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# Geochemical Modeling: A Comparison of Forward and Inverse Methods

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## Abstract

This paper discusses methods for learning quantitative details of the evolutionary reaction path of water and rock along recognized or hypothetical flow lines in ground water systems. The goals are: (1) to identify those minerals that are dissolving and/or precipitating along a recognized flow line, (2) to determine the regional variation in the number of moles of each mineral entering or leaving the ground water, and (3) to predict water quality and mass transfer in systems yet unstudied. Various concepts of geochemical modeling are reviewed and compared as they apply to the inverse problem and the forward problem. The inverse problem attempts to find a set of net mass transfer reactions that are thermodynamically feasible and satisfy the mass balance criteria using the available hydrochemical data. The forward problem involves *a priori* prediction of water composition and reaction path in hypothetical systems. The forward problem has the advantage of predicting details of thermodynamically valid reaction paths between the initial and final points, provided each path is constrained by the net mass transfer derived from the inverse problem. While defining the net mass transfer along the flow line, the inverse problem is not directly constrained by thermodynamics and results should be checked by the forward problem, or at least partially through thermodynamic speciation calculations at the initial and final points in the system.

In modeling reactions in regional ground water systems, for which appropriate hydrochemical data are available, most of the reaction information is gained through the inverse problems, i.e., through the combined use of mass balance and speciation calculations. The forward problem has perhaps its greatest value in estimating the previously unknown mass transfer and final water composition of systems yet unstudied. While the forward problem predicts the

chemical evolution that should occur along a hypothetical flow line, chemical modeling via the inverse problem requires details of ground water flow in selecting initial and final points along the same flow line. Various hydrologic, thermodynamic, mineralogic and kinetic factors (limitations) that should be considered in developing geochemical models are reviewed. The tools of geochemical modeling (speciation, mass balance and mass transfer/reaction path calculations) are discussed with special reference to the computer codes WATEQF, BALANCE and PHREEQE.

An example is made contrasting advantages and disadvantages of the forward and inverse methods. Using a given recharge water composition in a part of the Madison Limestone Aquifer of the Northern Great Plains, and assumptions regarding reversible and irreversible reactions in the system, an attempt is made to predict the mass transfer and water composition of Madison Limestone ground water via the forward problem. The forward method is successful in predicting observed trends in water quality as a function of temperature and irreversible reactions. But predicted water composition and mass transfer to any particular well shows a large uncertainty owing to lack of information on the extent of reaction and relative reaction rates. Via the inverse method, a series of reaction models are defined, all of which exactly predict the observed water composition, if treated as a forward problem. By including carbon and sulfur isotopic data in the inverse method, the extent of sulfate reduction is defined along with (1) a prediction of the sulfur isotopic composition of dissolving gypsum, (2) definition of the net mass transfer for a thermodynamically valid reaction path, (3) a geochemical model that predicts the observed  $^{13}\text{C}$  content, (4) corrected  $^{14}\text{C}$  ages, and (5) definition of flow velocities and rates of reactions along a flow line. For example, the inverse problem indicates that the Myssse water (east central Montana,  $\delta^{13}\text{C} = -2.2\text{‰}$ ) is approximately 22,600 years old and the net mass transfer reaction is

Recharge water (9.9 C) + 20.15 CaSO<sub>4</sub> + 0.87 CH<sub>2</sub>O +  
 3.54 CaMg(CO<sub>3</sub>)<sub>2</sub> + .09 FeOOH  
 + 15.31 NaCl + 2.52 KCl + 16.56 Na<sup>+</sup>-Exchange  
 - 8.28 Ca<sup>2+</sup>-Exchange  
 + 5.33 CaCO<sub>3</sub> + 0.09 FeS<sub>2</sub> + Mysse Water (63 C)

## Introduction

In developing geochemical models of ground water systems, we are interested in learning quantitative details of the evolutionary reaction path of water and rock along recognized or hypothetical flow lines. Specifically, we would like (1) to identify those minerals that are dissolving and/or precipitating along the flow line, (2) to determine the spatial variation in the number of moles of each mineral entering or leaving the ground water, and (3) to predict water composition and mass transfer in systems yet unstudied. This paper reviews and contrasts various concepts of geochemical modeling as they apply to (1) interpreting chemical reactions in ground water systems using the available hydrochemical data, and (2) *a priori* prediction of water composition and reaction path in hypothetical systems. Appropriate use of some of the computer programs available for modeling calculations is discussed and demonstrated through an example based on a recent modeling study of the Madison Limestone Aquifer of Montana, Wyoming and South Dakota, U.S.A. (Busby et al. unpublished). Further details of this approach to geochemical modeling are given by Plummer (1977), Wigley et al. (1978, 1979), Plummer and Back (1980), Parkhurst et al. (1980, 1982), and Plummer et al. (1983).

## Comparison of Forward and Inverse Methods in Geochemical Modeling

We may view the subject of modeling water-rock interaction in ground water systems either as a forward problem applying an assumed reaction model to an initial condition to predict the chemical composition of water and rock as a function of reaction progress, or as an inverse problem using observed chemical, isotopic, petrographic and hydrologic information at the initial and final points in the system to define mass balance reaction models that are consistent with the data. Both approaches lead to identical results in the net mass transfer between the initial and final points in the system provided the forward problem is so constrained (Plummer et al. 1983).

The forward problem has the advantage of predicting details of thermodynamically valid reaction paths between the initial and final points, provided each path is constrained by the net mass transfer derived from the inverse problem. But, without observed water chemistry data at the initial and final points, predicted water chemistry and mass transfer via the forward problem may be far from reality.

An advantage of the inverse problem is that any mass balance model found to be consistent with the available data is guaranteed to predict the final composition of the system if the derived mass transfer is

applied to the initial condition and solved as a forward problem. The inverse problem, however, is not constrained by thermodynamic considerations that must be checked by the forward problem, or at least partially through thermodynamic speciation calculations at the initial and final points in the system (Plummer et al. 1983).

In modeling reactions in regional ground water systems, for which appropriate hydrochemical data are available, most of the reaction information is gained through the inverse problem, i.e., through the combined use of mass balance and speciation calculations. Having defined the net mass transfer via the inverse problem, it is useful to treat the derived reaction model as a forward problem varying the relative rates of the irreversible reactions in order to examine possible variations in reaction path.

The forward problem has perhaps its greatest value in predicting the previously unknown mass transfer and final water composition of the system via hypothetical reaction models. The validity of the predicted mass transfer and final water composition derived from the forward problem depends on the accuracy of the assumed reaction model and thermodynamic data on which it is based.

## Review of Hydrologic, Thermodynamic, Mineralogic and Kinetic Factors to be Considered in Constructing Geochemical Models of Ground Water Systems

In constructing geochemical models of ground water systems, it is important to be aware of many of the hydrologic, thermodynamic, mineralogic and kinetic factors (processes) affecting the system.

### Hydrologic Considerations

First of all, as it is not meaningful to model changes in ground water composition between two unrelated waters, i.e., between two wells that are not located on the same flow path, a detailed knowledge of the flow system, is required, prior to development of the chemical model. The chemical model, once developed, can be used to check and refine aspects of the hydrologic model, such as through calculation of flow velocities (Back et al. 1983) and intrinsic permeability of the lithology (Konikow 1984; Back et al. 1984) from reaction-corrected <sup>14</sup>C ages, and quantification of vertical mixing (leakage) via interpretation of the water chemistry.

