Fourth Annual Conference on Carbon Capture & Sequestration

Developing Potential Paths Forward Based on the Knowledge, Science and Experience to Date

Session Title:

Geologic Sequestration (3)

Uncertainty in carbon dioxide sequestration capacity estimates in saline aquifers using geochemical models

Douglas E Allen*, Brian Strazisar, Yee Soong, Sheila Hedges, Robert M. Dilmore, PJ Pique

U.S. DOE NETL, *Salem State College

May 2-5, 2005, Hilton Alexandria Mark Center, Alexandria Virginia

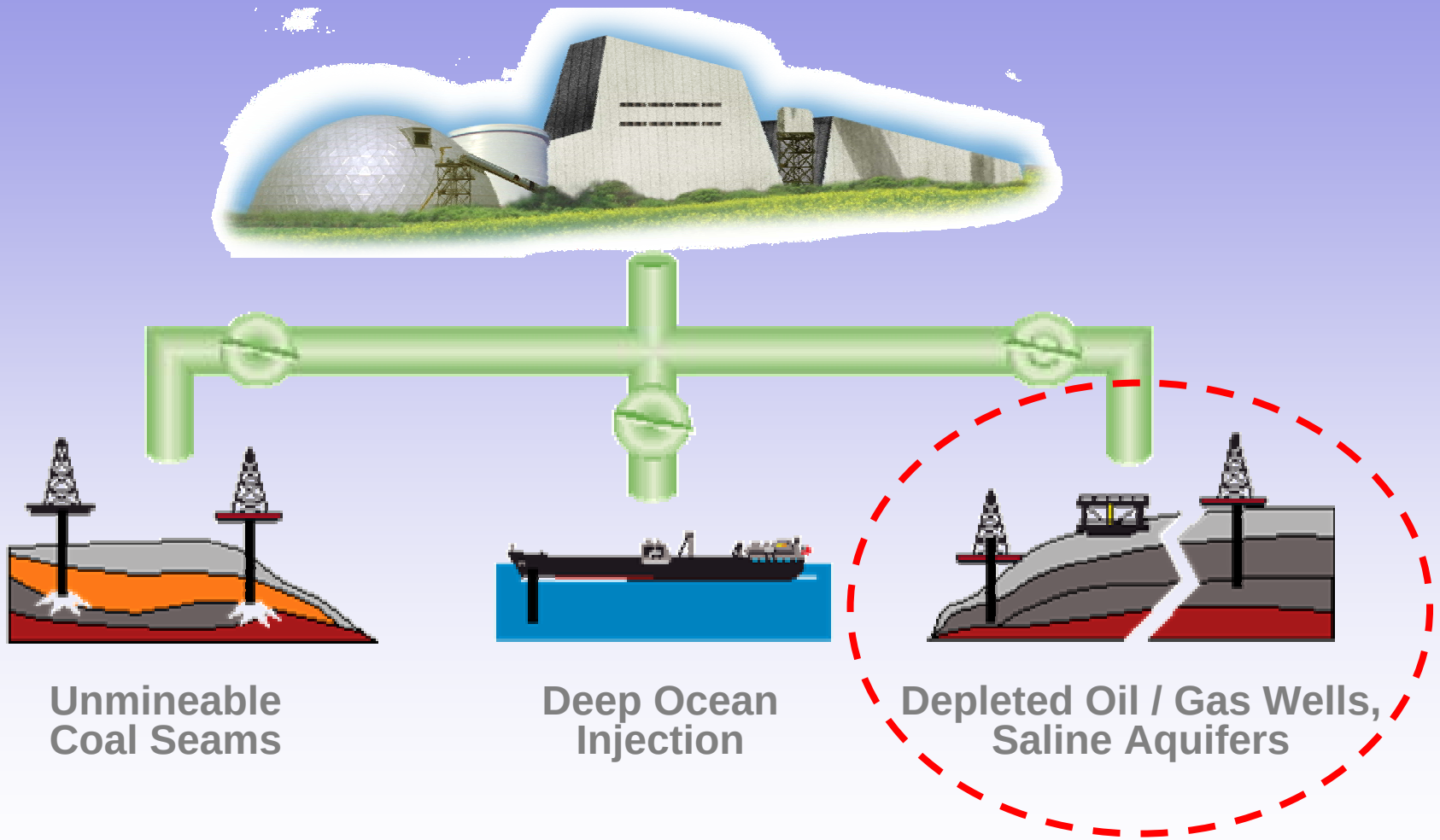
Paper 76

Overview

- Brine sequestration summary
- CO_2 capacity model overview
- Issues related to brine sequestration equilibrium modeling:
  - Fugacity coefficient model
  - Solubility model
  - Thermodynamic equilibrium data
  - Gas/water/rock interaction
- Comparison of model results
- Summary

