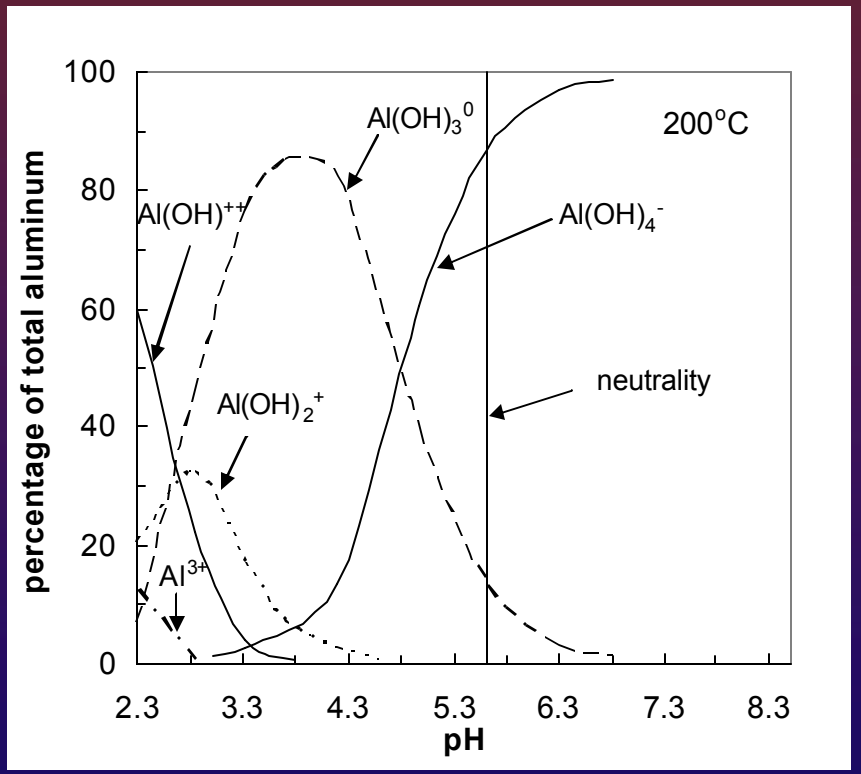
For example, in agreement with Castet et al., 1993:

- Al^{3+} is the dominant species up to about pH ~ 5 at 25°C.
- The amount of $Al(OH)^{2+}$ never exceeds 40% of the total aluminium species in solution from 25°C to 300°C.
- Increase of temperature favors the production of the lower charged hydrolysis species, $Al(OH)_3^o$ and $Al(OH)_4^-$.
- The $Al(OH)_4^-$ species dominates at temperatures = 25°C in solutions with a pH close to and above neutral. At 200°C, $Al(OH)^{2+}$ is a major species only in very acidic solutions (up to about pH=2.6), and the neutral $Al(OH)_3^o$ species is the dominant species at pH from ~ 2.6 to about 4.5.



Low temperature aluminum aqueous chemistry model successfully extended to 300ºC





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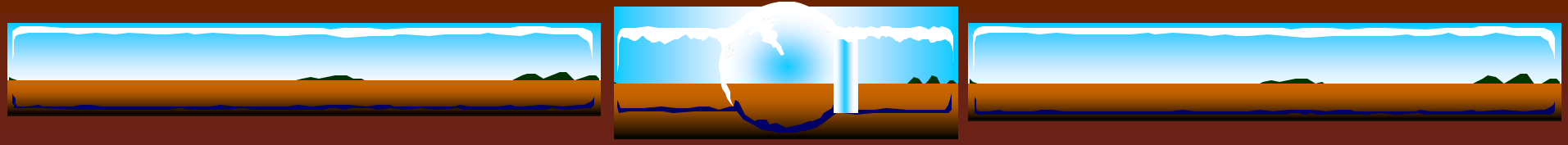
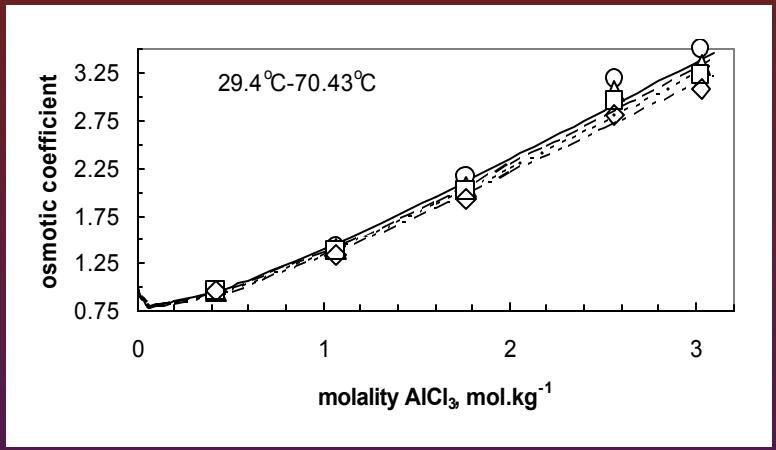


