U.S. DEPARTMENT OF ENERGY
OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

NUCLEAR WASTE TECHNICAL REVIEW BOARD
FULL BOARD MEETING

SUBJECT: **GEOCHEMICAL CODE EQ3/6**

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EQ3/6 is a Software Package for Modeling the Geochemistry of Water/Rock/Waste Systems

- **Treats the overall water/rock/waste interaction as the sum of many simpler processes (e.g., dissolution of a single mineral, formation of a single aqueous complex)**

- **Links complex applications to fundamental data:**

    Example: Models of experiments on UO_2 and spent-fuel dissolution, which incorporate data for the solubility of uranyl silicate minerals and for the stability of uranyl carbonate complexes

    Example: Models of experiments on hydrothermal tuff/J-13 water interactions, which incorporate data for the solubility and dissolution/growth kinetics of individual minerals

EQ3/6 Makes Two Different Kinds of Calculations

- ## Analytical calculations (EQ3NR code):

  - Chemical form of dissolved components (simple ions, complexes)
  - Saturation indices and affinities (states of the whole system and of individual reactions with respect to thermodynamic equilibrium)

- ## Simulation (prediction) calculations (EQ6 code):

  - Equilibrium states, titrations, groundwater-mixing, reaction paths
  - Mineral growth and dissolution, changes in water chemistry, including pH and Eh
  - Individual reactions controlled by kinetics, equilibrium, or locked

EQ3/6 Has Been Applied to a Variety of Problems Involving Water/Rock and Water/Rock/Waste Interactions

- **Originally developed to model seawater/basalt interactions in mid-ocean ridge hydrothermal systems**

- **Later developed for applications related to geologic repositories for high-level nuclear waste (Salt Repository Project, Yucca Mountain Project)**

- **Other areas of application:**
  - **Geothermal fields and hydrothermal systems, in general**
  - **Ore deposition**
  - **Petroleum reservoirs**
  - **Landfill geochemistry**
  - **DOE site cleanup**

Current and Planned Applications of EQ3/6 within the Yucca Mountain Project

- **LLNL - Analysis and simulation of water/rock and water/rock/waste interactions experiments pertinent to the near-field environment (low temperature and hydrothermal). Experimental design. Natural analog studies. Prediction of near-field interactions. Supporting prediction of the source term**

- **USGS - Analysis of ambient groundwater chemistry**

- **LANL - Analysis and simulation of water/rock/waste interactions experiments pertinent to far-field radionuclide migration. Supporting prediction of far-field migration**

- **PNL - Performance assessment**

Recent History of Releases of EQ3/6

- **Version 6.0 (Feb. 1988)**

- **Version 6.1 (Aug. 1988) (Fixes only)**

- **Version 7.0 (Nov. 1990)**

- **Version 7.1 (Aug. 1992) (Fixes only)**

- **Version 7 has been distributed to LANL, PNL, NAGRA, CNWRA, the NWTRB, and others**

- **No code development in FY91 or FY92. Start on Version 8 in FY93?**

QA Status of EQ3/6, Version 7

- Version 7 has not yet been certified as "qualified" for use in "quality-affecting work" on the Yucca Mountain Project

- Four manuals (totaling ~720 pages) have been written to meet the NUREG-0856 code documentation requirements. These manuals are about to be published

- There is a large library of test cases, many allowing comparison with other codes (especially PHREEQE and PHRQPITZ)

- An "independent" qualification effort was started in late FY92

EQ3/6, Version 7: Software Characteristics

- **Written in FORTRAN 77**

- **Version 7 export package:**
  - **7.5 megabytes total**
  - **Total lines of source code: 62,500**
  - **Largest executable code: 1 megabyte**
  - **Largest data file: 2 megabytes**

- **Host platform is a Sun SPARCstation (UNIX workstation)**

- **Also runs on Silicon Graphics and IBM RS6000 workstations**

- **Easily ported to a VAX or a 486 PC**

Version 7 of EQ3/6 has Five Thermodynamic Data Files to Support Applications

File Name	Source	γ Models	Temp. Range	Chem. Elem.	Aq. Sp.	Pure Mins.	Sol. Sols.	Gas Sp.
com	GEMBOCHS (LLNL)	EDH	0-300°C	78	846	891	13	76
sup	SUPCRT92	EDH	0-300°C	69	315	130	0	16
nea	NEA92	EDH	0-300°C	32	158	188	0	76
hmw	HMW84	Pitzer	25°C only	9	17	51	0	3
pit	PITZER79 & others	Pitzer	0-l00°C	52	68	381	0	38

