DOE GRANT DE-FG03-85ER13419

ADVECTIVE DIFFUSIVE/DISPERSIVE TRANSPORT IN GEOCHEMICAL PROCESSES

(H. C. Helgeson)

PROGRESS REPORT FYS 88-91

May 28, 1991

DOE/ER/13419--T1

DE91 013156

Comprehensive understanding of chemical transport in response to fluid flow and diffusion in geologic processes requires thermodynamic and transport properties of a wide variety of aqueous species at the temperature and pressure of interest, as well as mass transfer computer codes that provide simultaneously for fluid flow, diffusion, dispersion, homogeneous chemical reactions, and mineral solubilities. As a result of research carried out with support from DOE in prior years of this grant, considerable progress has been made in developing computer codes to calculate advective-dispersive-diffusional transport at both high and low pressures and temperatures (Lichtner, 1985, 1986, 1988; Lichtner *et al*, 1986a, b, 1987; Oelkers, 1990). These codes have become highly sophisticated, but their application to geochemical processes is limited by the availability of thermodynamic and transport data for the major solute species in the aqueous phase. As a consequence, research emphasis has been focused over the past several years on investigation of the thermodynamic and transport properties of aqueous species in hydrothermal solutions as functions of pressure, temperature, and solute composition. Recently developed speciation models and computer algorithms can be used to calculate interphase mass transfer in response to fluid flow, aqueous diffusion, and chemical reactions among minerals, organic species in petroleum, and organic and inorganic gases and aqueous species in geochemical processes. Such calculations should lead to improved understanding of these processes and facilitate enhanced development and production of energy resources.

MASTER

20
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Over the past three years, research carried out under the auspices of DOE grant DEFG03-85ER-13419 has been directed primarily toward characterizing the thermodynamic behavior of concentrated supercritical aqueous electrolyte solutions and predicting the diffusion coefficients of organic species in oil field brines. Related research has been concerned with characterizing the growth rate of hydrothermal alteration zones and assessing the relative importance of aqueous diffusion and heterogeneous reactions at mineral surfaces in geochemical processes. This research is described in detail below.

RESEARCH ACCOMPLISHED IN FYS 88-91

During FY 88-91, the following research goals were accomplished:

1. Diffusion coefficients were generated for organic aqueous species at temperatures from 0° to 350° C (Oelkers, 1989, 1991).
2. Computer code SUPCRT 91, which facilitates calculation of the standard partial molal thermodynamic properties of chemical reactions among coexisting minerals, aqueous species, and gases at temperatures from 0° to 1000° C and pressures from 1 to 5000 bars was completely revised and updated (Johnson *et al*, 1991). This computer code and the associated data file are currently being distributed to a large number of laboratories engaged in energy-related research.
3. Algorithms and parameters were derived from theoretical considerations and regression analysis of experimental data to compute the activity coefficients of charged and neutral 1:1 ion pairs in single electrolyte solutions at temperatures from 0 to 1000° C (Oelkers and Helgeson 1990, 1991).
4. Dissociation constants for triple ions in supercritical aqueous 1:1 electrolyte solutions were generated as functions of pressure, temperature, and the density of H₂O (Oelkers and Helgeson 1990).

5. The generation and growth rates of hydrothermal alteration halos were characterized with the aid of a combined chemical mass transport/kinetic computer algorithm called NEWCRANK (Oelkers 1990).
6. Analyses of the relative importance of mineral surface reactions and diffusive mass transfer were carried out for multicomponent systems (Murphy and Oelkers 1990).

These research accomplishments are described in detail below.

1. DIFFUSION COEFFICIENTS FOR AQUEOUS ORGANIC SPECIES AS FUNCTIONS OF TEMPERATURE TO 350 C

Analysis of aqueous tracer diffusion coefficients (D°) for normal alkanes, alcohols, amides, carboxylic acids, benzenes and naphthalenes reported in the literature (Longworth, 1952, 1953, 1954; Lewis, 1955; Bidstrup and Geankoplis, 1963; Vivian and King, 1964; Wise and Houghton, 1966; Huq and Wood, 1968; Bonoli and Witherspoon, 1968; Sahores and Witherspoon, 1970; Akgerman and Gainer, 1972; Maharajh and Walkley, 1973; Pratt and Wakeham, 1974, 1975; Tyn and Calus, 1975; Taira *et al.*, 1978; Tominaga *et al.*, 1984, 1986, 1990; Eastal and Woolf, 1985; Jahne *et al.*, 1987; Matthews and Akgerman, 1988) indicate that diffusional activation energies decrease with increasing temperature, reaching a constant limiting value of ~ 3.3 kcal/mole at temperatures $\geq 100^\circ$ C. This observation is consistent with the modified Arrhenius equation derived by Oelkers and Helgeson (1988b). The applicability of this equation to describe the tracer diffusion coefficients of aqueous organic species can be assessed with the aid of Fig. 1, where values of D° for methanol are plotted as a function of temperature. The symbols in this figure correspond to experimental values of D° , but the curve represents a fit of these data to the modified Arrhenius equation developed by Oelkers and Helgeson (1988b). The Kirkwood - Riseman equation (Kirkwood and Riseman, 1948) was used to predict the tracer diffusion

coefficients of many hydrocarbon polymers for which no experimental data are available. Combining these predictions with estimated activation parameters and the modified Arrhenius equation permits calculation of tracer diffusion coefficients for a large number of aqueous hydrocarbons at temperatures to 350° C and P_{SAT}^1 . The results of the calculations indicate that tracer diffusion coefficients for aqueous organic species are similar in magnitude to D° values previously calculated for aqueous ions (Oelkers and Helgeson, 1988b). Computed values of D° for the n-alkanes from methane to octane are depicted in Fig. 2 as a function of temperature from 0° to 350° at P_{SAT} . It can be seen in this figure that the tracer diffusion coefficient for a given hydrocarbon increases by more than an order of magnitude with increasing temperature from 0° to 350° C. For example, the tracer diffusion coefficient of aqueous hexane increases from 0.4 to $18.8 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ over this temperature range. Note that the computed tracer diffusion coefficients also decrease dramatically with increasing hydrocarbon chain length at high temperatures. At 200° C, the predicted tracer diffusion coefficient of methane is 16.8, compared to 7.0 for octane.