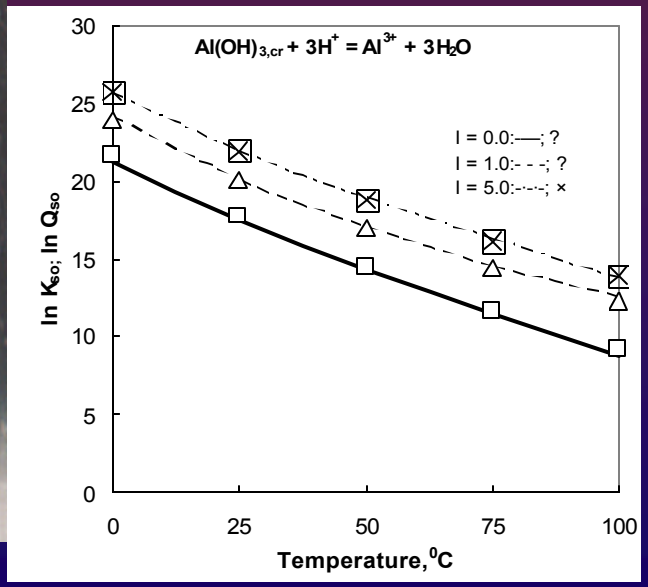
Conclusion: Can successfully add aluminum solid phase interactions to model.

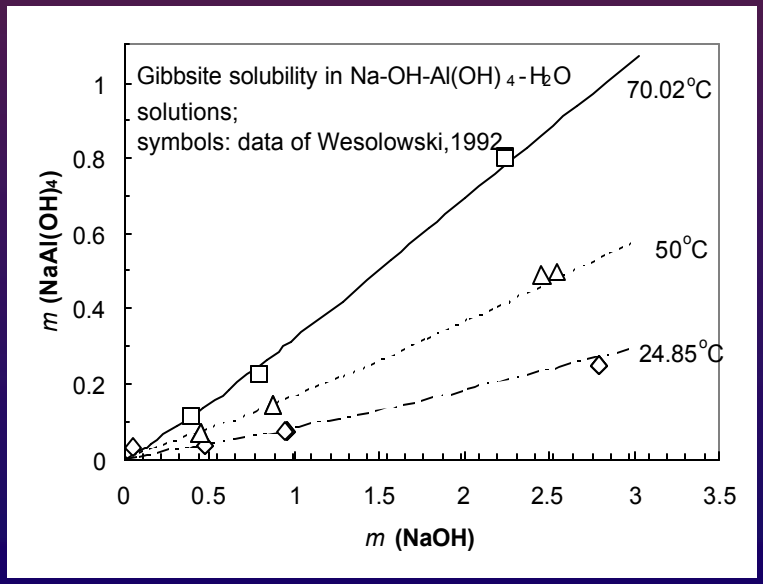
- Solution model parameterization compatible with TEQUIL silica parameterization.
- Solution model parameterization compatible with solubility data and thermodynamic databases for aluminum hydroxide and aluminiosilicate minerals.
- Parameterization process includes evaluation of data in the literature.

Low and high pH behavior included in model.

The aggressive hydrolysis chemistry of Al.