In contrast to the recognized physical boundaries of ground water systems, the definition of boundaries of chemical models of ground water systems depends on the questions being asked and the availability of data. For example, if we were primarily interested in chemical reactions during the recharge process, extensive sampling of rain and of the unsaturated zone would be required. Alternatively, if we were primarily interested in reactions deeper in the saturated zone, we could choose as our starting point ground water samples near the recharge area.

In the case of the forward problem, the end of the chemical model for a ground water system is determined by the modeler and may correspond, for example, to the point in reaction progress where a particular mass transfer of an irreversible reaction has been attained. Where this point in reaction progress fits into the flow system depends on the relationship of reaction progress to time (kinetics of reaction) and flow velocity.

For the inverse problem, the chemical model ends at the selected well farthest downgradient along the flow path of the starting water. While the forward problem predicts the chemical evolution that should occur along the flow path of the starting water, chemical modeling via the inverse problem is dependent on selection of initial and final points along the same flow path. Obviously, this is not always possible, even in detailed examination of a flow system, and thus, modeling results via the inverse problem must be tempered somewhat with knowledge and/or assumptions regarding the three-dimensional variation of water quality along adjacent flow lines.

Some hydrologic systems may not be amenable to chemical interpretation without incorporation of the effects of hydrodynamic dispersion, such as occurs in problems of injection and artificial recharge. It is presently thought that the effects of hydrodynamic dispersion can be neglected in many regional ground water systems (Appendix A, Wigley et al. 1978). If we had detailed knowledge of the reaction kinetics and flow velocity along a flow path, comparison of the final water composition predicted from the forward problem with the observed would give insight as to the importance of dispersion along the flow path.

Other hydrologic conditions that may seriously limit the success of chemical modeling in ground water systems include:

- Systems where there is significant fractured flow leading to the occurrence of water of very different residence times (and presumably different chemical character) at the same distance downgradient (Winoograd and Pearson 1976).
- Cases of hydrochemically undefined vertical mixing such as due to: (1) continued recharge to unconfined flow systems where, without knowledge of the quantity and chemical composition of the incoming water, it is not possible to separate effects of mixing from those of reaction in the flow system, and (2) leakage from underlying and overlying aquifers that may have heads greater than that of the system being considered.
- Chemically stratified flow systems where radically different water compositions occur as a function of depth. Again sufficient hydrochemical data may not be available to select wells opened to the proper depth to intersect the flow line and finally,
- Ground water systems that have been altered hydrochemically such as through injection, drawdown, sea water encroachment, etc., such that the water chemistry along the flow path is influenced by other reactions (or processes) not accounted for by the

chemical model being applied to the rest of the system. Included here are cases involving paleohydrology where past hydrochemical patterns are now inconsistent with the present-day flow system.

Given sufficient hydrochemical data, all of the above conditions could be treated competently with geochemical modeling techniques. The problem is that we usually do not have the details of the water chemistry and hydrology required for their resolution. Considering the availability of data, the modeling approach discussed here is usually best suited for large regional, confined flow systems.

### Thermodynamic Considerations

There are probably no ground water systems that are in overall chemical equilibrium with their host mineralogy. Even if all mineral-water reactions are rapid, there are usually temperature and pressure variations that cause shifts in the equilibrium composition of the system. Thus, in the sense of traveling along a flow path, even in an equilibrium system, there is the perception of reaction progress as a function of temperature and pressure changes. This is but one example of a partial equilibrium system, i.e., mineral-water equilibria shifting nearly reversibly in response to an irreversible process, changes in temperature and pressure in this case. There are many other examples of partial equilibrium systems where one or more minerals remain near equilibrium with the ground water, while one or more other chemical reactions proceed irreversibly.

It is often the case for partial equilibrium systems that minerals that appear to be in equilibrium are actually linked directly or indirectly to the irreversible reaction(s), such as through a common ion or via changing activity coefficients in the ground water. Thus, we may view a series of ground water samples that, based on thermodynamic speciation calculations, appear to be everywhere near equilibrium with one or more minerals, but may actually be continually reacting with these minerals in response to the irreversible reactions in the system.

If the saturation index of a mineral-water reaction is near zero in the system, evaluation of the saturation index along the flow path offers no clue as to whether the mineral is at equilibrium or continually reacting near equilibrium in response to irreversible reaction(s). Resolution of this distinction between equilibrium and what we will call apparent equilibrium reactions depends on the nature of the mass transfer. (The saturation index, SI, is defined as  $\log \frac{IAP}{K}$  where IAP is the ion activity product for the reaction in solution and K is the equilibrium constant.)

If the mineral is reacting at apparent equilibrium, its mass transfer along the flow path will not be zero. Evidence of non-zero mass transfer can come from various sources including petrographic observations of mineral abundance in the flow system, isotopic data for minerals and/or dissolved species, and in many cases from mass balance calculations via the inverse

problem, provided the net mass transfer along the flow path is not zero. If the net mass transfer along the flow path is zero, separating cases of equilibrium from apparent equilibrium requires knowledge as to whether the mineral mass transfer is non-zero along the true reaction path (as opposed to the net path determined via the inverse problem).

For purposes of modeling reactions along flow paths in ground water systems, we will conclude that a mineral present in the system is in equilibrium along the flow path if it is both saturated and has zero mass transfer. We will refer to cases of apparent equilibrium where the mineral appears to be saturated in the system, but has non-zero mass transfer along the flow path. In this latter case, the mineral is reacting in a partial equilibrium system.

If a mineral has non-zero mass transfer along the flow path, but is not saturated in the ground water, it is reacting irreversibly. In some cases irreversible reactions may proceed far enough that they reach equilibrium, or apparent equilibrium. Minerals that are not saturated in the system and have zero mass transfer are either not present along the flow path or, for kinetic reasons may be considered inert on the time scale of the flow system.

As a special case of a partial equilibrium system, consider an initial water in equilibrium with calcite, siderite, geothite, pyrite and gypsum at 25 C and 1 atm total pressure. In accordance with the mineralogic phase rule, we have arbitrarily selected an invariant system with six phases of compositions described by a minimum of six components:

Phases	Components
Calcite ( $\text{CaCO}_3$ )	$\text{CaCO}_3$
Siderite ( $\text{FeCO}_3$ )	$\text{FeCO}_3$
Geothite ( $\text{FeOOH}$ )	$\text{Fe}_2\text{O}_3$
Pyrite ( $\text{FeS}_2$ )	$\text{H}_2\text{S}$
Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )	$\text{H}_2\text{SO}_4$
Aqueous Phase	$\text{H}_2\text{O}$

At constant temperature and pressure the activities of all six components (and all other aqueous species derived from these components) are fixed in solution. If the minerals respond rapidly and reversibly with the aqueous phase, the composition of the aqueous phase will remain unchanged in response to all irreversible reactions with any other phase(s) whose composition can be described by one or more of the six components in the system at constant temperature and pressure. For example, Figure 1A shows the calculated composition of the aqueous phase as a function of irreversible reaction of oxygen, hydrogen and organic matter in the system. The activities of all species in solution remain constant for any amount of oxygen, hydrogen and  $\text{CH}_2\text{O}$  entering the equilibrium system. Similar results would be found in the aqueous phase for irreversible introduction of any other phase such as methane, FeS, sulfuric acid, aragonite, water, etc.),

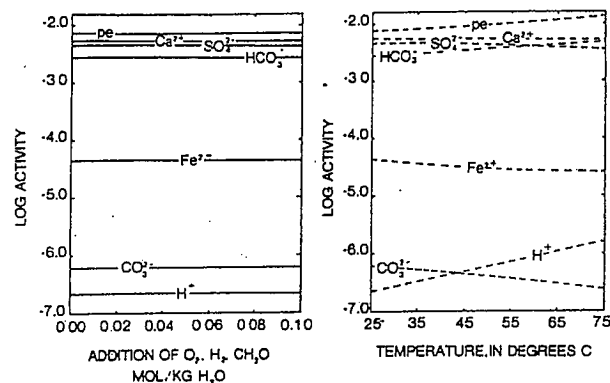


Figure 1. Calculated composition of an aqueous solution in equilibrium with calcite, siderite, geothite, pyrite and gypsum at 25 C and 1 atm total pressure (an invariant system) as a function of irreversible addition of  $\text{O}_2$ ,  $\text{H}_2$ , and  $\text{CH}_2\text{O}$  (A); and as a function of temperature (B) (one degree of freedom)

which have compositions that are functions of the six components chosen. (Calculations made using the geochemical simulation program PHREEQE, which is discussed in a later section of this paper.)