Direct Sequestration

Capture and Disposal of CO_2



CO_2 sequestration in saline aquifers

- **Hydrodynamic trapping :** traps the CO_2 into flow systems for geological periods of time
- **Solubility trapping :** traps the CO_2 as an aqueous component (H_2CO_3, HCO_3^-, $CO_3^=$,and $CO_{2(aq)}$)
- **Mineral trapping :** convert CO_2 to carbonate minerals (e.g., calcite, dolomite, siderite)

$$\mathbf{Ca^{++} + CO_3^{\ 2-} \longrightarrow CaCO_3 \ (calcite)}$$

$$\mathbf{Ca^{++} + Mg^{++} + 2\ CO_3^{\ 2-} \longrightarrow CaMg(CO_3)_2 \ (dolomite)}$$

$$\mathbf{Fe^{++} + CO_3^{\ 2-} \longrightarrow FeCO_3 \ (siderite)}$$

$$\mathbf{Mg^{++} + CO_3^{\ 2-} \longrightarrow MgCO_3 \ (magnesite)}$$

Equilibrium Models

- Stand Alone:
  - Designed specifically and exclusively to estimate CO_2 solubility
  - Gas/water interaction only (no rock interaction)
  - Very accurate (if data used is correct)
- Complex geochemical code
  - Calculates bulk equilibrium reaction equilibria between gas/rock/water at a variety of temperature, pressure, and solution compositions

Stand Alone Models

- **Enick & Klara** (Chem. Eng. Commun. 90, 1990)
  - Krichevsky – Kasarnovsky equation for CO_2 solubility in water
  - 25-250 ºC
  - 34-724 bars
  - CO_2 solubility as a function of salinity based on empirical fit of solubility data at a range of conditions
- **Duan & Sun** (Chem. Geol. 193, 2003)
  - 0 – 260 ºC
  - 0 – 2,000 bars
  - EOS to calculate solubility of CO_2 in pure water
  - Pitzer ion specific interaction to adjust solubility of CO_2 in fluids with high salinity

Complex Geochemical Models

- Geochemist's Workbench®
  - Simulate salting out behavior of CO_2 (default setting must be adjusted)
  - Requires adjusted ionic strength limit (default max set to 3 molal)
  - Input CO_2 pressure as fugacity
- PHREEQC
  - Assumes CO_2 behaves as an ideal gas (partial pressure = fugacity)