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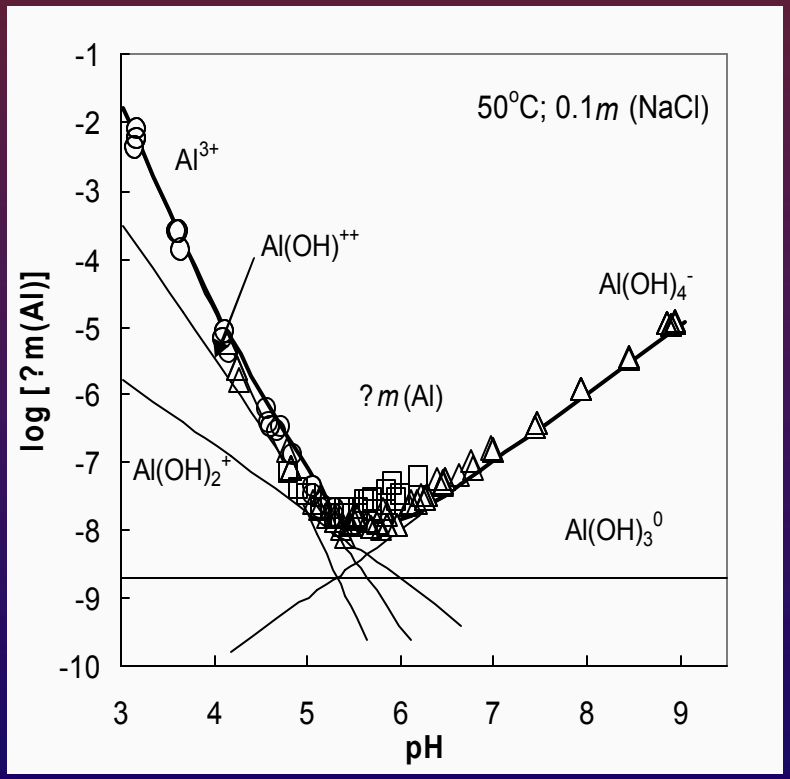
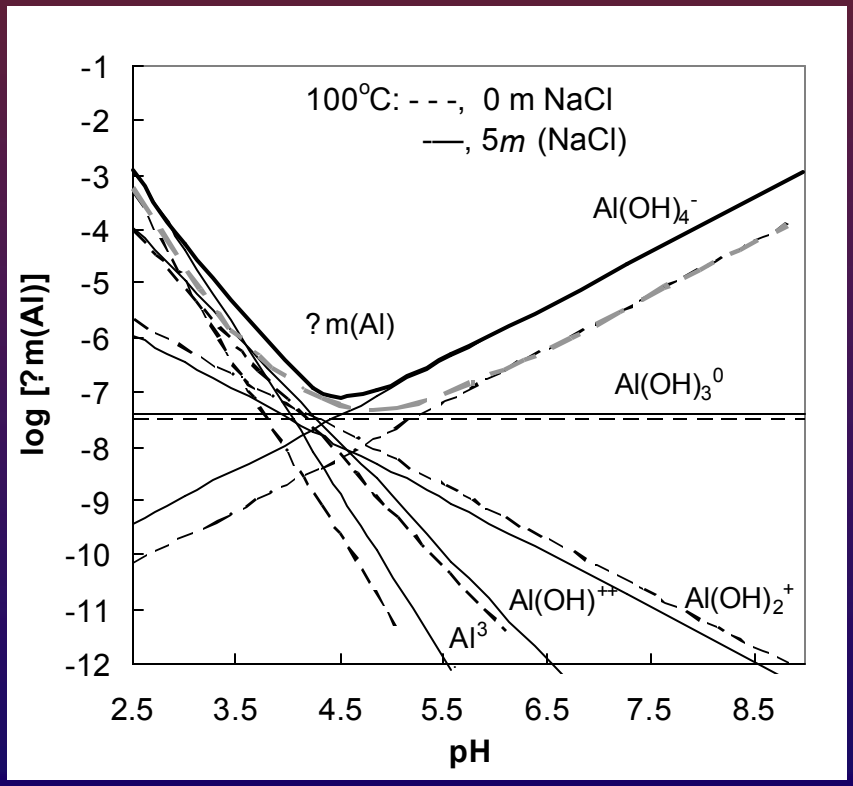
Solubility of gibbsite ($Al(OH)_3$) as a function of pH (pH = -log $aH+$)

The straight lines represent the concentrations of individual species. The heavy curves are the total concentration of all aqueous aluminum species