Although the activities of species and mineral saturation indices remain constant during irreversible reaction with oxygen, hydrogen and  $\text{CH}_2\text{O}$ , Figures 2A to 2C show there are large variations in the mass transfers of calcite, siderite, geothite, pyrite and gypsum. Furthermore, the mass transfer differs significantly with choice of irreversible reactions. But, even though there is significant reaction (mass transfer) among the five phases, thermodynamic analysis of the saturation indices of these phases in solution would show no evidence of reaction in this particular partial equilibrium system.

The example of Figures 1A and 2A to 2C describes partial equilibrium in an invariant system. If the irreversible reaction(s) involved phases with compositions not entirely a function of the six components for the system, such as would be the case if plagioclase feldspar were dissolving irreversibly in the preceding example, we would find a shift in ground water composition with reaction progress, while the saturation indices of calcite, siderite, geothite, pyrite and gypsum would again remain at zero offering no evidence of reaction for these phases. Notice in Figures 2A to 2C that for invariant systems the mineral mass transfer varies in constant proportion to the amount of irreversible reaction; this is not true, however, for systems with one or more degrees of freedom. For example, Figures 1B and 2D show variations in solution activities and mineral mass transfers, respectively, as one degree of freedom is added (temperature variations) to the partial equilibrium system of Figures 1A and 2A to 2C.

Invariant systems pose a special problem to chemical modeling via the inverse method because the changes in total concentrations of all elements in solution are zero throughout the system. Thus, in terms of

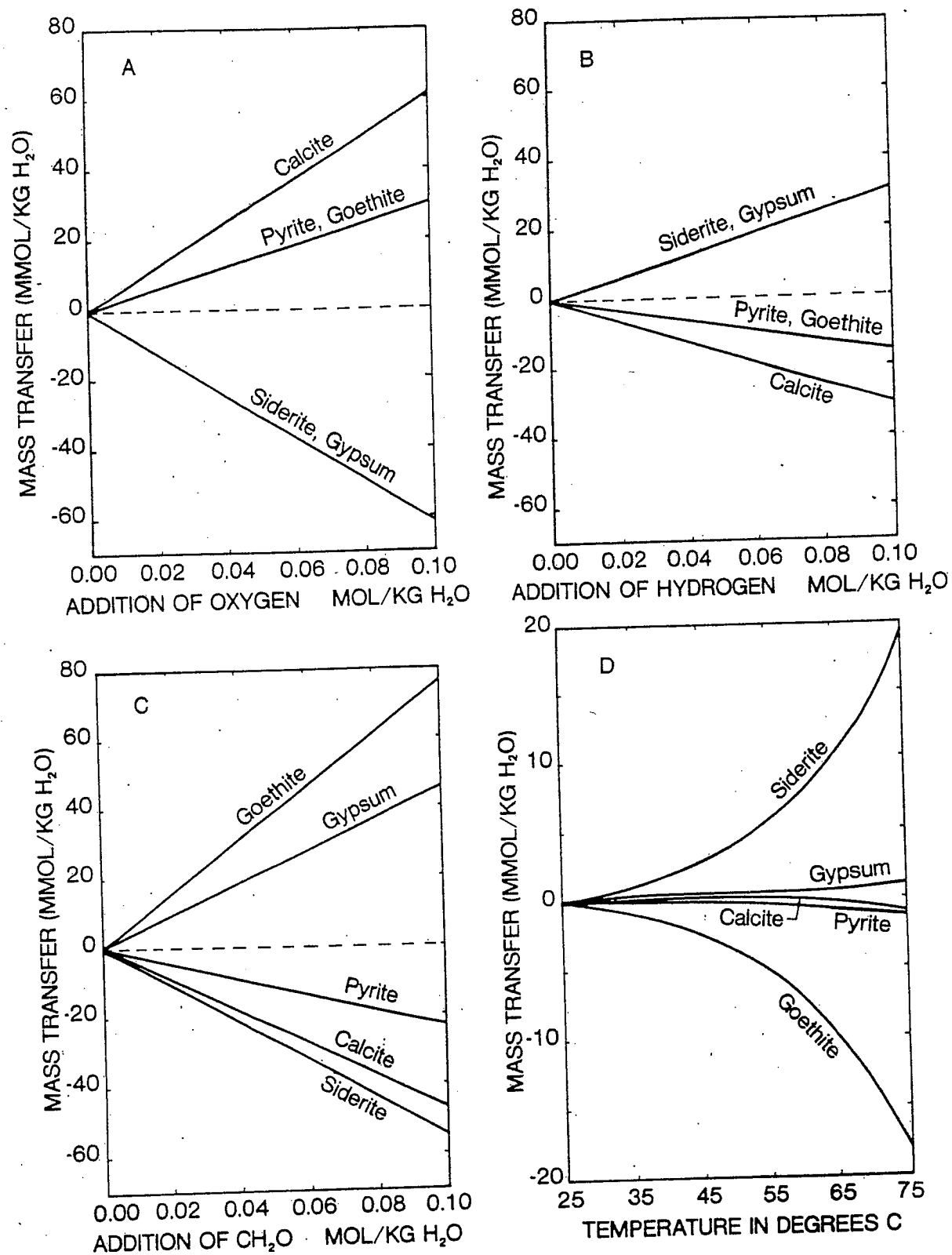
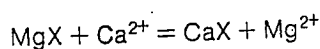


Figure 2. Variation in calcite, pyrite, goethite, siderite and gypsum mass transfers for the invariant system of Figure 1A as a function of irreversible addition of oxygen (A), hydrogen (B) and organic matter (C) and as a function of varying temperature (D) corresponding to Figure 1B

the inverse problem, there is no evidence of reaction without examining additional data for the system, such as isotopic or petrographic data. For example, if organic matter were reacting irreversibly, we might expect to find lighter and lighter  $\delta^{13}\text{C}$  values in solution downgradient even though the solution composition is fixed. Although many ground water systems are partial equilibrium systems, few are invariant in composition.

From the foregoing discussion, it can be concluded that constant near-zero values of the saturation index for a mineral-water reaction along a flow path is usually evidence of either equilibrium or apparent equilibrium control of water composition. This is not always the case, however, since it must also be known that the mineral is present and reactive in the system. Consider, for example, a water in equilibrium with calcite and a  $\text{Mg}^{2+}\text{-Ca}^{2+}$  ion exchange reaction at some  $\text{P}_{\text{CO}_2}$ . It may be possible to choose a clay with an equilibrium exchange constant for the reaction



such that the equilibrium solution satisfies the condition

$$a_{\text{Ca}^{2+}} a_{\text{Mg}^{2+}} a_{\text{CO}_3^{2-}} = K_D$$

and

$$a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}} = K_C$$

where  $K_D$  and  $K_C$  are the equilibrium constants of dolomite and calcite, even though dolomite is not present in the system. In this case, without mineralogic information, we might falsely conclude that we have either an equilibrium or apparent equilibrium system with respect to dolomite.