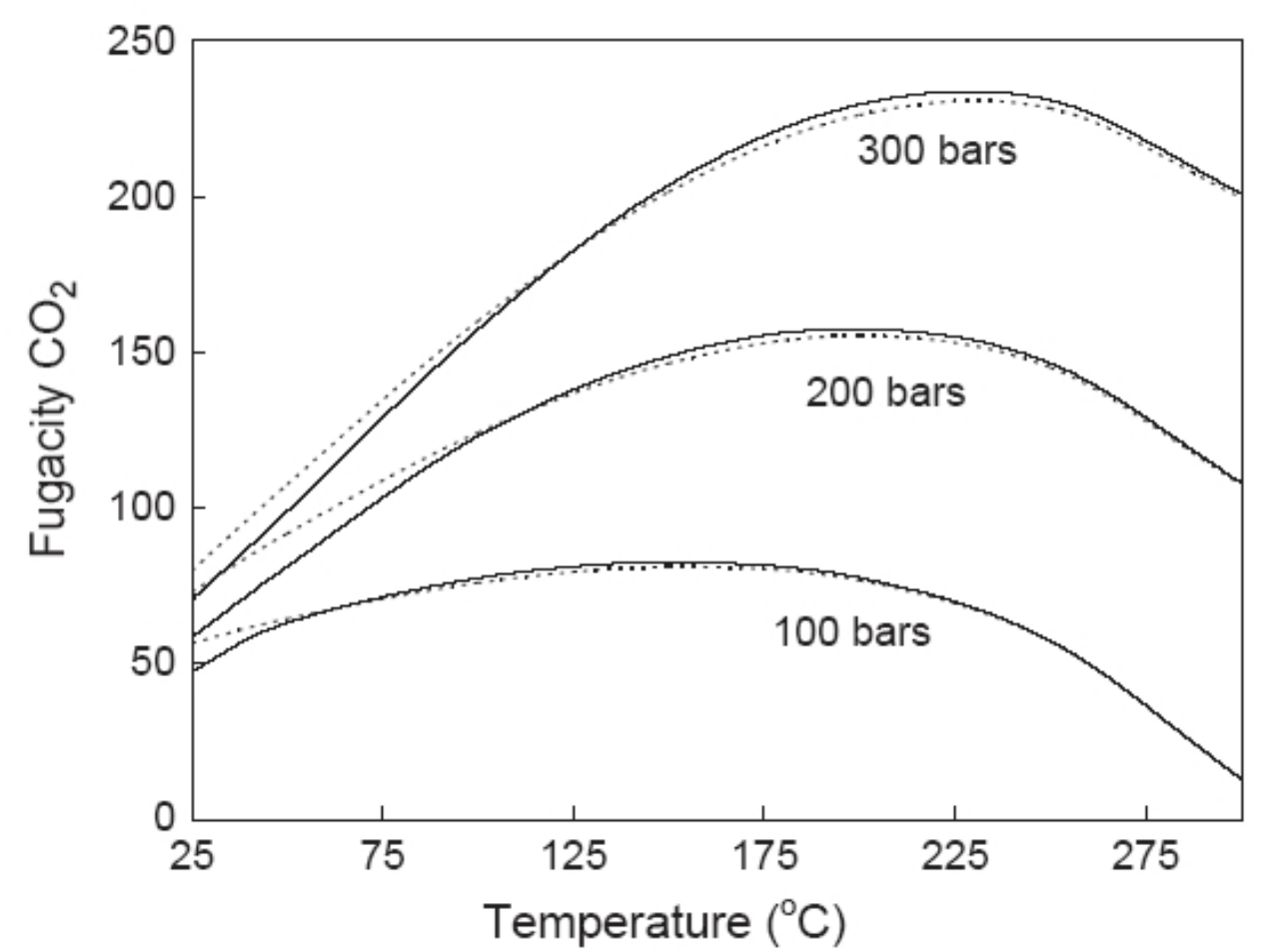
Partial Pressure vs. Fugacity

$$f_{CO2} = \varphi_{CO2} * P_{CO2}$$

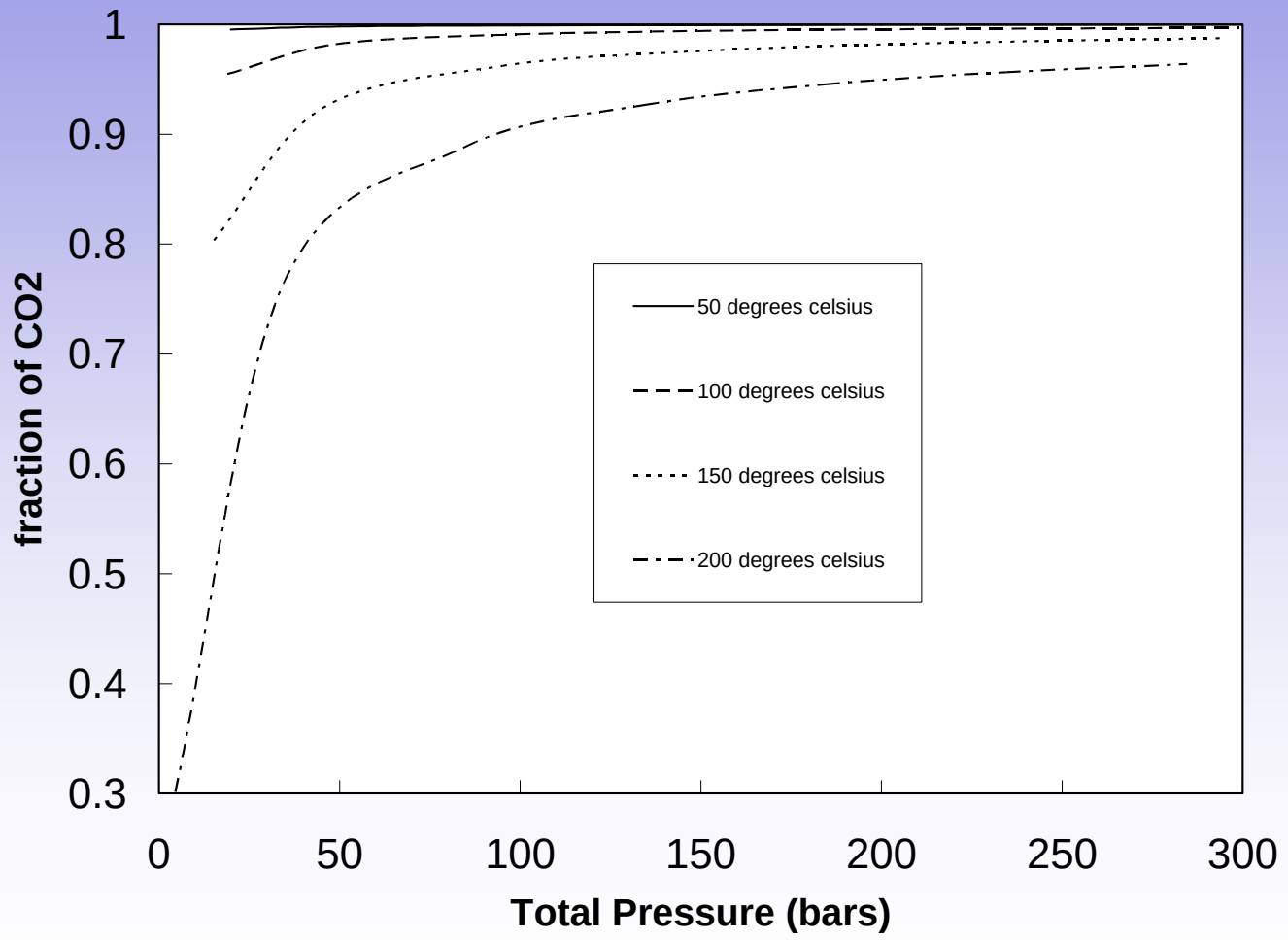
- At high P_{CO2}, CO_2 fugacity coefficient departs significantly from unity (φ departs fom unity)
- Under sequestration conditions, if T is relatively low, assume that P_{CO2} = Ptotal (H_2O vapor pressure is negligible)