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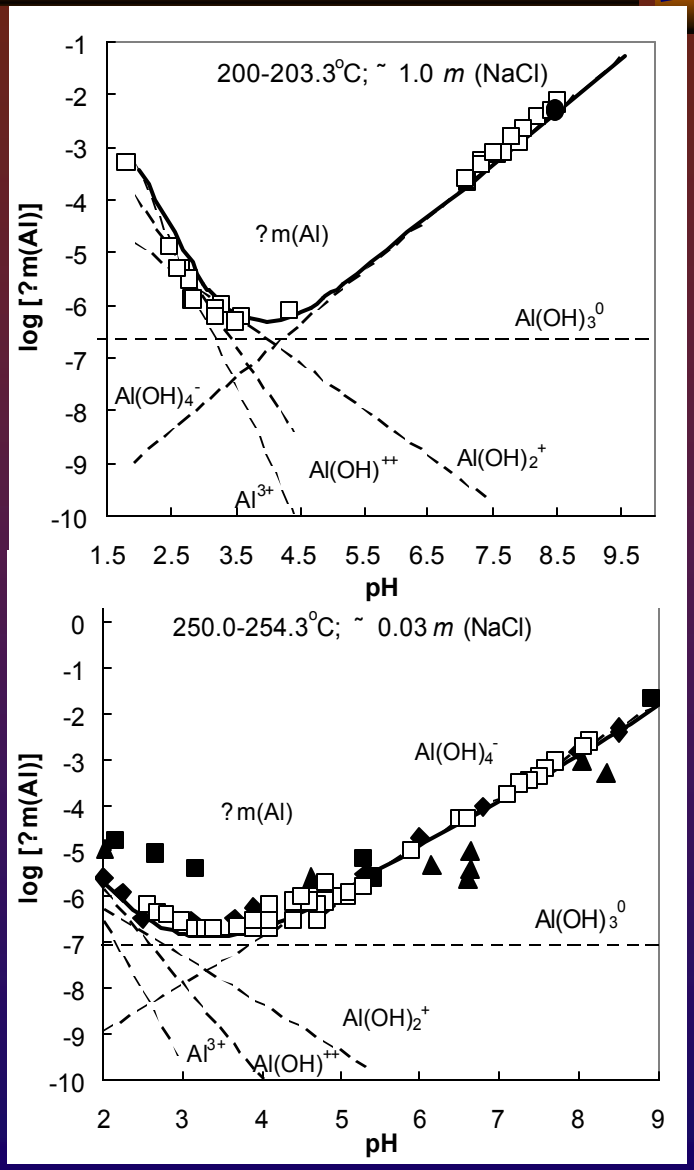
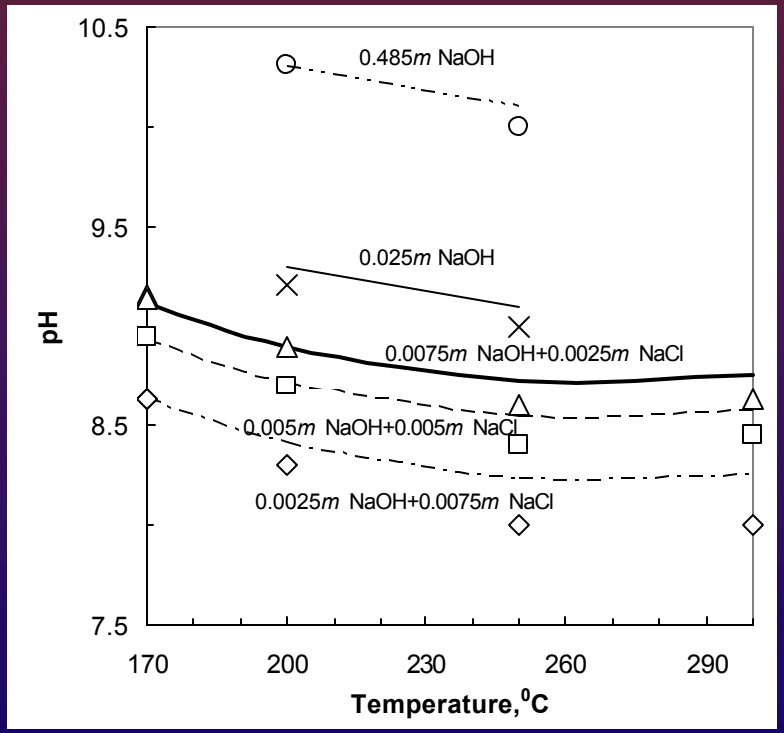
Boehmite (AlOOH) Solubility in NaCl Brines