As an example of how related mineral-water equilibria can fix the ion activity product of another mineral, which may or may not be present in the system, we consider selected results from a recent geochemical modeling study of the Mississippian Madison Aquifer System of Montana, South Dakota and Wyoming (U.S.A.). Using data of Busby et al. (1983), the speciation calculations show that the water is near equilibrium with aragonite and dolomite (Figure 3) during the irreversible dissolution of anhydrite; this is the dedolomitization reaction as discussed by Back et al. (1983). As the reaction proceeds, much of the water approaches saturation with gypsum and a celestite phase assumed to be slightly more stable than that shown in Figure 4.

For much of this Madison water, we have the following properties:

$$a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}} \approx K_A$$

$$a_{\text{Ca}^{2+}} a_{\text{SO}_4^{2-}} \approx K_G \text{ (taking } a_{\text{H}_2\text{O}} \approx 1.0)$$

$$a_{\text{Sr}^{2+}} a_{\text{SO}_4^{2-}} \approx K_{\text{cel}}$$

where  $K_A$ ,  $K_G$  and  $K_{\text{cel}}$  are the equilibrium constants of aragonite, gypsum and celestite, and  $a_i$  denotes activ-

ity in solution. By substitution it can be shown that the ion activity product (IAP) of strontianite (S) in this water is determined entirely by the celestite, aragonite, gypsum ion activity products in the system

$$\text{IAP}_S = a_{\text{Sr}^{2+}} a_{\text{CO}_3^{2-}} = \frac{\text{IAP}_A \text{IAP}_{\text{cel}}}{\text{IAP}_G}$$

and since the water is near equilibrium with these three minerals, we have

$$\text{IAP}_S \approx \frac{K_A K_{\text{cel}}}{K_G}$$

At 25 C  $\log K_A = -8.336$  (Plummer and Busenberg 1982),  $\log K_{\text{cel}} = -6.578$  (calculated from Gallo 1935), and  $\log K_G = -4.602$  (calculated from Marshall and Slusher 1966).

Thus, ignoring the effect of temperature on the equilibrium constants, we should find an approximately constant strontianite ion activity product in much of the Madison water, and if we did not have reliable thermodynamic data for the strontianite equilibrium constant ( $\log K = -9.27$ , Busenberg et al. 1984), we might interpret the constant strontianite IAP as evidence of equilibrium or apparent equilibrium control. Figure 5 shows that the strontianite saturation index for all Madison water is near the value -1.0,

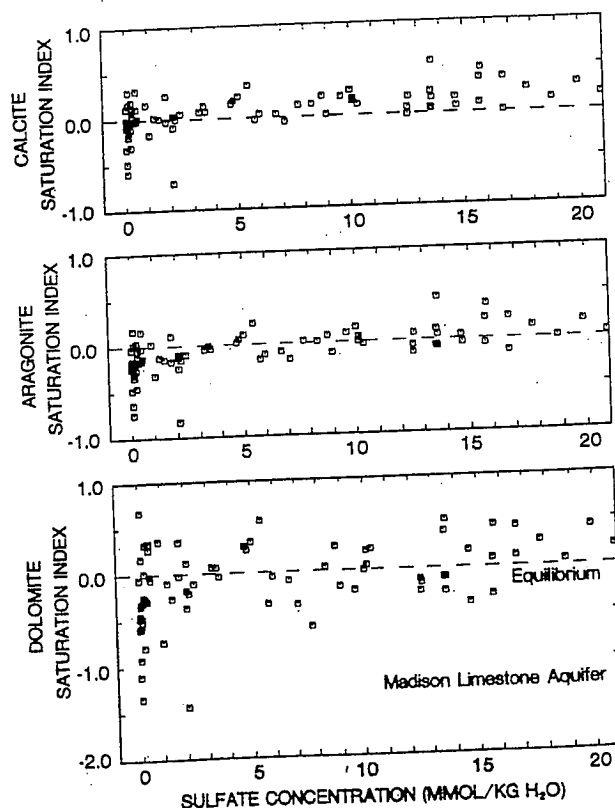


Figure 3. Comparison of the saturation indices of calcite, aragonite and dolomite in the Mississippian Madison Limestone Aquifer of parts of Wyoming, Montana and South Dakota, U.S.A.

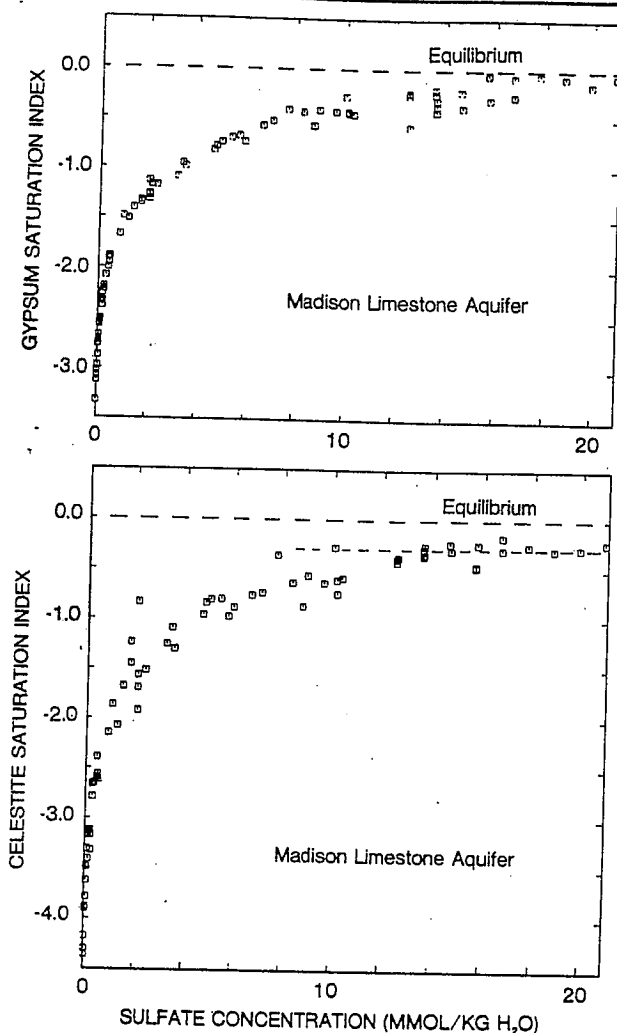


Figure 4. Comparison of gypsum and celestite saturation indices in the Madison Limestone Aquifer as a function of total dissolved sulfate. The water appears to approach equilibrium with gypsum and equilibrium with a celestite phase approximately 0.25 log  $K$  units more stable than that based on the experimental solubility data of Gallo (1935).

which is calculated from the gypsum, aragonite, celestite and strontianite equilibrium constants. Thus, if strontianite were present in the Madison system, it would dissolve irreversibly, causing precipitation of celestite and calcite, and dissolution of gypsum.

#### Mineralogic Factors

Almost without exception, chemical modeling studies of ground water systems have devoted far too little attention to mineralogy. Valuable insights on the reactions can be gained from careful examination of the mineralogy when combined with modeling of the water chemistry. The more information we have on the chemical and isotopic composition of the reactants and products, the more stringent the constraints that can be placed on the chemical models.