Fugacity as a function of T & P

(Duan & Sun - solid line, Spycher and Reed - dotted line)



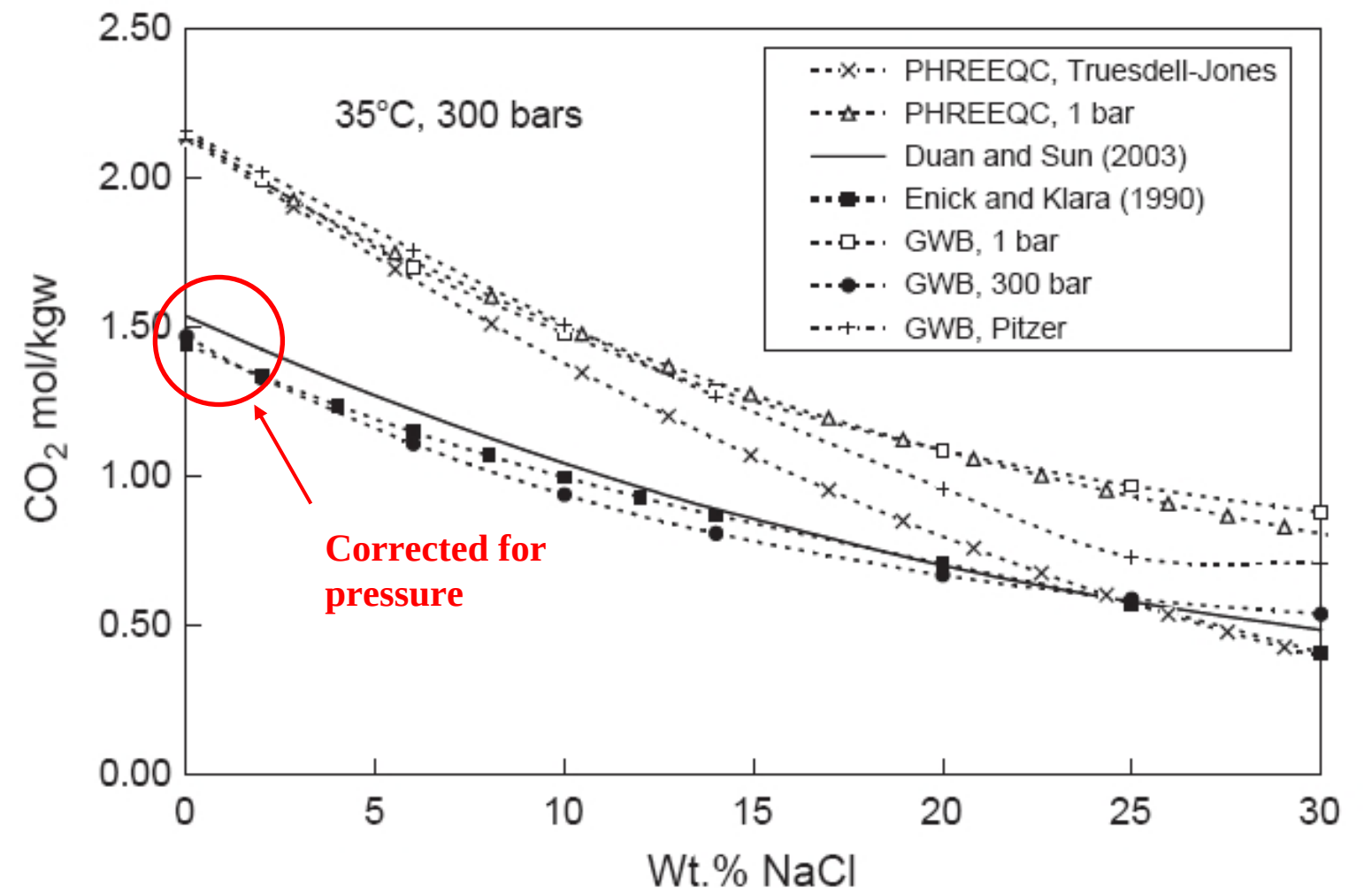
Fractional contribution of CO_2 to total pressure