EDH = Extended Debye-Hückel (Davies' equation or B-dot equation)

EQ3/6 Data Files are Created and Maintained at LLNL Using a Relational Data Base System Called GEMBOCHS

- **GEMBOCHS - Geologic and Engineering Materials: Bibliography of Chemical Species** *(Jim Johnson and Suzanne Lundeen)*

- **Contents: thermodynamic data for over 2000 chemical species (aqueous species, liquids, pure minerals, solid solutions, gases):**
  - Standard-state thermodynamic data in a variety of forms: equation-of-state parameters, species properties (e.g., $\Delta G^\circ_{f,i}$, $\Delta H^\circ_{f,i}$, $c_p{}^\circ_{,i}$), and reaction properties (e.g, $\log K$, ΔH°_r)
  - Activity coefficient parameters (e.g., Debye-Huckel parameters, hard-core diameters, interaction coefficients)

- **Allows control of mixing of data from various supersets (e.g., SUPCRT92, NEA92)**

- **D0OUT code uses the contents of GEMBOCHS to write EQ3/6 data files**

Some Features of Version 7 of EQ3/6

- **Three options for activity coefficients of aqueous species (B-dot equation, Davies' equation, Pitzer's equations)**

- **Limited range of solid solution models (important solid solutions include clays, zeolites, feldspars, and carbonates)**

- **Ability to model from 0-300°C on a standard pressure curve:**

    P = 1.013 bar (1 atm) up to 100°C; P = the liquid/vapor saturation pressure for pure water from 100-300°C

- **Control of mineral growth/dissolution via simple rate law expressions (EQ6)**

- **Ability to fix gas fugacities along reaction paths (EQ6)**

- **Pseudo-1-D fluid-centered flow-through system (EQ6)**

Version 7 of EQ3/6 is Adequate to Meet Some Technical Needs of the Yucca Mountain Project

- **More thermodynamic data, especially for radionuclide elements**

- **Continuing development of models for phenomena such as "sorption" and waste-form leaching**

- **Development of new versions of EQ3/6 or (?) with additional capabilities to address project needs in the following areas:**

  - **Near-field environment**
  - **Waste-form release**
  - **Source term**
  - **Far-field migration**

Additional Capabilities Anticipated to be Needed for Near-Field and Far-Field Environment Work

- "Sorption": Simple ion exchange model (generalized substrate with exchange capacity but no surface area) (Brian Viani and Carol Bruton)

- "Sorption": Surface chemistry models (generalized substrate, multiple substrates, specific solids as substrates)

- "Sorption": Expanded range of solid solution models (Brian Viani, Carol Bruton, and Bill Bourcier)

- "Sorption": Zoning of solid solutions (appropriate for feldspars and carbonates, but not clays or zeolites)

Additional Capabilities Anticipated to be Needed for Near-Field and Far-Field Environment Work

(Continued)

- Aqueous redox disequilibrium (and redox kinetics) (EQ6) *(e.g., metastable persistence of SO^{2-}_4 and NO^-_3*

- Pressure corrections to allow calculations off the standard pressure curve (up to ~500 bars off) *(Add partial molar volume data to EQ3/6 data files)*

- Volumetric properties (mg/l ←→ molality, solution density, porosity changes) *(use the same partial molar volume data)*

- Production or consumption of heat by chemical reaction and phase changes (EQ6) *(Add partial molar enthalpy data to EQ3/6 data files)*

Additional Capabilities Anticipated to be Needed for Near-Field and Far-Field Environment Work

(Continued)

- Gas phase model (EQ6)

- Models of mineral dissolution and precipitation kinetics and of redox kinetics with explicit links to mineral surface chemistry (EQ6)

- Pseudo-1-D rock-centered flow-through system (EQ6)

- Coupled 1-D transport model (EQ6) (?)

- Stable isotope mass transfer (EQ6) (?)

EQ3/6 and Other Geochemical Modeling Codes

- **Various other codes (e.g., MINTEQAQ2, MICROQL, PHREEQE, PHRQPITZ, CHILLER, Gt/React) exist and can also be used to model rock/water and rock/water/waste systems**

- **Each code tends to have its own strengths and weaknesses. No code now in existence covers everything needed for Yucca Mountain Project applications. No other codes are being developed by the Yucca Mountain Project**

- **Other codes may be useful for**

  - **Submodel evaluation (e.g., surface chemistry models)**
  - **Code-to-code verification (especially MINTEQAQ2, PHREEQE, PHRQPITZ, and React)**
  - **Applications, if capabilities are sufficient and if QA requirements can be met**

Why is Geochemical Modeling Important to the Yucca Mountain Project ?