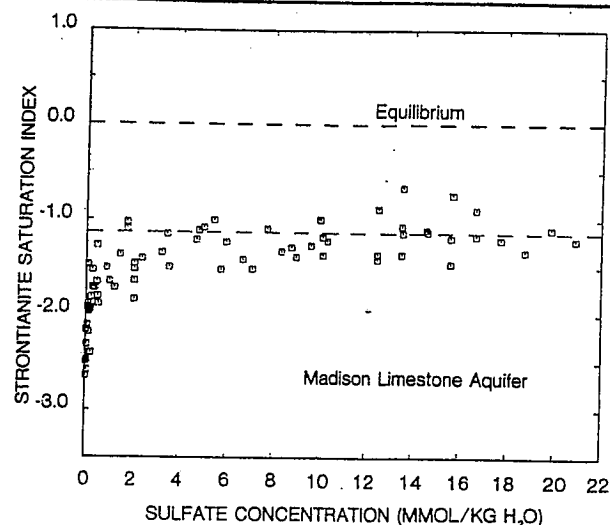


Figure 5. The apparent constant undersaturation with respect to strontianite in the Madison Limestone Aquifer is determined by  $\text{CaCO}_3\text{-SrSO}_4\text{-CaSO}_4$  equilibria (see text)

In our examination of the mineralogy of ground water systems we need to be asking questions such as:

1. What minerals are present and what are their abundances?
2. How does mineral abundance, including trace mineralogy, vary spatially in the system?
3. What is the actual composition (elemental substitution, exchangeable ions, etc.) of each mineral and how does this vary spatially?
4. What is the isotopic composition of the minerals and how does this vary spatially?
5. Are there any regional trends in mineralogy or composition that can be related to direction of flow?
6. From thin section or SEM examination, which minerals appear to be secondary and which are being replaced?
7. Is there evidence of coatings or zoned crystals? And, if so, how does the composition of the coating vary in the crystal?
8. Is the mineralogy of more permeable rocks in the system different from that in more impermeable zones?

With better understanding of the spatial variation in mineralogy and isotopic composition of ground water systems, we would no doubt be able to refine the geochemical reaction models and reach more advanced conclusions about phenomena such as chemical fronts and transition zones, which are often observed in ground water (Baedeker and Back 1979; Champ et al. 1979; Thorstenson et al. 1979; Chapelle and Knobel 1983). Fronts or transition zones probably represent the position on the flow path where the mass of an irreversible reactant either appears abruptly or becomes limiting. Typical examples include: (1) the point where oxygenated recharge water becomes depleted in oxygen leading to, for example, the abrupt



appearance of  $\text{Fe}^{2+}$  and/or  $\text{Mn}^{2+}$  fronts in solution, (2) the appearance of hydrogen sulfide in solution, which may coincide with the point downgradient where organic matter, originally deposited everywhere with the sediment has yet to be removed, (3) the point downgradient where clay minerals deposited in a marine environment are still in their original sodium form leading to the abrupt uptake of calcium and magnesium and the appearance of sodium bicarbonate water farther downgradient, or (4) uranium role front deposits (Reynolds and Goldhaber 1983).

In a qualitative sense, the following conditions promote sharp fronts in ground water systems: (1) abundant supply of an irreversible reactant (such as organic matter or evaporite minerals) in the substrate readily available for reaction, (2) fast reaction rates, and (3) slow flow velocities. The opposite of these conditions tends to spread out fronts and lead to broader transition zones. Obviously, with continued ground water flow, we can expect the position of the front or transition zone to continue to move downgradient.

As ground water diagenesis continues and the mineralogy matures, we would expect to see emergence of regional trends in mineral abundance—the more unstable minerals being depleted on the upgradient side of fronts and more abundant downgradient. Variations in the primary depositional pattern must also be taken into account, as well as the possibility that trends in composition may be due to previous paleohydrologic conditions.

#### Kinetic Factors

Apparent rates of reactions can be derived from ground water systems via the inverse problem if the mass transfer results are combined with estimates of water age such as through  $^{14}\text{C}$  dating (Plummer 1977; Plummer and Back 1980; Back et al. 1983; Paces 1983). Because it is difficult to determine the surface area of reactants and products in contact with a kg of  $\text{H}_2\text{O}$  extracted from a given volume of pore space, apparent rates of reaction derived from hydrochemical data are usually expressed in  $\text{mmol/kg H}_2\text{O/yr}$ . As a consequence of this choice of unit of rate, variations in mineral abundance will have a dramatic effect on the calculated rate.

Because the relative proportions of stable and unstable reactants and products change with age of the ground water system, we might expect to find for a mature ground water system, slower apparent rates of reaction near recharge areas where the proportion of unstable reactants is depleted, and faster apparent rates of reactions farther downgradient where the unstable reactants may not have been completely removed. This appears to be the case for the apparent rate of anhydrite dissolution in the Madison Aquifer System of Montana, Wyoming and South Dakota (Figure 6); as calculated from the data of Busby et al. (1983). The apparent rate of anhydrite dissolution varies from  $2.2$  to  $32.6 \times 10^{-4} \text{ mmol/kg H}_2\text{O/yr}$  in the Madison system and shows systematic increases with

distance of flow downgradient. Several groupings of apparent rate vs. distance are suggested by Figure 6 and may represent variations in anhydrite abundance in the system.

From laboratory studies, the rate of dissolution of gypsum (Liu and Nancollas 1971) and presumably anhydrite is expected to be instantaneous on the hydrologic time scale of the Madison System. That the Madison water is not in equilibrium with anhydrite throughout is evidence that mineral abundance is rate-limiting. Water that shows very rapid anhydrite dissolution (Figure 6) probably flows in part through bedded evaporites. Water showing very low rates probably flows through areas where much of the anhydrite has already been dissolved. The low rates probably represent the dissolution of nodules or pockets of anhydrite within the dolostone, which, through dolomite dissolution, occasionally come into contact with the ground water. Once exposed, dissolution is probably very rapid. Seen from a regional viewpoint, the average effect is perceived as one of slow anhydrite dissolution.

There is potential to learn a great deal about the kinetics of mineral water reactions from ground water systems, but the data will remain somewhat empirical and of questionable transfer value to other systems without knowledge of the reactive surface area in contact with a unit volume of water flowing through the pore spaces. From laboratory studies we know that rates of mineral water reactions per unit surface area vary by orders of magnitude between different minerals in the same solution, therefore, in treating the forward problem, it is not appropriate to relate relative rates of reaction to the proportion of mineral abundance.

Ultimately, we would like to treat ground water

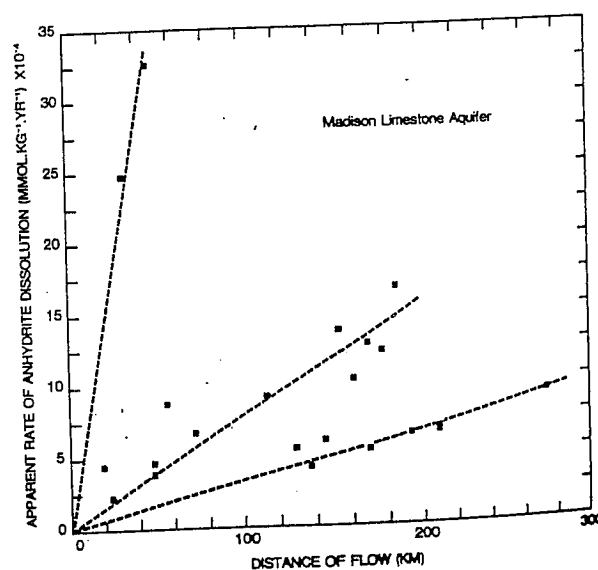


Figure 6. Computed apparent rates of gypsum/anhydrite dissolution in the Madison Limestone Aquifer as a function of distance of ground water flow from the recharge area.

systems as a forward problem predicting water quality in time and space. From a kinetic standpoint, we are far from realizing this goal. Laboratory studies have shown that rates of mineral water reactions are significantly influenced by water composition, including trace metals. The inhibiting effect of foreign ions is most pronounced near equilibrium such as found in many ground water systems. We will not be able to predict the paths of chemical reactions in ground water without details of the reaction kinetics (including mineral surface area) and thermodynamics for all relevant mineral water reactions as a function of fluid composition (including possible inhibiting trace elements), temperature, and, in some cases, pressure. Unfortunately, we are far from realizing this goal presently, and our best hope of obtaining useful kinetic information for predictive purposes in ground water systems is via the inverse problem.