Equilibrium Constants at Elevated Pressures

- Stand alone model
  - Built-in method to correct equilibrium constants as *f(T,P)*
- Geochemical Modeling Packages
  - Equilibrium constants provided for set conditions
    - 1 bar, 0-100ºC and at steam saturation presure thereafter
  - Correct by direct modification of database to reflect accurate prediction of K as *f(T,P)*
  - SUPCRT92 w/1998 database update used for K of all gasses, aqueous species and minerals

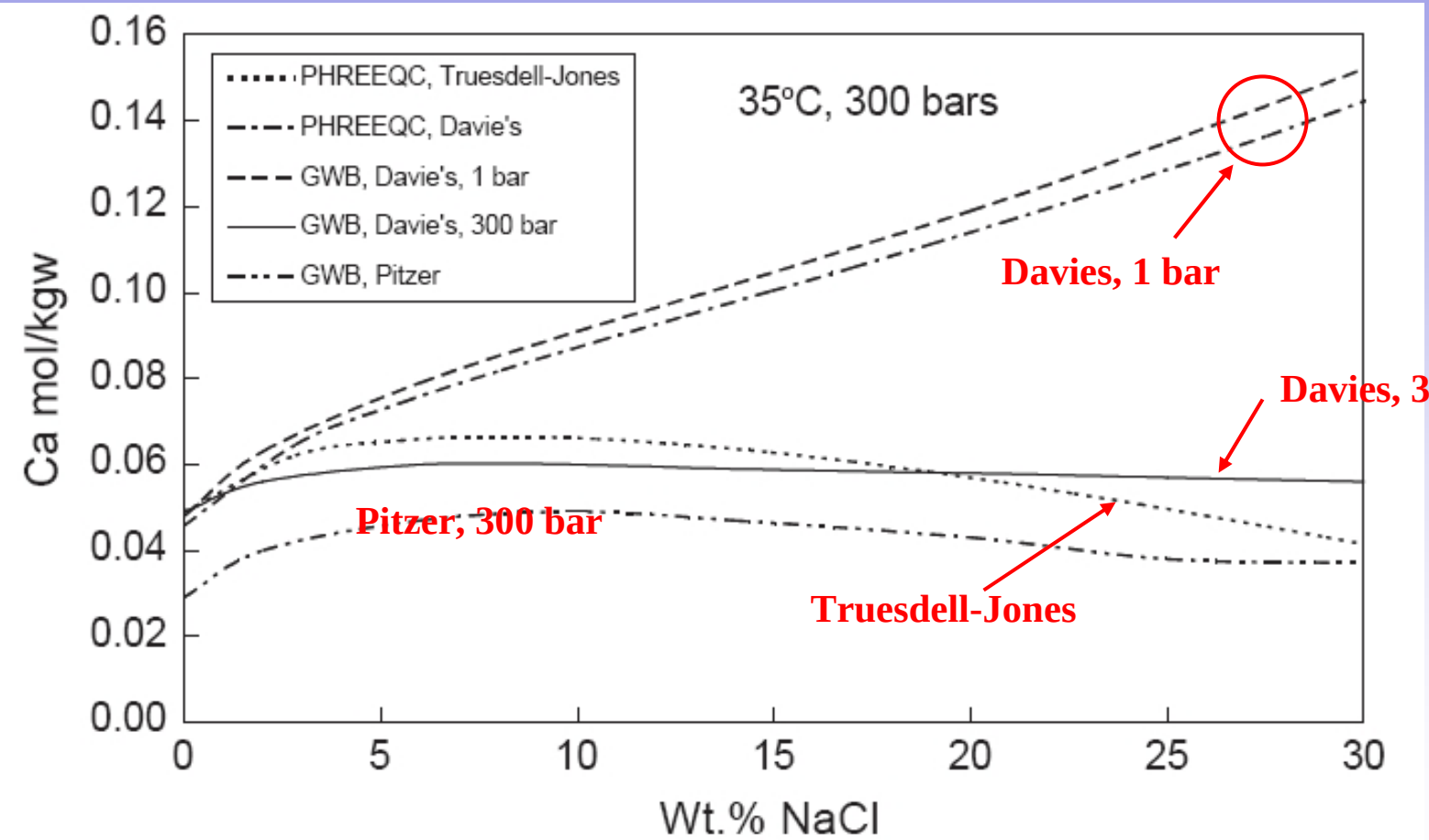
Calculated CO_2 solubility as a function of salinity