2. DEVELOPMENT OF THE SUPCRT 91 COMPUTER CODE

Thermodynamic constraints on chemical equilibrium among mineral, gases, and aqueous species in the Earth's crust can be characterized as functions of temperature and pressure with the aid of SUPCRT 91, which is a revision and update of the original SUPCRT computer code written prior to 1975 (Helgeson *et al.*, 1978, 1981). Recent advances in describing the temperature and pressure dependence of the thermodynamic and electrostatic properties of H_2O (Haar *et al.*, 1984; Levelt Senger *et al.*, 1983; Johnson and Norton, 1991) and aqueous species (Tanger and Helgeson, 1988; Shock and Helgeson, 1988, 1990;

¹ P_{SAT} represents pressures corresponding to liquid-vapor equilibrium for the system H_2O , except at temperatures < 100° C where it refers to a reference pressure of 1 bar.

Shock *et al.*, 1989, 1991; Sverjensky *et al.*, 1991) have been incorporated into the SUPCRT 91 code, which permits accurate description of the standard partial molal thermodynamic properties of a large number of aqueous species over wide ranges of pressure and temperature. In addition, the SUPCRT code has undergone extensive modification to improve its user interface, computational efficiency, and adaptability to diverse hardware and operating systems. The current SUPCRT 91 data file contains parameters to compute the thermodynamic properties of 135 minerals, 15 gases, and 451 inorganic and organic aqueous species at temperatures from 0° to 1000° C and pressures from 1 to 5000 bars. All of the thermodynamic properties in the SUPCRT 91 data file are internally consistent with one another and documented in the literature. SUPCRT 91 is currently being distributed worldwide in response to requests from more than 60 scientific laboratories.

3. ACTIVITY COEFFICIENTS OF NEUTRAL AND CHARGED AQUEOUS SPECIES IN ELECTROLYTE SOLUTIONS AT HIGH PRESSURES AND TEMPERATURES

Although hydrothermal solutions at high temperatures and low pressures where the solution density is low are widely regarded as highly associated alkali chloride solutions in which neutral ion pairs are the predominant solute species, reconsideration of experimental conductance data reported by Quist and Marshall (1968a, b, c), Dunn and Marshall (1969) and Frantz and Marshall (1984) for 1:1 electrolytes suggests that this may not be the case (Oelkers and Helgeson, 1991). Quist, Marshall, and their coworkers interpreted their high temperature/pressure conductance data in part by considering the activity coefficients of the neutral species to be negligibly different from unity in dilute solutions. However, these data can also be interpreted by regarding the logarithm of the activity coefficients of neutral complexes ($\bar{\gamma}_n$) to be a linear function of effective ionic strength ($\bar{I}$), which is consistent with both the Setchenow (1892) and Hückel (1925) equations (Helgeson *et al.* 1981).

Accordingly, supercritical conductance data for five electrolytes were regressed using the Hückel, Setcheñow, and Shedlovsky (1938) equations for the molality scale of concentration, together with the law of mass action and values of the limiting equivalent conductances of the electrolytes taken from Oelkers and Helgeson (1989) for the temperatures and pressures of the experiments to generate simultaneously the logarithms of dissociation constants ($\log K_1$) and Setcheñow coefficients ($b_{\gamma,n}$) for the neutral 1:1 complexes. The resulting values of $\log K_1$ are in close agreement with corresponding values originally reported by Marshall and coworkers. However, the regression calculations also indicate that $b_{\gamma,n}$, and thus the activity coefficients of neutral species in concentrated electrolyte solutions increase dramatically with increasing temperature and decreasing pressure, which opposes the effect on ion pair formation of the accompanying decrease in $\log K_1$. This contrasting behavior is depicted in Fig. 3, where values of $\log K_1$ and $b_{\gamma,n}$ for NaCl are plotted as a function of temperature at constant pressure. Comparison of Figs. 3A and B illustrates the different behavior of the dissociation constants and Setcheñow coefficients for NaCl° at supercritical temperatures and pressures. Distribution of species calculations using the values of $\log K_1$ and $b_{\gamma,n}$ shown in Fig. 3, with and without provision for the formation of triple ions (Oelkers and Helgeson, 1990) indicate that the degrees of formation of neutral 1:1 ion pairs in NaCl solutions maximize at stoichiometric ionic strengths of ~0.2 molal, and become negligible at stoichiometric ionic strengths greater than ~0.8 molal in the temperature range 400° to 800° C at pressures to 4 kb. Figs. 3A and 3B are typical of other alkali chlorides. It thus appears that neutral aqueous species may account for only a minor part of the solute in concentrated hydrothermal solutions at supercritical temperatures and pressures.

Equations to compute the activity coefficient of NaCl consistent with the revised HKF (Helgeson, Kirkham, and Flowers, 1981) equations of state for the standard partial molal

thermodynamic properties of aqueous species (Tanger and Helgeson, 1988; Shock and Helgeson, 1988; Shock *et al.*, 1991) were also developed with support from DOE Grant DEFG03-85ER-13419 (Oelkers and Helgeson, 1990). The requisite equation of state parameters for NaCl were obtained by regression of experimental heat capacity, volume, and expansibility data. The regression results permit calculation of the mean ionic activity coefficients of NaCl at temperatures from 0° to 1000° C and pressures from 1 to 5000 bars. The equations and parameters can be used together with the geochemical approximation (Helgeson *et al.*, 1981) and the effective electrostatic radii of ions (Shock *et al.*, 1991) to predict the activity coefficients of a wide variety of aqueous species in NaCl-dominated hydrothermal solutions at high pressures and temperatures.

4. TRIPLE ION FORMATION IN SUPERCRITICAL AQUEOUS SOLUTIONS OF SINGLE ELECTROLYTES

The thermodynamic behavior of supercritical alkali metal halide solutions plays a significant role in various industrial and natural processes, including corrosion of metals, mineral solubilities, solvent extraction, synthetic crystal growth, and the formation of hydrothermal ore deposits. Consideration of dissociation constants representing the standard partial molal Gibbs free energy changes resulting from the electrostatic interaction of aqueous species indicates that triple ions such as NaCl_2^- and Na_2Cl^+ are major species in concentrated alkali metal halide solutions at high temperatures and low pressures where the dielectric constant of H_2O is ≤ 15 (Oelkers and Helgeson, 1990). This observation is supported by revised interpretation of conductance measurements reported in the literature (Franck, 1956a, b; Quist and Marshall, 1968a, b, c; Ritzert and Franck, 1968; Dunn and Marshall, 1969; Frantz and Marshall, 1984), which indicate that the solute in these electrolyte solutions is present predominately as single ions and neutral ion pairs only in the dilute concentration range at supercritical pressures and temperatures (Oelkers and

Helgeson, 1991).