### Methodology of Reaction Modeling

As judged from the foregoing discussion, geochemical modeling of ground water systems is largely a mental process, but is facilitated, however, by three types of calculations: (1) speciation calculations, (2) mass balance calculations, and (3) calculations of mass transfer and reaction path.

### Speciation Calculations

The speciation calculations are based on a chemical equilibrium model of the aqueous solution and thermodynamic data for all relevant mineral water reactions. Depending on the accuracy and reliability of the thermodynamic and analytical data, speciation calculations can tell us whether a particular mineral present in the system should tend to dissolve or precipitate. The question of whether the mineral is actually reacting in the environment, however, cannot be answered by speciation calculations alone.

There is a large and growing literature on speciation calculations and their application to geochemical environments. Nordstrom et al. (1979) reviewed and compared results from more than 30 computerized speciation models. Recently, Nordstrom and Ball (1983) have reported that the list of such models has grown to more than 50. No single code has been developed capable of treating the wide range of environmental problems to which equilibrium calculations have been applied, nor would such a code be practical.

From all indications, most speciation codes do well with the major inorganic element chemistry (Na-K-Ca-Mg-Cl-SO<sub>4</sub>-C) in dilute water characteristic of many ground water systems (ionic strength < 0.1), but thermodynamic equilibrium constants for many minerals, particularly the aluminosilicates, vary widely. Most speciation programs are on weak ground in modeling the minor element chemistry (particularly redox species), higher ionic strength water (particularly brines) and higher temperature water (> 75 °C).

Nordstrom and Ball (1983) have attempted to classify the various codes by capability including applications to brines, trace elements and high temperature

geothermal problems. Based in part on this classification, there are several standout models that deserve special attention.

For thermodynamic calculations in high ionic strength salt solutions (including mixed electrolytes), the model of Harvie et al. (1984), which is an extension of the work of Harvie and Weare (1980) to the system Na-K-Ca-Mg-Cl-SO<sub>4</sub>-OH-HCO<sub>3</sub>-CO<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O is unsurpassed. The model is based on the Pitzer (1973) equations for aqueous electrolyte solutions and is capable of reliably calculating saturation indices, pH, and gas and mineral solubility in brines to 20m. The Pitzer approach utilized by Harvie and Weare predicts the osmotic coefficient (and thus activity of water) and mean activity coefficient of neutral compounds in mixed electrolyte solutions. Although this approach is unparalleled for thermodynamic calculations of mineral-water reactions, it cannot predict the activities or concentrations of individual ions or ion pairs, and thus has limited application to problems requiring this information, such as toxicity, biological uptake, reaction mechanisms, which are thought to depend on the concentrations or activities of individual ions in solution. The data base of the Harvie et al. (1984) model is currently valid at 25 °C (only) and unfortunately a computer code utilizing this model is not publicly available. Future developments of this model will include expansion to hybrid models combining the Pitzer equations with ion pairing models for minor elements, and provision for variations in temperature and pressure (Ananthaswamy and Atkinson 1984).

For calculations at geothermal temperatures (to 300 °C) the programs SOLMNEQ (Kharaka and Barnes 1973) and EQ3NR (Wolery 1983) are notable standouts. Both codes use data developed largely by H.C. Helgeson and colleagues over the past 15 years. The EQ3NR code draws heavily from the more recent SUPCRT program/data base (Helgeson and Kirkham 1974a, 1974b, 1976; Helgeson et al. 1978, 1981) for log K values of aqueous redox reactions and mineral-water reactions, and utilizes Helgeson (1969) for aqueous species dissociation constants, as well as other sources mentioned in Wolery (1983) (Wolery 1979, 1980, 1984).

Depending, of course, on the accuracy and reliability of the thermodynamic data, speciation codes with large numbers of aqueous species and complexes included in the model will have a greater likelihood of application to a wider range of problems. Unfortunately, there are many uncertainties in the accuracy of thermodynamic data and analytical procedures for trace elements. As a result, speciation calculations of trace elements are rarely comparable in accuracy to those obtained for the major elements. Several codes that appear to have done well with trace element speciation include GEOCHEM (Mattigod and Sposito 1979), which has some 2,000 species including selected organics. GEOCHEM was designed initially for application to soil-water systems, but is presently not available for distribution (Mattigod, written communication 1984). Also included here is WATEQ2 (Ball et al. 1979,

1980) and related programs WATEQ3 (Ball et al. 1981) and MINTEQ (Felmy et al. 1983), which are well suited for treating both major and minor elements in the ground water environment.

Most aqueous models in use today are based on the ion pairing concept. The solution is assumed to contain both free ions and ion pairs. The formation of ion pairs from the free ions is described by a mass action equilibrium expression for the association reaction. The unknowns that are solved by the speciation code are the concentrations, activities and activity coefficients of all the free ions and ion pairs in solution. Activity is related to concentration by an individual ion activity coefficient,  $\gamma_i$ ,  $a_i = m_i \gamma_i$ , where  $m_i$  denotes molality and  $a_i$  is activity of the  $i^{\text{th}}$  free ion or ion pair. The activity coefficients are usually calculated from various forms of the extended Debye-Hückel equation (Stumm and Morgan 1981). Other expressions for  $\gamma_i$  contain adjustable parameters that have been fitted to mean salt data such as in WATEQ (Truesdell and Jones 1974) and WATEQF (Plummer et al. 1976) and are more reliable to higher ionic strengths particularly in chloride-dominated solutions. But because these expressions were derived from single salt (chlorides) solutions, their application to mixed electrolyte solutions can introduce large errors at high ionic strength.

The speciation problem is constrained by mass balance for each element and charge balance for the solution. For a solution containing  $J$  elements, we may write  $J$  mass balance expressions, which specify that the sum of the molalities of all species containing a particular element, taking into account species stoichiometry, must be equal to the known (analyzed) molality of that element in solution. The charge balance expression requires that the sum of the molalities of all species multiplied by their charge be zero in solution. Combining the number of mass balance equations with the charge balance constraint, there are  $J + 1$  independent equations that must be specified in solving the speciation problem. There are usually many more than  $J + 1$  unknowns in the speciation problem but this number is reduced by solving for "master species"; one predominant species for each element. The activities of ion pairs are then calculated from the activities of the master species using the mass action expressions and the known ion association equilibrium constants.

Because of the analytical difficulties, it is usually not practical to write mass balance equations for hydrogen and oxygen. Furthermore, when dealing with chemical analyses of natural water, the data may not be complete for all the elements present and there are always uncertainties in the analytical procedures such that it is also not appropriate to include the charge balance equation among the  $J + 1$  equations required to solve the speciation problem. Thus, only  $J - 2$  mass balance equations can be written. The remaining three equations required in speciation calculations are usually satisfied by fixing the mass of water at 1 kg (molal concentrations), and specifying pH and Eh (or pe). Therefore, in addition to the thermodynamic data base

of the model, the data required in performing the speciation calculation are usually concentrations of the major elements (and any minor elements of interest), pH, Eh and temperature.