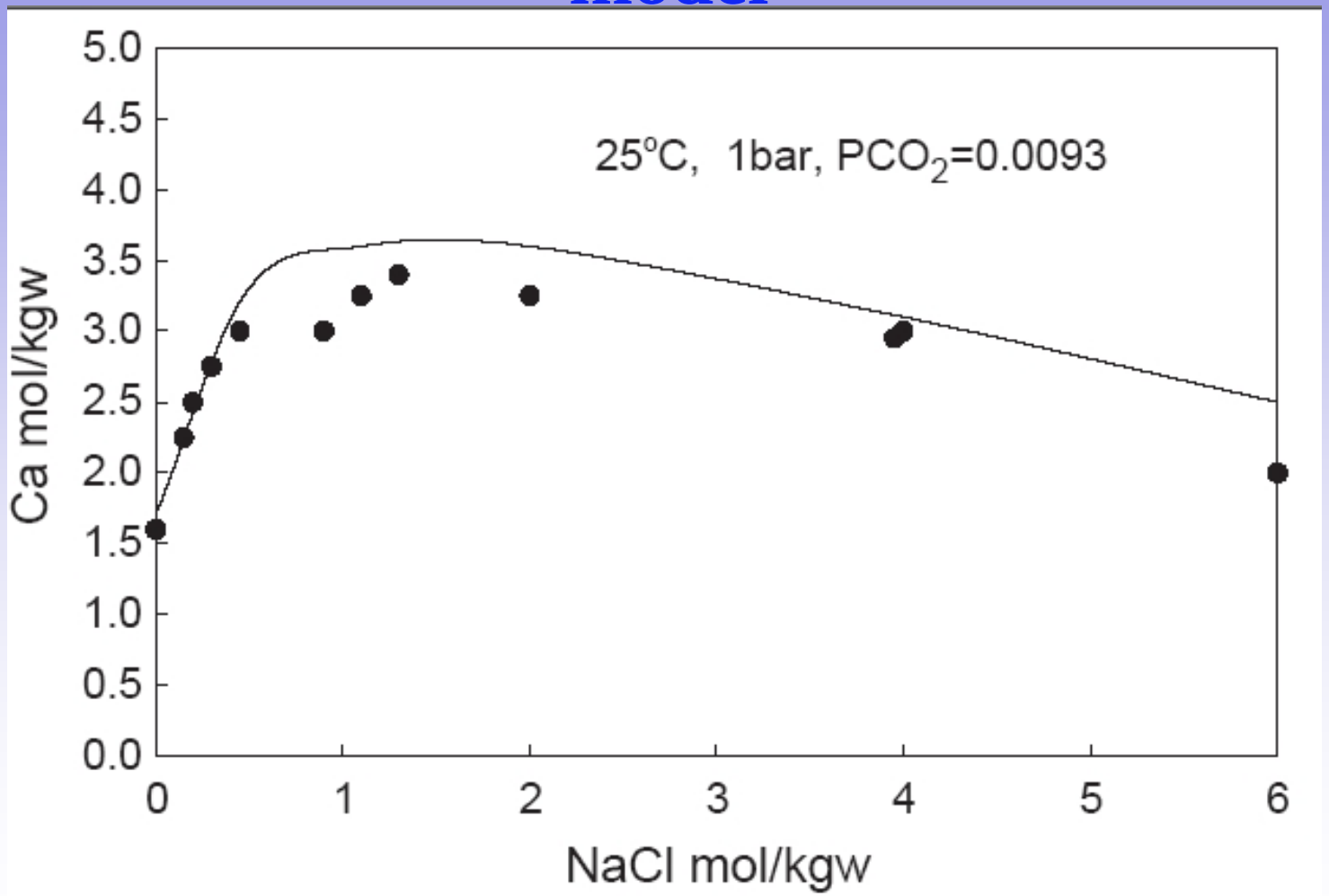
Activity Calculation

- Activity coefficients are estimated by activity models
- Extended forms of the Debye-Hückel model– treat ion as spheres with central charge that interacts with each other through columbic forces
  - Davies Equation (accurate below 1 molal)
  - Truesdell-Jones (accurate @ high salinity, low pressure)
  - B-Dot Equation (accurate below 1 molal)
- Pitzer coefficients-ion specific interaction to account for high salinities, no Al, Si considered

Calculated Calcite solubility as a function of salinity (35 °C, 300 bars of CO_2 pressure)



Calcite Solubility as a function of salinity at atmospheric conditions using the Pitzer model