Molal triple ion dissociation constants were computed for temperatures from 400° to 800° C at pressures from 500 to 4000 bars using equations taken from Fuoss and Kraus (1933a), together with values of the effective electrostatic radii of aqueous ions generated from algorithms developed by Tanger and Helgeson (1988) and Shock *et al.* (1991). The logarithms of the calculated second stepwise dissociation constants ($\log K_2$) for 14 alkali metal halide triple ions typically decrease at 500 bars from ~ 0.0 at 400° to ~ -3.0 at 700° C, but they increase with increasing pressure. This behavior is illustrated in Fig. 4, where computed values of $\log K_2$ for NaCl are depicted as a function of temperature at constant pressure. Distribution of species calculations were carried out using these $\log K_2$ values, together with dissociation constants for 1:1 ion pairs (Oelkers and Helgeson, 1988a) and activity coefficients generated by adopting the revised HKF equations of state (Tanger and Helgeson, 1988) to calculate extended term parameters in the Hückel equation (Helgeson *et al.*, 1981; Oelkers and Helgeson, 1990). The calculations indicate that triple ions may be the major ionic species in low-pressure supercritical aqueous electrolyte solutions at concentrations ≥ 1 m. For example, it can be seen in in Fig. 5 that the calculated degree of neutral ion pair formation in NaCl solutions at 700° C and 2 kb maximizes with increasing concentration at ~ 0.15 m and becomes negligible at higher concentrations (1m) where triple ions predominate. It thus appears that supercritical aqueous solutions of alkali metal halides are dominated successively by single ions, neutral ion pairs and triple ions with increasing solute concentration. As a consequence, polynuclear complexes such as KNaCl^+ , MgKCl_2^+ , ZnNaCl_2^+ , FeKCl_2^+ , $\text{Na}_2\text{SO}_4\text{Cl}^-$, Na_2SCl^- etc. may have a significant effect on the solubilities of minerals in concentrated hydrothermal brines at high temperatures and low pressures where many geochemical processes occur. Furthermore, by analogy with the behavior of electrolytes in low dielectric constant solvents at low temperatures

and pressures (Fuoss and Kraus, 1933b; Copenhafer and Kraus, 1951; Young and Kraus, 1951) and the results of molecular dynamical calculations (Gillan, 1983; Pitzer and Schreiber, 1987), it appears likely that in addition to triple ions, higher order complexes such as quadruple, quintuple, sextuple, and higher order species sequentially predominate with increasing concentration in concentrated supercritical solutions of single electrolytes (see below).

5. GENERATION AND GROWTH OF HYDROTHERMAL ALTERATION ZONES

Conventional finite difference algorithms for describing advective and diffusional transport of chemically reacting species are generally restricted to relatively small time steps and/or systems with only a few chemical components. As a consequence, with a few notable exceptions (e.g. Steefel and Lasaga, 1990; Steefel and Van Cappellen, 1990; Dewers and Ortoleva, 1990; Lichtner, 1991) most research concerned with quantitative description of fluid/rock interaction has been concerned with idealized systems (Rubin, 1983; Lasaga, 1984; Walsh *et al.*, 1984; Lichtner, 1985; Kirkner *et al.*, 1985; Lichtner *et al.*, 1986a, b, 1987; Ortoleva *et al.*, 1987; Mundell and Kirkner, 1988). To overcome these restrictions, Lichtner (1986, 1988) developed (with support from DOE Grant DEFG03-85ER-13419) a quasi-stationary state approximation to compute chemical mass transfer among minerals and advecting fluids over geologic time frames. The quasi-stationary state assumption is based on the observation that the rate at which the reactant surface areas of minerals change is slow compared to the rate of advective and diffusional mass transfer. Under these conditions, the evolution of hydrothermal alteration zones can be computed from a series of steady state approximations to the mass transport equations.

During FYs 88-91, a diffusional analog of Lichtner's quasi-stationary state approach was used to generate a computer code called NEWCRANK to compute diffusional mass transfer accompanying kinetically controlled homogeneous and heterogeneous reactions

among minerals and aqueous species as a function of distance and geologic time. A numerical algorithm incorporating Lasaga's (1979) equations for diffusive flux in multi-component electrolyte solutions is used in the NEWCRANK code to provide simultaneously for homogeneous equilibrium and solute diffusion in the aqueous phase, which is coupled to reversible and irreversible mineral dissolution/precipitation reactions.

During FYs 88-91, mass transfer calculations were carried out to replicate the mineralogy of alteration zones like those associated with hydrothermal veins in porphyry copper deposits (Meyer, 1950; Hemley and Jones, 1964; Meyer and Hemley, 1967; Meyer *et al.*, 1968; Rose and Burt, 1979). Taking account of the thermodynamic properties of minerals (Helgeson *et al.*, 1978) and those of aqueous species consistent with the revised HKF equations of state developed by Tanger and Helgeson (1988), Shock and Helgeson (1988, 1990), Shock *et al.* (1989, 1991), and Sverjensky *et al.*, (1991), together with rate constants for mineral hydrolysis reported by Helgeson *et al.* (1984) and Murphy and Helgeson (1987, 1989) and diffusion coefficients taken from Oelkers and Helgeson (1988b), the NEWCRANK code was used to characterize quantitatively the generation, evolution, and growth rate of lateral hydrothermal alteration zones as a function of time and distance along flow paths in hydrothermal systems. The specified boundary conditions differ from those used in other studies of hydrothermal alteration zones (Fisher, 1973; Fltecher and Hoffman, 1974; Frantz and Mao, 1976, 1979; Weare *et al.*, 1976) by providing for kinetic rate laws based on transition state theory to represent the hydrolysis of silicates as a function of time (Helgeson *et al.* 1984; Murphy and Helgeson, 1987, 1989).

Calculations of the kind described above were carried out for the chemical interaction of hydrothermal solutions with minerals in the system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{HCl}-\text{H}_2\text{O}$ at 250° C and 1 kb. A schematic illustration of the finite difference grid used to compute the growth of the hydrothermal alteration zones in this system is shown in Fig. 6. The

consequences of reaction of a rock consisting initially of 27 volume percent quartz, 23 percent orthoclase, 46 percent albite and 4 percent porosity with a fissure fluid of constant composition is shown in Figs. 7-9. The aqueous fissure fluid was assumed to be a 1 molal NaCl solution with a molality of KCl equal to 0.1 and a constant pH of 3.2. The fluid was considered to be in local equilibrium with kaolinite and quartz at the fluid/rock interface immediately adjacent to the fissure. The proportions of the minerals in the reactant rock correspond to those in the unaltered quartz monzonite at the Butte porphyry copper deposit (Meyer *et al.*, 1968). In accord with field observations (Hemley and Jones, 1964), the original aluminosilicate mineral assemblage was considered in the calculations to be out of equilibrium with the hydrothermal fluid, but local equilibrium was assumed to prevail among alteration products and the interstitial fluid in the alteration zones. This assumption is consistent with transport control of reaction rates (Steefel and Lasaga, 1990; Steefel and Van Cappellen, 1990; Lichtner, 1991).