?, data of Benezeth et al.(.03m) and Palmer et al. (1m).,? Diakonov et al, ¦ Kuyonko, ? Bourcier et al., ? Castet et al





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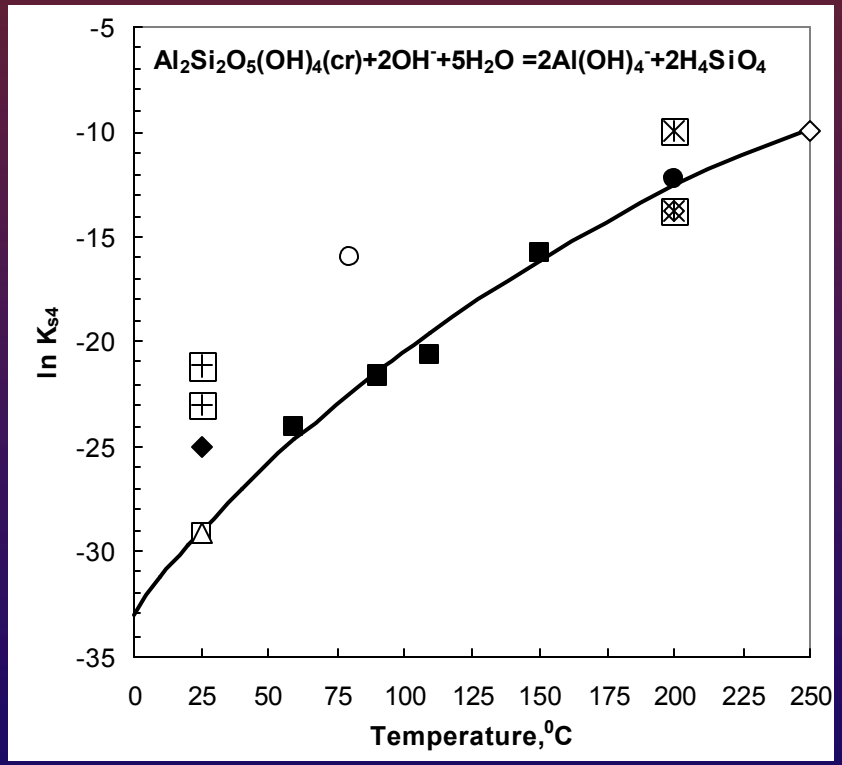
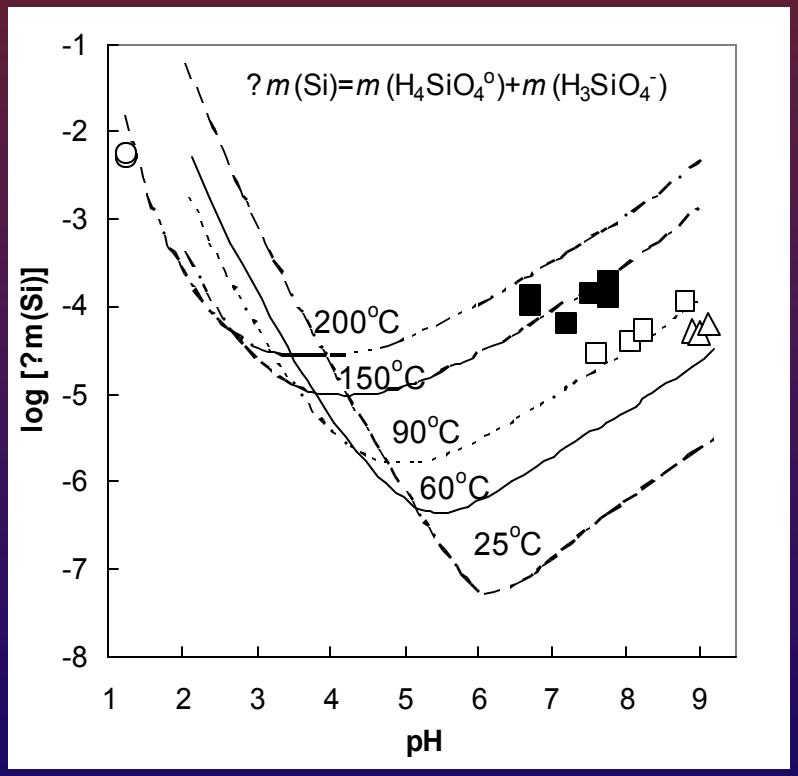
Kaolinite ($Al_2Si_2O_6(OH)_4$ Solubility