- Primary means of figuring out water/rock/waste interactions in a repository is based on doing short-term experiments (lab or field)

- Must predict (with confidence) interactions (e.g., involving the source term and migration) over much longer time scales

- The evidence suggests that extrapolating short-term results to predict long-term results is possible but requires consideration of certain factors, which may not manifest themselves in short-term experiments. Prediction must account for these "non-linearities"

Why is Geochemical Modeling Important to the Yucca Mountain Project ?

(Continued)

- Short-term experiments have a tendency to give results at least partially inconsistent with natural systems that evolved over long time-periods (e.g., hydrothermal seawater/basalt experiments yield smectite-dominated mineral assemblages, but the process in nature yields assemblages dominated by chlorite or chlorite/epidote)

- Tuff/J-13 water hydrothermal experiments run ~3 months give water chemistries that appear to reach steady-state. Thermodynamic calculations clearly demonstrate that these water compositions are supersaturated with respect to a variety of minerals; hence, are metastable

- Modeling is required to account for differences between short-term and long-term results. Long-term results adhere more closely to what one would predict using thermodynamic equilibrium : how verify ?

Summary of LLNL Applications of EQ3/6 Through FY92

- Tuff/J-13 water hydrothermal interactions experiments (Joan Delany, Kevin Knauss, et al.) -- use of kinetics to model experiments

- Calculation of pH buffer compositions for single-mineral dissolution kinetics measurements (Kevin Knauss, Tom Wolery)

- Glass waste-form dissolution (Bill Bourcier) -- kinetic models of experiments

- Spent-fuel dissolution (Carol Bruton and Henry Shaw) -- scoping study of equilibrium step calculations to identify potential secondary phases; led to understanding the importance of uranyl silicate minerals

- Development of ion exchange models for clinoptilolite and smectite in Yucca Mountain tuffs (Brian Viani, Carol Bruton)

Tuff/J-13 Water Hydrothermal Interactions Experiments (Joan Delany, Kevin Knauss, et al.)

- **Experiments done in Dickson rocking autoclaves**

- **Topopah Springs tuff -- devitrified to an assemblage of cristobalite, quartz, Na-K feldspar, plagioclase (similar studies later done with glassy tuffs)**

- **Modeling approach:**
  - **Take rate laws and rate constants for the dissolution of the tuff-bearing minerals from the literature; extrapolate/estimate, as necessary**
  - **Partition measured surface area of the tuff among the individual minerals**
  - **Run model, allowing secondary minerals to form according to equilibrium constraints**
  - **Iterate, locking reactions for specific secondary mineral formation until a reasonable fit is obtained. For example, quartz cannot be allowed to precipitate (solution is near equilibrium with cristobalite)**

# Tuff/J-13 Water Hydrothermal Interactions Experiments

(Continued)

- Reasonable results obtained for 150°C experiments with little or no adjustment of rate-constant values

- Not necessary to invoke secondary mineral growth kinetics models. Actual secondary mineral formation either very rapid or too slow to observe on the experimental time scale

- Experiments at higher temperatures (250°C) could not be modeled due to precipitation of the zeolite dachiardite, which was not in the EQ3/6 data base