The chemical reaction between the wall rock and the fissure fluid described above resulted in three distinct reaction zones consisting of kaolinite + quartz adjoining the fissure, an intermediate muscovite + quartz zone, and an orthoclase + quartz zone next to the fresh rock, which is the mineralogy and sequence observed in the advanced argillic stage of rock alteration at Butte (Rose and Burt, 1979). The growth rates of these alteration zones are depicted in Fig. 7, where the calculated positions of the alteration zone boundaries are plotted as a function of time. It can be seen in this figure that all three alteration zones are formed as soon as the fissure fluid comes in contact with the fresh wall rock, and each persists throughout the alteration process. Note that the predicted relative thickness of each of the alteration zones remains approximately constant with time, which is consistent with field observations (Rose and Burt, 1979). The relative abundances of minerals in the system after 15,400 years of elapsed time are depicted in Fig. 8. Again in

accord with field observations, the boundaries between the mineral assemblages are sharp, and the volume percent of each mineral tends to be independent of distance within each alteration zone. The relative growth rates of these alteration sequences is a consequence of the relative rates of diffusion of chemical species into and out of the fluid-filled fissure, which are coupled to one another by homogeneous equilibrium constants. Diffusional concentration profiles of 4 aqueous species are depicted in Fig. 9. It can be seen in this figure that K^+ and H^+ diffuse into the wall rock, but Na^+ and $Al(OH)_4^-$ diffuse toward the fissure. A large number of computer experiments are currently under way to predict the sequence and growth rate of these and other alteration mineral assemblages in porphyry copper deposits and metamorphosed dolomites for which analytical data are available (Meyer *et al.*, 1968; Rose and Burt, 1979; Frisch and Helgeson, 1984).

6. EFFECTS OF CONCENTRATION GRADIENTS ON SURFACE REACTIONS IN MULTICOMPONENT SYSTEMS

Reaction rates and the formation and distribution of secondary minerals in hydrothermal systems generally depend on dissolution/growth processes at mineral surfaces which are coupled to diffusional and advective mass transport of species in the aqueous phase (Steeffel and Van Cappellen, 1990). Nevertheless, chemical mass transfer in these systems is commonly modeled as if it were a non-spatial process by assuming that the rate of aqueous diffusion is faster than chemical reaction rates. However, concentration gradients associated with crystal growth from an aqueous phase may occur on the scale of pores. As a consequence, irreversible reaction paths may be affected, especially at high temperatures where reaction rates are known to be faster than aqueous diffusion rates (Murphy and Helgeson, 1987, 1989; Oelkers and Helgeson, 1988b; Murphy *et al.*, 1989). To investigate these phenomena, numerous attempts have been made to analyze the effects of diffusional

concentration gradients on mineral surface reaction rates in one component systems (Berner, 1978; Prigogine and Lefever 1978; Dibble and Tiller, 1981; Sjoberg and Rickard, 1984; Murphy *et al.*, 1989). Over the past several years, these efforts have been augmented with support from DOE grant DEFG03-85ER-13419 to assess the consequences of diffusional concentration gradients on mineral reaction rates in multi-component systems. The effects of diffusional concentration gradients on mineral dissolution/precipitation rates were investigated for two limiting cases: a symmetrical pore space and a stratigraphic column. One-dimensional analogs of these two cases are depicted schematically in Fig. 10, where it can be seen that each consists of a reactive mineral surface at one side of the system and a zero flux boundary at the other side.

To quantify the effect of diffusional concentration gradients on mineral dissolution/precipitation reactions, comparisons were made between the results of non-spatial mass transfer calculations for a closed system, which were carried out using the EQ3/6 computer code (Wollery, 1986), and the results of analogous calculations that took into account solute diffusion coupled with mineral surface reactions. For congruent mineral dissolution, the calculations indicate that diffusional concentration gradients may significantly slow overall reaction rates. In systems where secondary minerals precipitate, the calculations demonstrate that diffusional concentration gradients cause product minerals to form at faster rates. Calculations were also carried out for albite dissolving into an aqueous phase in a 1-meter wide porous rock at 25° C (Fig. 10B). The porous rock was taken to have a 1 percent porosity, a tortuosity of 10, and contain initially a pore fluid consisting of a dilute (5×10^{-4} molal) sodium bicarbonate solution with a pH of 7.5. The rate of albite hydrolysis was computed using the kinetic rate law developed by Murphy and Helgeson (1987), but the dissolution/precipitation rate of secondary minerals was assumed as a first approximation to be controlled by local equilibrium. The dissolution of albite in

this system led to sequential precipitation of gibbsite, kaolinite, pyrophyllite and clinoptinolite. The timing of appearance and the relative abundances of these secondary minerals were computed with provision for diffusional concentration gradients using the NEWCRANK computer code. The results are depicted in Fig. 11. The logarithm of the number of moles of secondary phases (cm^2 of reactive surface area) $^{-1}$ at the reactive interface is plotted in this figure as a function of the logarithm of time. The results of a corresponding calculation carried out without provision for diffusional concentration gradients is depicted in Fig. 12. Comparison of Figs. 11 and 12 reveals the contribution by diffusional concentration gradients to the time of appearance and relative abundances of the various secondary phases. It can be seen that gibbsite first precipitates after ~ 2 hours, reaching a maximum abundance of $10^{-8.8}$ moles cm^{-2} after ~ 7 days in the coupled dissolution/surface reaction calculation. In contrast, the calculations carried out assuming a homogeneous pore fluid indicate that gibbsite first precipitates after ~ 2.5 days, reaching a maximum abundance of $\sim 10^{-7.5}$ moles cm^{-2} after ~ 6 months. Despite the fact that the secondary minerals form at earlier times in the coupled diffusion/surface reaction calculations, albite took approximately 2 percent more time to reach equilibrium than in the EQ3/6 calculations. Numerous such comparisons are currently being carried out to better assess the impact of diffusional concentration gradients on mass transfer in multicomponent systems.