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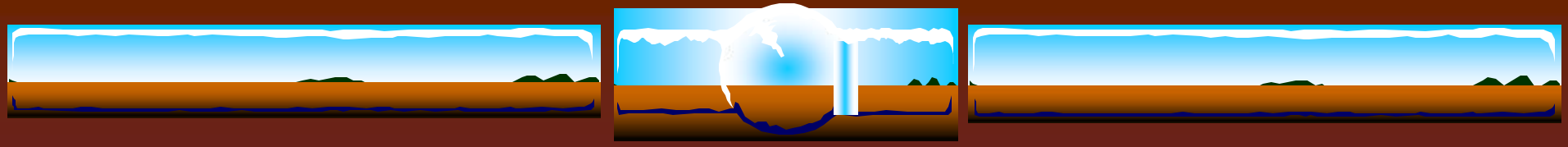
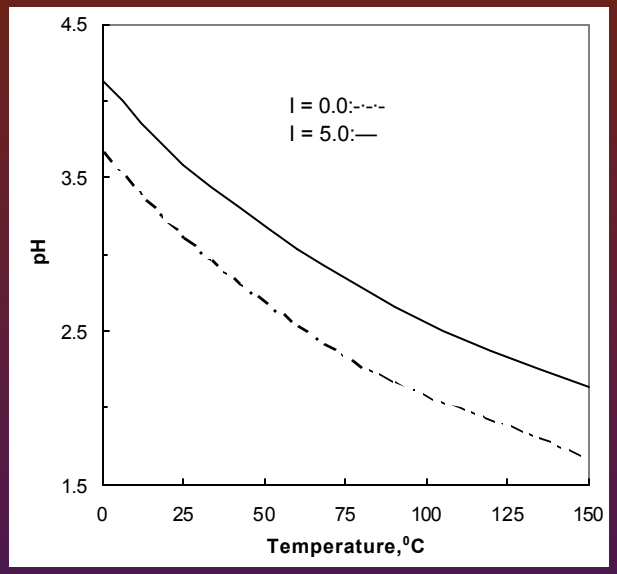
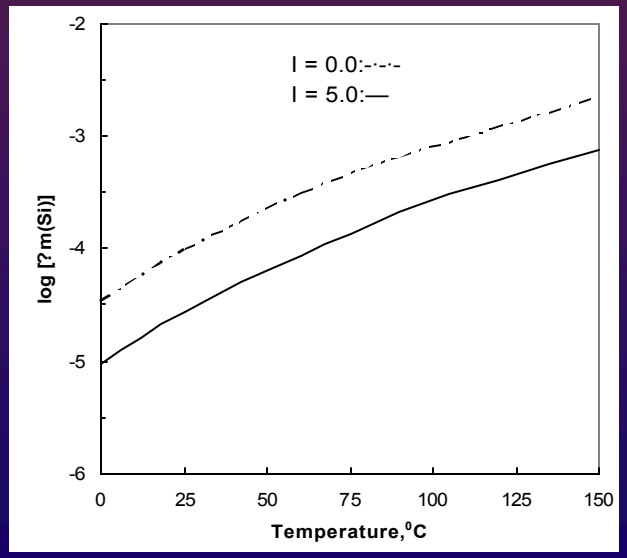
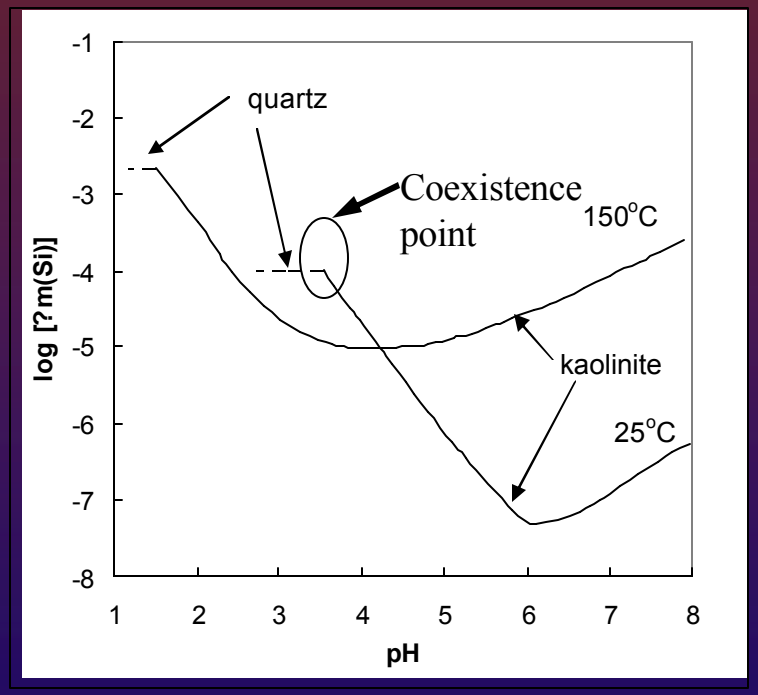