The results usually include the modeled concentrations and activities of the dissolved species and a calculation of appropriate gas partial pressures and mineral saturation indices. In addition, the speciation calculation provides several other numbers that are often required in chemical modeling via the inverse problem. These include the molal scale total concentrations of the elements including total inorganic carbon, which is usually derived from titration alkalinity, and pH, and a summation of the "redox state" of the solution. The redox state is a parameter used to keep track of electron transfer in mass balance reaction models. The redox state, RS, is defined:

$$RS = \sum_{i=1}^I v_i m_i$$

where  $v_i$  is termed the "operational valence" of the species. See Parkhurst et al. (1980) and Plummer et al. (1983) for further details of operational valence.

Before reaction modeling of a ground water system is attempted, it is almost always useful to perform the speciation calculation on the analytical data. As a final caution though, it must be remembered that the results of the speciation calculation are no better than the thermodynamic and analytical data on which they are based.

A first guide to reliable analytical data is to check for charge imbalance, as a percentage. Percent charge imbalance is defined as:

$$\% \text{ charge imbalance} = \left[ \frac{\sum_{i=1}^I (m_i z_i)_{\text{cations}} - \sum_{i=1}^I (m_i z_i)_{\text{anions}}}{\sum_{i=1}^I (m_i z_i)_{\text{cations}} + \sum_{i=1}^I (m_i z_i)_{\text{anions}}} \right] 100$$

where  $m_i$  denotes molality and  $z_i$  the absolute value of charge of the  $i^{\text{th}}$  ion. As a general rule, good analyses often balance within 1 percent and water with more than 5 percent charge imbalance should be checked carefully.

It is usually more difficult to assess the reliability of the thermodynamic data used in a particular model. Users of speciation codes are cautioned not to blindly accept any thermodynamic data used by any code. Before calculations should be made, it is recommended that the data base be carefully evaluated through checking appropriate literature sources as well as examining calculated saturation indices of water known to be in equilibrium with the minerals of interest (such as from laboratory solubility studies).

One of the greatest problems with thermodynamic data used in speciation codes is the lack of internal consistency of mineral-water equilibrium constants with the aqueous model. The most reliable equilibrium constants for calculation of saturation indices are those derived from application of the speciation model to laboratory or field solubility data.

In evaluating the results of speciation calculations, the uncertainties in computed mineral saturation indices must be considered. Individually taking into account all the uncertainties in the analytical and thermodynamic data for each mineral. As a result, we will always know some saturation indices better than others. For example, in a recent study of the Madison Aquifer system (Busby et al. unpublished), it was estimated that the saturation indices of calcite, aragonite, gypsum and anhydrite could not be determined to better than  $\pm 0.1$ . Uncertainties of  $\pm 0.2$  were assigned to the saturation indices of dolomite, celestite and strontianite, and much larger uncertainties on the order of  $\pm 0.5$  SI were assigned to barite and siderite. Calculation of the saturation index of FeOOH in water where dissolved iron is predominantly in the ferrous oxidation state is particularly uncertain when total ferric iron has not been determined in the field. In assigning uncertainties to saturation indices, it is also important to consider the additive effect of analytical uncertainties in dealing with complex stoichiometries of minerals such as apatite or a smectite. Here the same analytical uncertainty leading to  $\pm 0.1$  SI for a simple solid might compound to  $\pm 2.0$  or more for a mineral of complex compound stoichiometry.

#### Mass Balance Calculations

Mass balance reaction models are used to define the net masses of minerals dissolved and/or precipitated along each flow path between the recharge area and each downgradient well. This type of modeling is called the inverse problem and has been considered in detail by Plummer et al. (1983). As shown by these authors, the chemical evolution of the water along the flow path is constrained by relationships of conservation of mass and electrons, which are represented by the equations

$$\sum_{p=1}^P \alpha_p b_{p,k} = \Delta m_{T,k} \quad k = 1, j \quad (1)$$

and

$$\sum_{p=1}^P u_p \alpha_p = \Delta RS \quad (2)$$

Equation 1 requires that the change in total moles of the  $k^{\text{th}}$  element in solution along the flow path,  $\Delta m_{T,k}$  (final water minus initial water) be equal to the sum of the net moles of that element entering and/or

leaving solution from dissolution, precipitation, biological degradation, gas transfer, etc. of P phases (minerals) along the flow path, where the mass transfer coefficient,  $\alpha_p$ , is the number of moles of the  $p^{\text{th}}$  mineral entering (positive) or leaving (negative) the solution, and  $b_{p,k}$  is the stoichiometric coefficient of the  $k^{\text{th}}$  element in the  $p^{\text{th}}$  mineral. Equations of the form of Equation 1 may be written for the J-2 elements (excluding hydrogen and oxygen), which are required to define the composition of the P phases considered in the model. Thus a reaction model is a particular choice of phases that react to give the observed final water composition. If the reaction also includes changes in oxidation state, Equation 2 provides an additional constraint on the reaction. Equation 2 follows from the fact that hydrated electrons do not exist in effective concentrations in solution (Thorstenson 1984) so that if electron transfer does take place (i.e., there is a redox reaction), the electrons transferred are conserved among the dissolved species,  $\Delta RS$ , and the mass transfer,  $\alpha_p$ , of the P phases in the model. In Equation 2  $\Delta RS$  is calculated from the analytical data, as are the  $\Delta m$  values, and includes the (operational) valence,  $v_i$  of the  $i^{\text{th}}$  species in solution. The term  $\Delta RS$  is defined as:

$$\Delta RS = \sum_{i=1}^I v_i m_i (\text{final}) - \sum_{i=1}^I v_i m_i (\text{initial}) \quad (3)$$

where  $m_i$  is the molality of the  $i^{\text{th}}$  species in solution. (The initial condition refers to the recharge area or upgradient well and final indicates the downgradient well). The change in the redox state of the solution,  $\Delta RS$ , is then equal to the number of electrons transferred among the P phases where  $u_p$  is the operational valence of the  $p^{\text{th}}$  phase.

The data required to solve a mass balance reaction model are (1) the set of phases thought to be reacting along the flow path, and (2) the concentrations of the elements in the initial and final water that correspond to the composition of the chosen phases.

In solving the mass balance model, values of  $\Delta m_{T,k}$  and  $\Delta RS$  are defined by the analytical data and are usually expressed in mmols/kg  $H_2O$ . Values of  $b_{p,k}$  and  $u_p$  depend on the choice of plausible phases being included in the mass balance model. Solved by the mass balance equations are the net mass transfer coefficients of each phase,  $\alpha_p$ , in mmol/kg  $H_2O$  between the initial and final points. The mass transfer results define a balanced chemical reaction in the form:

Initial Solution Composition + "Reactant Phases" –  
Final Solution Composition + "Product Phases"

Mass balance calculations used in conjunction with speciation calculations, can tell us a great deal about the reactions occurring, provided hydrologic data are available to identify initial and final water along the same flow path. If hydrologic dispersion is significant along the flow path, the computed mass transfer coef-

ficients incorporate both the effects of reaction and flow. Separation of the dispersive and reactive effects would require an independent detailed model of fluid flow.

The most difficult aspect of mass balance modeling is the usually non-unique nature of modeled results. In solving mass balance problems we may consider only J-2 phases (or J-1 phases in redox problems), i.e., we may include one phase for each equation we can write. Usually the number of plausible phases we could consider is larger than J-1 leading to the non-unique nature of the results. The inverse problem becomes one of solving multiple mass balance hypotheses and then utilizing additional isotopic, thermodynamic and mineralogic information for the system in identifying models that are inconsistent with the data. It is rarely proven that a particular reaction model is unique, and more common to recognize sets of plausible phases and associated mass transfers, which are consistent with all available data.