REFERENCES

- Akgerman, A. and Gainer, J. L. (1972) Predicting gas-liquid diffusivities *J. Chem. Eng. Data*, 17, 372 - 377.
- Berner R. A. (1978) Rate control of mineral dissolution under Earth surface conditions. *Am. J. Sci.* 287, 1253 - 1252.
- Bidstrup, D. E. and Geankoplis, C. J. (1963) Aqueous molecular diffusivities of carboxylic acids. *J. Chem. Eng. Data* 8, 170 - 173.
- Bonoli, L. and Witherspoon, P. A. (1968) Diffusion of aromatic and cycloparaffin hydrocarbons in water from 2 to 60°. *J. Phys. Chem.* 72, 2532 - 2534.
- Copenhafer and Kraus (1951) Properties of electrolytic solutions. LIII. Molecular weight of salts in Benzene by the cryoscopic method. *J. Am. Chem. Soc.* 73, 4557 - 4561.
- Dewers, T. and Ortoleva, P. (1990) A coupled reaction/transport/mechanical model for intergranular pressure solution, stylolites, and differential compaction and cementation in clean sandstones. *Geochim. Cosmochim. Acta* 54, 1609 - 1626.
- Dibble Jr. W. E. and Tiller W. A. (1981) Non-equilibrium water/rock interaction, I. Model for interface-controlled reactions. *Geochim. Cosmochim. Acta* 45, 79 - 92.
- Dunn, L. A. and Marshall, W. M. (1969) Electrical conductances of aqueous sodium iodide solutions and the comparative thermodynamic behavior of aqueous sodium halide solutions to 800° C and 4000 bar. *J. Phys. Chem.* 73, 723 - 728.
- Easteal, A. J. and Woolf, L. A. (1985) Pressure and temperature dependence of tracer diffusion coefficients of methanol, ethanol, acetonitrile and formamide in water. *J. Phys. Chem.* 89, 1066 - 1069.
- Fisher, G. W. (1973) Nonequilibrium thermodynamics as a model for diffusion controlled metamorphic processes. *Am. J. Sci.* 273, 897 - 924.

- Fletcher, R. C. and Hoffman, A. W. (1974) Simple models of diffusion and combined diffusion/infiltration metasomatism. in *Geochemical Transport and Kinetics* A. W. Hoffman ed. Carnegie Institution of Wash. Pub. 634, 243 - 259.
- Franck E. U. (1956a) Hochverdichteter Wasserdampf I. Elektroytische Leitfähigkeit in KCl - H₂O Lösungen bis 750° C *J Zeit. fur Physik Chemie* 8, 92 - 106.
- Franck E. U. (1956b) Hochverdichteter Wasserdampf III. Ionendissoziation von KCl, KOH und H₂O in überkritischem wasser *Zeitschr. Phys. Chemie* 8, 192 - 206.
- Frantz, J. D. and Mao, H. K. (1976) Bimetasomatism resulting from intergranular diffusion: I. A theoretical model for monomineralic reaction zone sequences. *Am. J. Sci.* 276, 817 - 840.
- Frantz, J. D. and Mao, H. K. (1979) Bimetasomatism resulting from intergranular diffusion: II. Prediction of multimineralic zone sequences. *Am. J. Sci.* 279, 302 - 323.
- Frantz, J. D. and Marshall, W. M. (1984) Electrical conductances and ionization constants of salts, acid and bases in supercritical aqueous fluids. I: Hydrochloric acid from 100° to 700° C and at pressures to 4000 bars. *Am. J. Sci.* 284, 651 - 667.
- Frisch C. and Helgeson H.C. (1984) Metasomatic phase relations in dolomites of the Adamello Alps. *Amer. J. Sci.* 284, 121-185.
- Fuoss, R. M. and Kraus, C. A. (1933a) Properties of electrolytic solutions. IV. The conductance minimum and the formation of triple ions due to the action of coulomb forces. *J. Am. Chem. Soc.* 55, 1019 - 1028.
- Fuoss, R. M. and Kraus, C. A. (1933b) Properties of electrolytic solutions. IX. Conductance of some salts in Benzene. *J. Am. Chem. Soc.* 55, 3614 - 3620.
- Gary-Bobo, C. M. and Weber, H. W. (1969) Diffusion of alcohols and amides in water from 4 to 37 *J. Phys. Chem.* 73, 1155 - 1156.

- Gillan, M. J. (1983) Liquid-vapor equilibrium in the restricted primitive model for ionic liquids. *Mol. Phys.* 49, 421 - 442.
- Haar, L., Gallagher, J. S. and Kell, G. S. (1984) NBS/NRC Steam Tables. Hemisphere Publishing Co., Washington, 320 p.
- Helgeson, H. C., Delany, J. M., Nesbitt, H. W. and Bird, D. K. (1978) Summary and critique of the thermodynamic properties of rock forming minerals. *Am. J. Sci.* 278a, 229p.
- Helgeson H.C., Kirkham D.H., and Flowers G.C. (1981) Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600° C and 5 kb. *Amer. J. Sci.* 281, 1249-1516.
- Helgeson, H. C., Murphy, W. M. and Aagard, P. (1984) Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions. II. Rate constants, effective surface area, and the hydrolysis of feldspar. *Geochim. Cosmochim. Acta* 48, 2405 - 2432.
- Hemley J.J. and Jones W.R. (1964) Chemical aspects of hydrothermal alteration with emphasis on hydrogen metasomatism. *Econ. Geol.* 59, 538-569.
- Hückel E. (1925) Zur theorie konzentrierter wässriger lösungen starker elektrolyte *Phys. Zeitschr.* 26, 93-147.
- Huq, A. and Wood, T. (1968) Diffusion coefficient of ethylene gas in water *J. Chem. Eng. Data* 13, 256 - 259.
- International Critical Tables (1929) Coefficients of diffusion in liquids. McGraw-Hill, New York. V, 63 - 76.