Kaolinite-Quartz Mineral Coexistence







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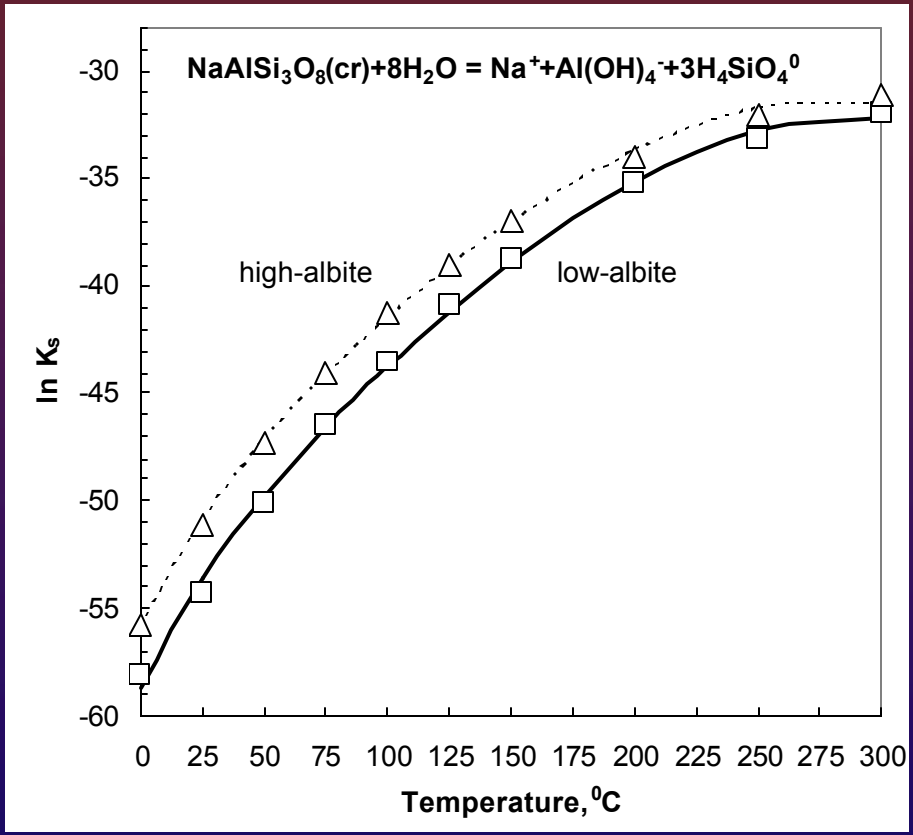
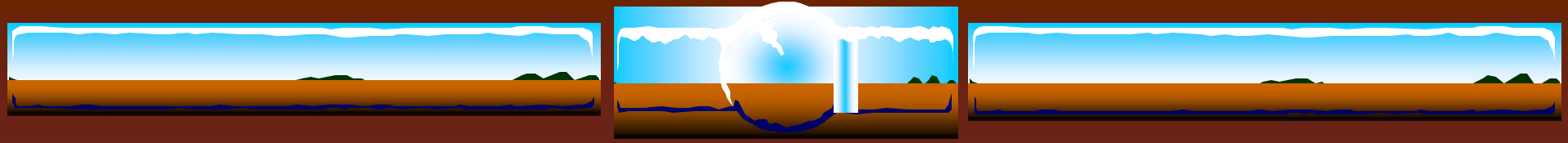
Albite ($NaAlSi_3O_8$) Equilibrium Constant