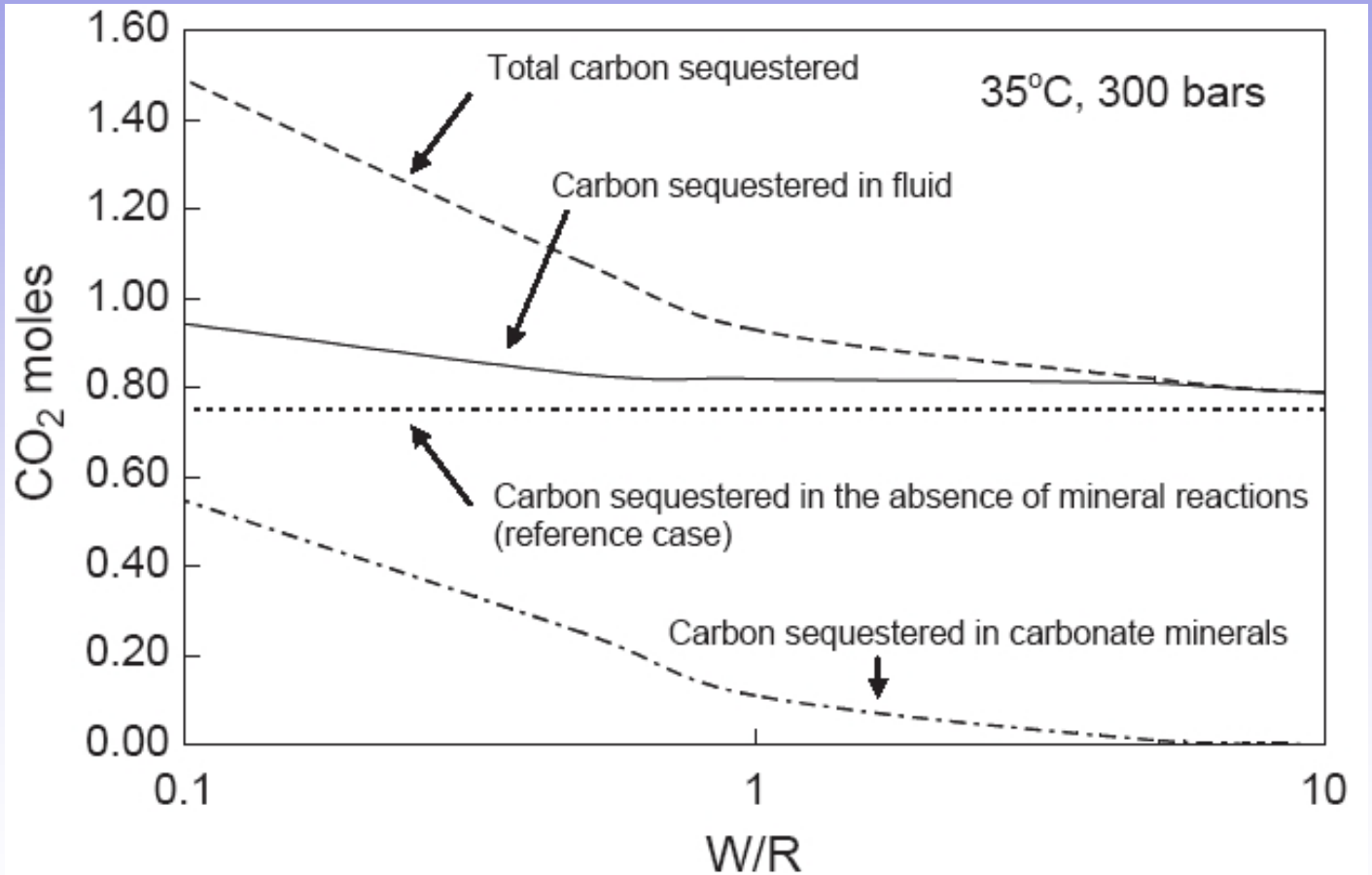


***Source*: M. Wolf, O. Breitkof, R. Puk, Solubility of calcite in different electrolytes at temperatures between 10 and 60 8C and at CO_2 partial pressures of about 1 kPa, Chem. Geol. 76 (1989) 291– 301.**

Significance of Rock/Water Interaction

- Simulated sandstone – quartz (85%, wt.), K-feldspar (10%), albite (2%), and Kaolinite (3%)
- Representative high salinity brine (high Na, Ca, Cl)
- 300 bars, 35 ºC
- Vary Rock/Water ratio
- Calcium/magnesium carbonate formation increases sequestration capacity
- Modification of fluid chemistry will enhance CO_2 solubility

Equilibrium CO_2 Capacity Model with and without rock-water interaction



Outstanding Problems

- Models based on Debye-Hückel type equations are not applicable to high salinity systems.
- The Pitzer coefficients are largely untested at temperatures above 25°C and pressures above 1 atmosphere.
- Although the Pitzer model does well to simulate high salinity conditions, there are currently no interaction coefficients for Al and Si available. Therefore, rock/water/gas interaction calculations involving alumino-silicate assemblages at elevated pressures and salinities are not currently accurate !!

(Including the very important Al-bearing mineral **Dawsonite**)

Summary

- Errors in the estimates of CO_2 sequestration capacity in saline aquifers are likely
- To produce reliable results, choose carefully:
  - Fugacity coefficient model
  - Solubility model
- Correct thermodynamic equilibrium data for temperature and pressure
- Stand alone models do not account for fluid interaction with rock
- Difficult to accurately model Al- and Si-bearing systems

Selected References

- D.E. Allen B.R.Strazisar, Y. Soong, S.W. Hedges, Modeling carbon dioxide sequestration in saline aquifers: Significance of elevated pressures and salinities (article in press)
- DOE, 1999. Carbon Sequestration Research and Development. DOE/SC/FE-1.
- S. Bachu, W.D. Gunter, E.H. Perkins, Aquifer disposal of CO_2: hydrodynamics and mineral trapping, Ener.Conv. Man. 35 (1994) 269– 279.
- C.M. Bethke, Geochemical reaction modeling: concepts and applications, Oxford University Press, 1996, 397 pp.
- R.M. Enick, S.M. Klara, CO_2 solubility in water and brine under reservoir conditions, Chem. Eng. Commun. 90 (1990) 23– 33.
- Z. Duan, R. Sun, An improved model calculating CO_2 solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar, Chem. Geol. 193 (2003) 257–271.
- J.W. Johnson, E.H. Oelkers, H.C. Helgeson, SUPCRT92—A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 bar to 5000 bar and 0 8C to 1000 8C, Comput. Geoscie. 18 (1992) 899–947.
- K.S. Pitzer, Thermodynamics of electrolytes: I. Theoretical basis and general equations, J. Phys. Chem. 77 (1973) 268– 277.
- A.H. Truesdell, B.F. Jones, WATEQ, a computer program for calculating chemical equilibrium of natural waters, J. Res. U.S. Geol. Surv. 2 (1974) 233–248.
- S. Bachu, J.J. Adams, Sequestration of CO_2 in geological media in response to climate change: capacity of deep saline aquifers to sequester CO_2 in solution, Environ. Conserv. Manag. 44 (2003) 3151– 3175.
- M. Wolf, O. Breitkof, R. Puk, Solubility of calcite in different electrolytes at temperatures between 10 and 60 8C and at CO_2 partial pressures of about 1 kPa, Chem. Geol. 76 (1989) 291– 301.

QUESTIONS?

Douglas E Allen
Department of Geological Sciences
Salem State College

dallen@salemstate.edu

(978) 542-6653