- Jahne, B., Heinz, G. and Dietrich, W. (1987) Measurement of the diffusion coefficients of sparingly soluble gases in water. *J. Geophys. Res.* 92, 10767 - 10776.
- Johnson, J. W. and Norton, D. L. (1991) Critical Phenomena in hydrothermal systems: I: State, thermodynamic and electrostatic properties of H₂O in the critical region. *Am. J. Sci.* (in press).
- Johnson, J. W., Oelkers, E. H. and Helgeson, H. C. (1991) SUPCRT91: A software package for calculating the standard molal thermodynamic properties of reactions among minerals, gases, and aqueous species as functions of temperature and pressure. Submitted to *Computers and Geosciences*.
- Kircher, K., Schaber, A. and Obermeier, E. (1981) Binary diffusion coefficients of alcohol water mixtures at higher temperatures by a diaphragm cell method. *Proc. 8th Symp. Thermophys. Prop., ASME* 1, 297 - 302.
- Kirkner, D. J., Jennings, A. A. and Theis, T. L. (1985) Multisolute mass transport with chemical interaction kinetics. *J. Hydrology* 76, 107 - 117.
- Kirkwood, J. G. and Riseman, J. (1948) The intrinsic viscosities and diffusion constants of flexible macromolecules in solution. *J. Chem. Phys.* 16, 565 - 573.
- Korzhinskii D.S. (1959) Physicochemical basis of the analysis of the paragenesis of minerals, Consultants Bureau, Inc., New York, 142 pp.
- Lasaga, A. C. (1979) The treatment of multi-component diffusion and ion pairs in diagenetic fluxes. *Am. J. Sci.* 279, 324 - 346.
- Lasaga, A. C. (1984) Chemical kinetics of water-rock interaction. *J. Geophys. Res.* 89, 4009 - 4025.
- Levelt Sengers, J. M. H., Kamgar-Parsi, B., Balfour, F. W. and Sengers, J. V. (1983) Thermodynamic properties of steam in the critical region. *J. Phys. Chem. Ref. Data.* 12,

1-28.

- Lewis, J. B. (1955) Some determinations of liquid-phase diffusion coefficients by means of an improved diaphragm cell. *J. Appl. Chem.* 5, 228 - 237.
- Lichtner, P. C. (1985) Continuum model for simultaneous chemical reactions and mass transport in hydrothermal systems. *Geochim. Cosmochim. Acta* 49, 779 - 800.
- Lichtner, P. C. (1986) Multiple reaction path model describing mass transfer in geochemical systems. in Proceedings of the workshop on Geochemical modeling, Fallen Leaf Lake, Jackson, K. J. and Bourcier, W. L. eds. CONF-8609134, Lawrence Livermore National Laboratory, Livermore, California, 3 - 9.
- Lichtner, P. C. (1988) The quasi-stationary state approximation to coupled mass transport and fluid/rock interaction in a porous media. *Geochim. Cosmochim. Acta* 52, 143 - 165.
- Lichtner, P. C. (1991) Redox front geochemistry and weathering: Theory with application to the Osamu Utsumi uranium mine, Pocos de Caldas, Brazil. *Chem. Geol.* (in press).
- Lichtner, P. C., Oelkers, E. H. and Helgeson, H. C. (1986a) Comparison of exact and numerical finite difference calculations to the moving boundary problem resulting from aqueous diffusion coupled to precipitation/dissolution of a stationary solid phase. *J. Geophys. Res.* 91, 7531 - 7544.
- Lichtner, P. C., Oelkers, E. H. and Helgeson, H. C. (1986b) Interdiffusion with multiple precipitation/dissolution reactions: Transient model and the steady state limit. *Geochim. Cosmochim. Acta* 50, 1951 - 1966.
- Lichtner, P. C. Helgeson, H. C. and Murphy, W. M. (1987) Lagrangian and Eulerian representations of metasomatic alteration of minerals. in Proceedings of the NATO

- Advanced Study Institute on Chemical Transport on Metasomatic Processes. Helgeson, H. C. ed. Reidel, Dordrecht, Holland, 519 - 545.
- Longworth, L. G. (1952) Diffusion measurements, at 1°, of ammino acids, peptides and sugars. *J. Am. Chem. Soc.* 74, 4155 - 4159.
- Longworth, L. G. (1953) Diffusion measurements, at 25°, of ammino acids, peptides and sugars. *J. Am. Chem. Soc.* 75, 5705 - 5709.
- Longworth, L. G. (1954) Temperature dependence of diffusion in aqueous solutions. *J. Phys. Chem.* 55, 770 - 773.
- Maharajh, D. M. and Walkley, J. (1973) The temperature dependence of the diffusion coefficients of Ar, CO₂, CH₄, CH₃Cl, CH₃Br and CHCl₂F in water. *Can. J. Chem.* 51, 944 - 952.
- Matthews, M. A. and Akgerman, A. (1988) Infinite dilution diffusion coefficients of methanol and 2-propanol in water. *J. Chem. Eng. Data* 33, 122 - 123.
- Meyer, C. (1950) Wall rock interaction at Butte, Montana. unpublished Ph. D. thesis, Harvard Univ.
- Meyer C. and Hemley J. J. (1967) Wall rock interaction in Geochemistry of hydrothermal ore deposits. H. L. Barnes ed. Holt, Rinehart and Winston, New York. 166 - 235.
- Meyer *et al.* (1968) Ore deposits at Butte, Montana. in Ore deposits of the U. S., 1933 - 1967. J. D. Ridge ed. Am. Inst. Eng., New York. 1373 - 1416.
- Mundell, J. A. and Kirkner, J. D. (1988) Numerical studies of dissolution induced moving boundary problems from aqueous diffusion in porous media. *J. Geophys. Res.* 93, 10,397 - 10,407.
- Murphy, W. M. and Helgeson, H. C. (1987) Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions. III. Activated complexes and

the pH dependence of the rates of feldspar, pyroxene, wollastonite and olivine hydrolysis. *Geochim. Cosmochim. Acta* 51, 3137 - 3153.

Murphy, W. M. and Helgeson, H. C. (1989) Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions. IV. Retrieval of rate constants and activation parameters for the hydrolysis of pyroxene, wollastonite, olivene, andalusite, quartz and nepheline. *Am. J. Sci.* 289, 17 - 101.

Murphy, W. M., Oelkers, E. H. and Lichtner, P. C. (1989) Surface reaction rate versus diffusion of aqueous species in the control of irreversible mineral hydrolysis in geochemical processes: *Chemical Geology* v. 78, p. 357 - 380.

Murphy, W. M. and Oelkers, E. H. (1990) Concentration gradient effects on surface reactions in multicomponent geochemical systems. V. M. Goldschmidt Conference, Program and Abstract, p 67.

Oelkers, E. H. (1989) Calculation of diffusion coefficients of aqueous organic species in hydrothermal systems at temperatures to 350° C. Geological Society of America, ABSTRACTS WITH PROGRAMS, V. 21, p A-49.