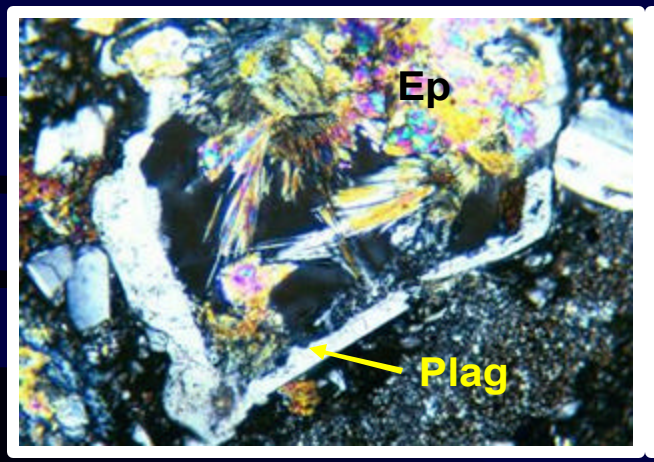
Project objective (slide 2) will be achieved by Project Completion Date.

- This research program will produce the first high accuracy variable temperature EOS models, tailored to the solution mixing properties in the composition-T-P region of interest to EGS, that include the most common hydrothermal solution and mineral components.

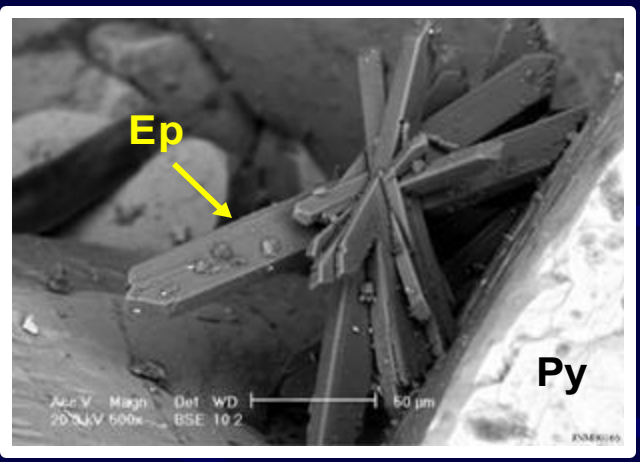
- Easy to use chemical models facilitate the economical production of EGS energy sources by providing the industry rapid predictive capability to: 1) characterize EGS resource and energy production chemistry; 2) predict chemical reactions between common formation minerals and hydrothermal fluids and/or injectates; 3) estimate effects of temperature changes and fluid mixing on mineral precipitation and dissolution and thereby on formation permeability and fluid circulation; 4) test thermodynamic databases in literature.

Test Model Against Natural Mineral Assemblages

Propylitic Zone: Epidote

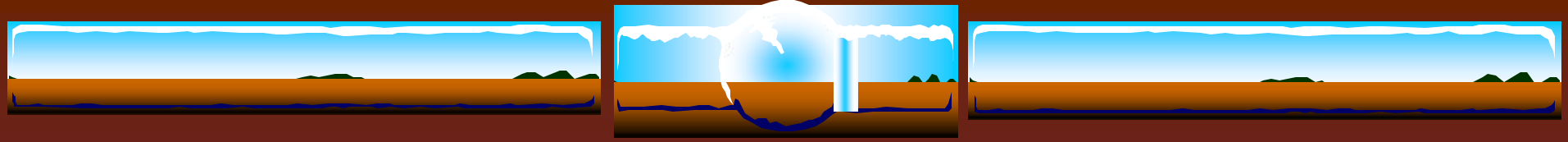


T-8



T-2; 3215 ft.

EGI



The End