- The final state in the experiments appears to be near steady-state. Thermodynamic analysis shows this to be metastable. Modeling of the long-term process would require consideration of nucleation/growth kinetics
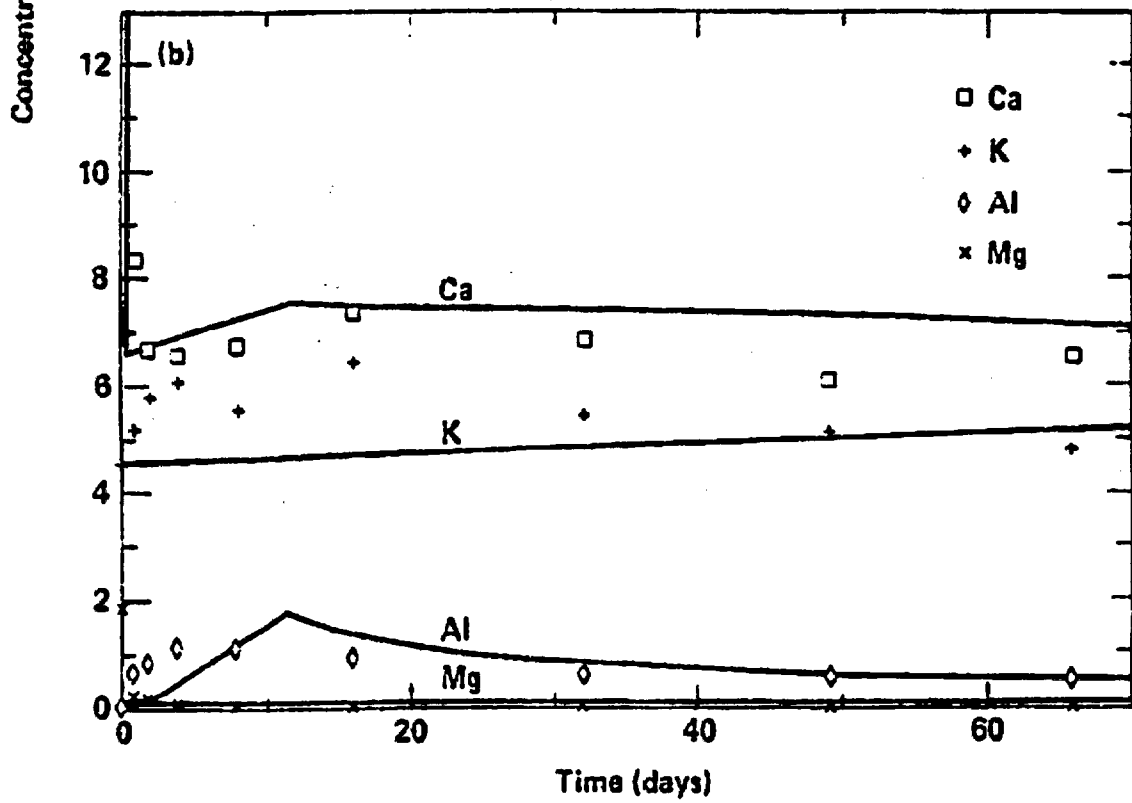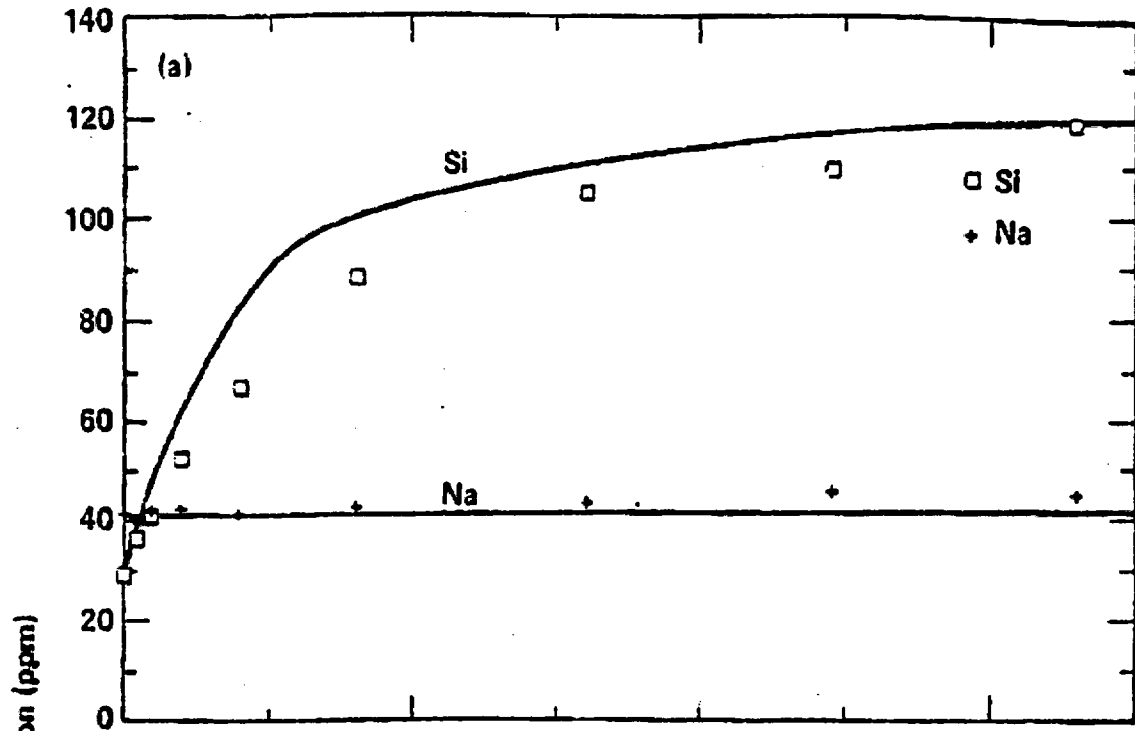
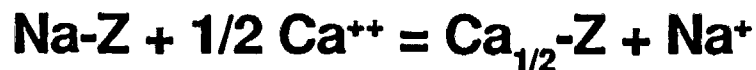# Cation-Exchange Modeling: Exchange Models