Oelkers, E. H. (1990) Calculation of the growth rates of hydrothermal alteration bands using the quasi-stationary state approximation. V. M. Goldschmidt Conference, Program and Abstract, p 70.

Oelkers, E. H. (1991) Calculation of diffusion coefficients for aqueous organic species at temperatures from 0 to 350° C. Submitted to *Geochimica et Cosmochimica Acta*.

Oelkers, E. H. and Helgeson, H. C. (1988a) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Dissociation constants for supercritical alkali metal halides at temperatures from 400 to 800° C and pressures from 500 to 4000 bar. *J. Phys. Chem.* 92, 1631 - 1639.

- Oelkers, E. H. and Helgeson, H. C. (1988b) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Aqueous tracer diffusion coefficients of ions to 1000° C and 5 kb. *Geochim. Cosmochim. Acta* 52, 63 - 85.
- Oelkers, E. H. and Helgeson, H. C. (1989) Calculation of the transport properties of aqueous species at pressures to 5 KB and temperatures to 1000° C : *Journal of Solution Chemistry*, 18, 601 - 640.
- Oelkers, E. H. and Helgeson, H. C. (1990) Triple-ion anions and polynuclear complexing in supercritical electrolyte solutions. *Geochim. Cosmochim. Acta* 54, 727 - 738.
- Oelkers, E. H. and Helgeson, H. C. (1991) Calculation of activity coefficients and degrees of formation of neutral ion pairs in supercritical electrolyte solutions. *Geochim. Cosmochim. Acta* 55, 1235 - 1251.
- Ortoleva, P., Merino, E., Moore, C., and Chadam, J. (1987) Redox reaction fronts and banding modalities. *Am. J. Sci.* 287, 979 - 1007.
- Pitzer K. S. and Schreiber D. R. (1987) The restricted primitive model for ionic fluids: Properties of the vapor and the critical region. *Molec. Phys.* 60, 1067 - 1078.
- Pokrovskii, V. A. and Helgeson, H. C. (1991) Thermodynamic properties of aqueous species and the solubilities of minerals at high pressures and temperatures. A thermodynamic interpretation of mineral equilibria in the systems $K_2O-Al_2O_3-SiO_2O-H_2O-HCl$ and $Na_2O-Al_2O_3-SiO_2-H_2O-HCl$ at temperatures to 700° C and pressures to 5 kb. (in preparation).
- Pratt, K. C. and Wakeham, W. A. (1974) The mutual diffusion coefficient of ethanol-water mixtures by a rapid new method. *Proc. R. Soc. London A.* 336, 393 - 406.

- Pratt, K. C. and Wakeham, W. A. (1975) The mutual diffusion coefficient for binary mixtures of water and the isomers of propanol. *Proc. R. Soc. London A.* 342, 401 - 419.
- Prigogine, I. and LeFever, R. (1978) Coupling between diffusion and chemical reactions. *Adv. Chem. Phys.* 44, 1 - 17.
- Quist, A. S. and Marshall, W. M. (1968a) Electrical conductances of aqueous sodium chloride solutions from 0-800° C and at pressures to 4000 bars. *J. Phys. Chem.* 72, 684 - 703.
- Quist, A. S. and Marshall, W. M. (1968b) Electrical conductances of sodium bromide solutions from 0-800° C and at pressures to 4000 bars. *J. Phys. Chem.* 72, 1545 - 1552.
- Quist, A. S. and Marshall, W. M. (1968c) Electrical conductances of aqueous hydrogen bromide solutions from 0-800° C and at pressures to 4000 bars. *J. Phys. Chem.* 72, 2100 - 2105.
- Ritzert, G. and Franck E. U. (1968) Elektrische Leitfähigkeit wässriger Lösungen bei hohen Temperaturen und Drucken, I. KCl, BaCl₂, Ba(OH)₂ und MgSO₄ bis 750°C und 6 Kbar. *J. Bunsengesell. für Physik. Chemie Ber.* 72, 798-807.
- Rose A.W. and Burt D.M. (1979) Hydrothermal alteration. In *Geochemistry of hydrothermal ore deposits 2nd ed.*, (ed. H.L.Barnes), 173-235, Holt, Rinehart and Winston, Inc., New York.
- Rubin, J. (1983) Transport of reacting solutes in porous media: Relation between mathematical nature of problem formulation and chemical nature of reactions. *Water Resources Res.* 19, 1231 - 1252.
- Sahores, J. J and Witherspoon, P. A. (1970) Diffusion of light paraffin hydrocarbons in water from 2° C to 80° C. in *Advances in Organic Geochemistry*, Hobson, G. D. and Speers, G. C. eds. Pergammon Press, Oxford, 219 - 230.

- Setchénow M. (1892) Action de l'acide carbonique sur les solutions des sels `a acides forts. *Ann. Chim. Phys.* 25, 225-270.
- Shedlovsky, T. (1938) The computation of ionization constants and limiting conductance values from conductivity measurements. *J. Franklin Institute* 225, 739 - 743.
- Shock, E. L. and Helgeson, H. C. (1988) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Correlation algorithms for ionic species and equation of state predictions to 5 kb and 1000° C. *Geochim. Cosmochim. Acta*, 52, 2009 - 2036.
- Shock, E. L. and Helgeson, H. C. (1990) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of organic aqueous species. *Geochim. Cosmochim. Acta*, 54, (in press).
- Shock, E. L., Helgeson, H. C. and Sverjensky, D. A. (1989) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of inorganic neutral species. *Geochim. Cosmochim. Acta*, 53, 2157 - 2183.
- Shock, E. L., Oelkers, E. H., Johnson, J. W., Sverjensky, D. A. and Helgeson, H. C. (1991) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Effective electrostatic radii to 1000° C and 5 kb. submitted to J. C. S. Faraday Transactions.
- Sjöberg, E. L. and Rickard, D. T. (1984) Temperature dependence of calcite dissolution kinetics between 1 and 62° C at pH 2.7 to 8.4 in aqueous solutions. *Geochim. Cosmochim. Acta* 48, 485 - 493.