- ## Ideal Vanselow model:

  Activity of component = mole fraction of exchange cation
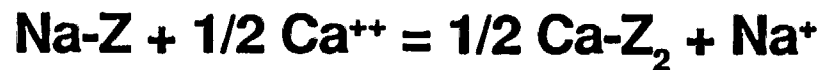
  $$Na\text{-}Z + 1/2\ Ca^{++} = 1/2\ Ca\text{-}Z_2 + Na^+ \qquad K_{ex} = \frac{X_{Ca\text{-}Z_2}^{1/2}\ a_{Na^+}}{X_{Na\text{-}Z}\ a_{Ca^{++}}^{1/2}}$$

- ## Ideal Gapon Model:

  Activity of component = equivalent fraction of exchange cation

  $$Na\text{-}Z + 1/2\ Ca^{++} = Ca_{1/2}\text{-}Z + Na^+ \qquad K_{ex} = \frac{E_{Ca_{1/2}\text{-}Z}\ a_{Na^+}}{E_{Na\text{-}Z}\ a_{Ca^{++}}^{1/2}}$$
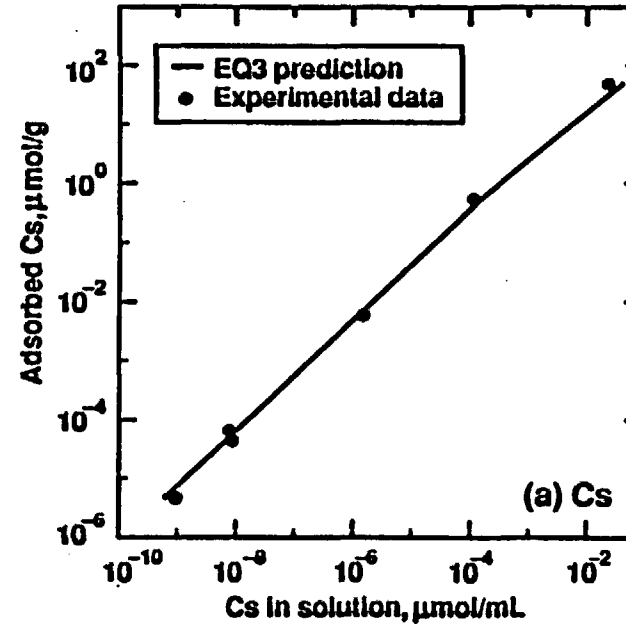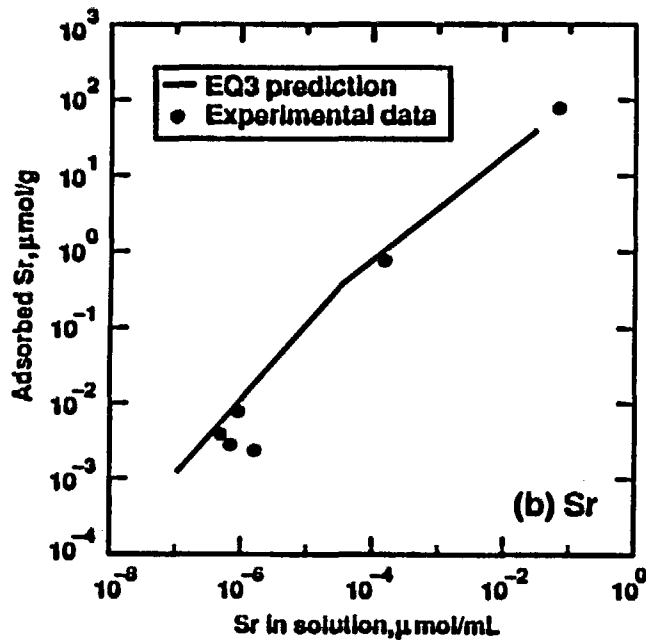
Cation-Exchange Modeling Examples: Cs and Sr Sorption on Zeolite and Smectite-Bearing Tuff