- Steefel, C. I. and Van Capellen, P. (1990) A new kinetic approach to modeling water-rock interaction: The role of nucleation, precursors, and Oswald ripening. *Geochim. Cosmochim. Acta* 54,
- Steefel, C. I. and Lasaga, A. C. (1990) Evolution of dissolution patterns: Permeability change due to coupled flow and reaction. In Chemical modelling in aqueous systems II. D. C. Melchior ed. A. C. S. Symp. Series 416, 212 - 225.
- Sverjensky, D. A. Shock, E. L. and Helgeson, H. C. (1991) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Inorganic metal-ligand complexes. (in preparation).
- Taira, Y., Matsuda, K. and Nakanishi, K. (1978) Diffusion coefficients of argon in aqueous ethanol and 1,4-dioxane solutions and of methane in aqueous ethanol solutions. *Bull. Chem. Soc. Japan* 51, 1639 - 1643.
- Tanger, J. C. and Helgeson, H. C. (1988) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Retrieval of equation of state parameters and prediction of the standard molal properties of electrolytes. *Am. J. Sci.* 288, 19 - 98.
- Tominaga, T., Yamamoto, S. and Tananaka, J.-I. (1984) Limiting interdiffusion coefficients of benzene, toluene, ethylbenzene and hexafluorobenzene in water from 298 to 368 K *J. Chem. Soc., Faraday Trans. I.* 80, 941 - 947.
- Tominaga, T., Matsumoto, S. and Ishii, T. (1986) Limiting interdiffusion of some aromatic hydrocarbons in water from 265 to 433 K *J. Phys. Chem.* 90, 139 - 143.
- Tominaga, T. and Matsumoto, S. (1990) Limiting interdiffusion of some hydroxylic compounds in water from 265 to 433 K *J. Chem. Eng. Ref. Data* 35, 45 - 47.

- Tyn, M. T. and Claus, W. F. (1975) Diffusion coefficients in dilute binary liquid mixtures. *J. Chem. Eng. Data* 20, 106 - 109.
- Vivian, J. E. and King, C. J. (1964) Diffusivities of slightly soluble gases in water. *A. I. Ch. E. Journal* 10, 220 - 221.
- Walsh, M. P., Bryant, S. L., Schecter, R. S. and Lake, L. W. (1984) Precipitation and dissolution of solids attending flow through porous media. *A. I. C. E. Jour.* 30, 317 - 327.
- Weare, J. H., Stephens, J. R. and Eugster, H. P. (1976) Diffusion metasomatism and mineral reaction zones: General principles and application to feldspar alteration. *Amer. J. Sci.* 276, 767 - 816.
- Wise, D. L. and Houghton, G. (1966) Diffusion coefficients of ten slightly soluble gases in water 10 - 60° C *Chem. Eng. Sci.* 21, 999 - 1010.
- Wollery T. (1986) EQ3/6 - Status and future development. In Workshop on Geochemical Modeling. Lawrence Livermore Natl. Lab., Livermore Calif., Doc. CONF-8609134.
- Young, H. S. and Kraus, C. A. (1951) Properties of electrolytic solutions LIV. The conductance and molecular weight of some salts in benzene at higher concentrations. *J. Am. Chem. Soc.* 73, 4732 - 4735.

Figure Captions

- Fig. 1. Aqueous tracer diffusion coefficients for methanol depicted as a function of temperature at P_{SAT} . The symbols represent experimental data reported in the literature, but the curve represents a fit of these data to the modified Arrhenius equation developed by Oelkers and Helgeson (1988b).
- Fig. 2. Predicted tracer diffusion coefficients for n-alkanes as a function of temperature at P_{SAT} . The labels on the curves represent the number of moles of carbon atoms in one mole of the n-alkanes.
- Fig. 3. Logarithms of the dissociation constants (A) and Setchénow coefficients (B) of $NaCl^{\circ}$ as a function of pressure at constant temperature (labeled in $^{\circ}C$). Except where otherwise noted, the symbols correspond to values generated by Oelkers and Helgeson (1991) from conductance data reported in the literature (see text). The curves represent smooth interpolation and extrapolation of the values represented by the symbols.
- Fig. 4. Logarithm of the dissociation constant for $NaCl_2^{-}$ and Na_2Cl^{+} ($\log K_{Na_2Cl^{+}} = \log K_{NaCl_2^{-}}$) as a function of temperature at constant pressure computed from equations given by Oelkers and Helgeson (1990).
- Fig. 5. Degree of formation (α) of single ions, neutral ion pairs, and triple ions in NaCl solutions as a function of the logarithm of the total molality of NaCl at 700 $^{\circ}$ C and 2 kb. The curves were generated using the dissociation constants and Setchénow coefficients depicted in Figs. 3 and 4, together with activity coefficients for the ionic species taken from Oelkers and Helgeson (1990).
- Fig. 6. Schematic illustration of the spatial model and finite difference grid used to compute the growth rate of hydrothermal alteration zones (see text).

Fig. 7. Positions of the hydrothermal alteration zone boundaries as a function of time in the computer experiment described in the text.

Fig. 8. Distribution of secondary minerals as a function of distance from the fluid-filled fissure depicted in Fig. 6 after 15,400 years of elapsed time (see text).

Fig. 9. Solution pH and the molalities of Na^+ , K^+ , and $\text{Al}(\text{OH})_4^-$ in the pore fluid as a function of distance from the fluid-filled fissure shown in Fig. 6 after 15,400 years of elapsed time (see text).

Fig. 10. Schematic representation of one-dimensional zero-flux boundary models.

A. Pore model: Symmetrical opposite boundaries of the pore consist of the same reactive mineral. Because of the symmetry, the transient concentration gradients are zero at the center of the pore, which constitutes the zero flux boundary.

B. Strata model: An impervious reactive stratum is separated from an impervious inert stratum by a layer of inert porous rock. The boundary between the impervious inert stratum and the porous stratum constitutes the zero flux boundary for diffusion of reactive aqueous species.

Fig. 11. Logarithm of the number of moles of secondary minerals (cm^2 of surface area) $^{-1}$ at the reactive stratum/porous rock interface (λ) as a function of the logarithm of time (t). The curves were generated by simultaneously solving for diffusional concentration gradients in the porous rock and the rate of mineral hydrolysis using the NEWCRANK computer code (see text).

Fig. 12. Logarithm of the number of moles of secondary minerals (cm^2 of surface area) $^{-1}$ at the reactive stratum/porous rock interface (λ) as a function of the logarithm of time (t). The system is the same as that represented by Fig. 11, but in contrast to the curves shown in this figure, those shown above were generated by assuming the pore

fluid within the porous rock to be homogeneous (i.e. no diffusional concentration gradients are present) using the EQ3/6 computer code (Wollery, 1986 -- see text).

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 9.

A. SYMMETRICAL PORE MODEL

B. STRATA MODEL

Figure 10.

Figure 11.

Figure 12.