Model inputs and assumptions

- Assumed one-site Vanselow model

- Used published energies of exchange for major cations and Sr and Cs on clinoptilolite and smectite

- Used reported sample mineralogical composition and exchange capacity to define exchanger quantities

- Used reported composition of exchange cations and aqueous phase to define initial exchanger and fluid compositions

Cation-Exchange Modeling Examples: Comparison of Predicted with Experimental Isotherms

(b) Sr

(a) Cs

Cation-Exchange Modeling Examples: Comparison of Predicted with Experimental Partition Coefficients
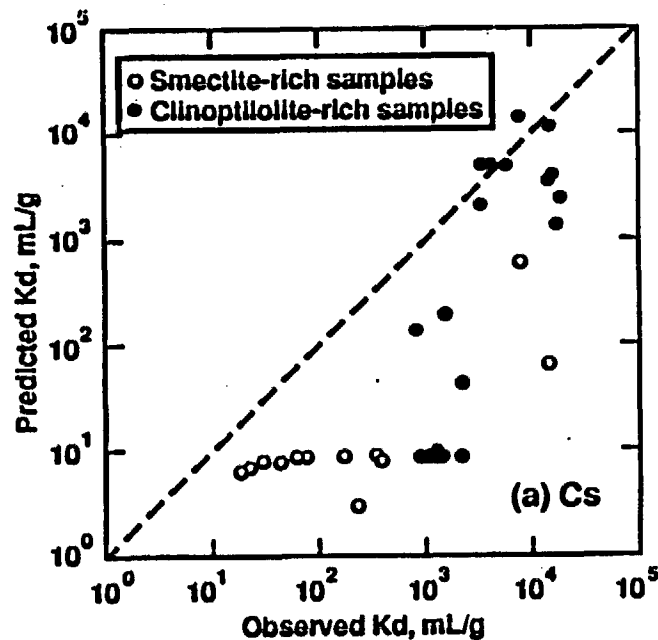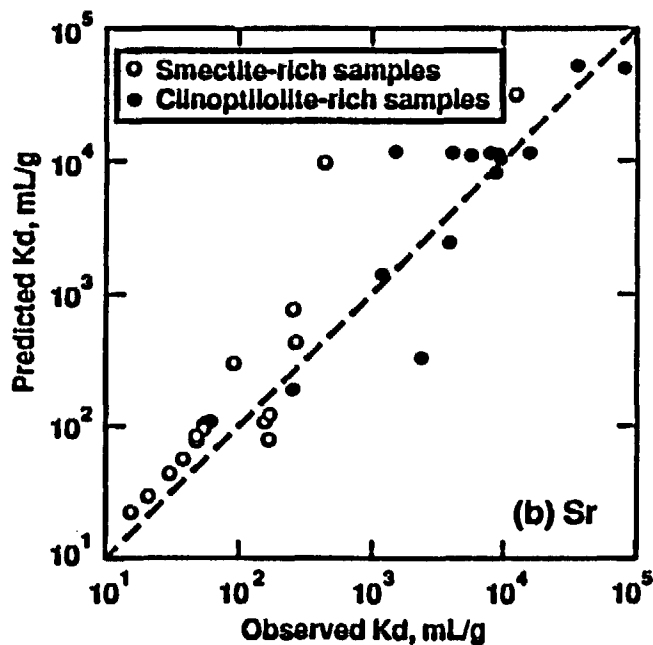
Some Code Documents for EQ3/6, Version 7

- EQ3/6, A Software Package for Geochemical Modeling of Aqueous Systems: Package Overview and Installation Guide (Version 7.0), by **T. J. Wolery (65 p.)**

- EQPT, A Data File Preprocessor for the EQ3/16 Software Package: User's Guide and Related Documentation (Version 7.0), **by S. A. Daveler and T. J. Wolery (83 p.)**

- EQ3NR, A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: Theoretical Manual, User's Guide, and Related Documentation (Version 7.0), **by T. J. Wolery (244 p.)**

- EQ6, A Computer Program for Reaction Path Modeling of Aqueous Geochemical Systems: Theoretical Manual, User's Guide, and Related Documentation (Version 0), **by T. J. Wolery and S. A. Daveler (327 p.)**