There are several ways of eliminating reaction models from further consideration. First, we would expect the computed mass transfer to be consistent with the saturation indices determined via the speciation calculations. For example, if the mass balance calculations indicate net dissolution of a mineral, the speciation calculations should show undersaturation at least somewhere along the flow path. Usually we can only check saturation indices at the initial and final points being modeled. If the mass transfer varies monotonically as a function of reaction progress, as is usually the case in regional flow systems, then we can expect the speciation calculation of saturation indices to be consistent with the mass balance results for all thermodynamically valid reaction models.

The distinction being recognized here is the difference between the reaction path implied by the net mass transfer calculated between the initial and final points, and the actual path taken by the reaction along the same flow line. It is possible, for example, that a mineral that shows a net dissolution over the length of the flow path may only dissolve over a limited portion of the path and may precipitate over other parts of the path, but resulting in the calculated positive net mass transfer. Mass balance calculations tell us nothing of the details of reaction path between the initial and final points. In spite of this, mass balance calculations are of considerable value in interpreting reactions in ground water systems, particularly regional ground water systems, because major variations in reaction path are uncommon. If important changes in reaction path are suspected between initial and final points, these may be determined through the mass balance calculations by selecting additional well(s) intermediate to the initial and final points. Clearly then, as the initial and final points are selected at shorter intervals along the flow path, the net mass transfer more closely corresponds to the actual mass transfer.

Other criteria used to eliminate mass balance reaction models include petrographic data supporting which minerals are reactants and products along the

flow path, and isotopic data for the water and mineralogy. Because the isotopic data provide an independent check on the computed mass transfer, it is often useful to compare computed isotopic values for the final water with the corresponding observed values. Details of modeling isotopic evolution are given in Wigley et al. (1978, 1979) and Plummer et al. (1983). If treated as a forward problem, the correct reaction model must predict both the observed chemical and isotopic composition of the final water.

Computationally, mass balance calculations are simple to perform and can often be solved by hand or by a programmable calculator. More elaborate reaction models may be solved using the computer program BALANCE (Parkhurst et al. 1982), which formulates and solves a set of simultaneous equations. See Parkhurst et al. (1982) and Plummer et al. (1983) for further examples of mass balance calculations including methods of solving problems involving mixing of water with chemical reaction and ways of incorporating isotope dilution equations with the mass balance calculations.

### Mass Transfer Calculations

Included under the definition of mass transfer are all calculations for which there is a recomputation of the distribution of species in response to changes in the composition, temperature and/or pressure of the fluid. This includes phenomena such as mineral solubility, dissolution, precipitation, irreversible reactions in partial equilibrium systems, adsorption, mixing of water, etc. Mass transfer calculations are based on a thermodynamic model of the mineral-water system and are subject to many of the same uncertainties as the speciation calculations on which they depend. But unlike the speciation calculations, which can only indicate the thermodynamic potential for minerals to react, the mass transfer calculations predict what the chemical composition of the aqueous solution should be and the amounts of minerals transferred among aqueous, gaseous and solid phases if a particular set of irreversible reactions and/or thermodynamic constraints are operative.

Some of the more important uses of mass transfer calculations are in (1) testing the thermodynamic feasibility of reaction models derived from (non-thermodynamic) mass balance calculations, (2) estimating the mass transfer and water composition along flow paths intermediate to wells of known composition, and (3) a *priori* calculation of reaction paths and solution composition for an unlimited number of hypothetical reactions (the forward problem).

Because the mass balance models are not constrained by thermodynamics, it is necessary to turn to the mass transfer calculations to try and find at least one thermodynamically valid reaction path between the initial and final points that is consistent with the net mass transfer derived from the mass balance calculations. If at least one valid reaction path exists, the mass

balance reaction model cannot be eliminated. For regional ground water systems of generally monotonic reaction behavior, i.e., no abrupt changes in reaction path over large flow path distances, it is possible to use mass transfer calculations and the mass balance model to predict water composition at points intermediate to wells of known composition where no data otherwise exist.

Finally, the most commonly recognized use of the mass transfer calculations is in the forward problem: prediction of hypothetical reaction paths, finding the composition of equilibrium and apparent equilibrium solutions, evaluating effects such as changing temperature, open systems, mixing of water, etc.

In modeling a forward problem it is first necessary to define the starting condition. This may be pure water, such as might be appropriate in modeling a reaction path beginning with rain water, or in constructing theoretical equilibrium or laboratory solutions, or a ground water sample near the recharge area of a regional aquifer. Regardless of the selected starting solution, it is essential that some appropriate adjustment be made to the starting solution to ensure electrical neutrality. Charge balance adjustments are particularly important when the starting solution is defined by a water analysis, which is almost certainly not electrically neutral to the precision required by most mass transfer codes (such as  $10^{-12}$  equivalents per kg  $H_2O$ ). Initial electrical neutrality is required because as the mass transfer calculations begin, the charge balance constraint is utilized in the governing equations and any initial charge imbalance will erroneously offset the computed distribution of species and mass transfer. Electrical neutrality is usually obtained by adjusting the concentrations of one of the elements in solution, adjusting the starting pH, or, in the case of PHREEQE (Parkhurst et al. 1980), and EQ6 (Wolery 1984), provision is also included to carry the initial charge imbalance through all subsequent calculations, as if a totally inert species had been added to solution. This latter option ensures the integrity of the analytical data of the starting condition.

The next step in modeling the forward problem is to recognize any irreversible reactions that may be occurring. Examples of irreversible reactions in geochemical systems include:

- The oxidation of organic matter, such as that accompanying bacterially mediated sulfate reduction
- The dissolution of minerals that rarely reach equilibrium in the ground water environment such as primary silicates like pyroxenes and plagioclase feldspars, or trace minerals that have such low surface area contact with the aquifer that there is the perception of a very slow dissolution reaction
- Introduction (or loss) of gases from (to) other reservoirs such as leakage of methane into an aquifer from subsurface oil field brines, diffusion of oxygen into sulfide-rich spoils piles associated with various mining practices, or transport of  $CO_2$  to the saturated zone by recharge water percolating through the unsaturated zone.

If there is only one irreversible reaction occurring, only one reaction path exists (for any particular starting solution and set of accompanying equilibrium constraints). But if there is more than one simultaneous irreversible reaction, then an unlimited number of reaction paths may be defined corresponding to the number of possible choices in relative rates of irreversible reactions. Definition of the true reaction path requires knowledge of the rates of each irreversible reaction and data on the surface area of each reactant in contact with a unit volume of pore fluid.

In modeling reaction paths between wells of known composition along a flow line, one may use the mass balance results as a starting point in assigning realistic relative rates of reaction. The computed final water will match the observed only when the starting water is identical to the observed and the net mass transfer along the computed reaction path is identical to the mass balance result. But in the absence of the mass balance models, or kinetic information, definition of relative rates of reaction and reaction path is completely arbitrary, as is then the computed reaction path and final water composition.

Mass transfer reactions are usually followed as a function of a reaction progress variable. Examples of a reaction progress variable include the total moles of one of the irreversible reactants entering or leaving a kg of water, temperature, or the proportion of an end-member water in mixtures of two end-member waters. Until geochemical models are modified to include kinetic information and coupled with flow models, it will not be possible to use time or distance as the progress variable.

The model of the forward problem is complete when all appropriate equilibrium or apparent equilibrium mineral-water reactions are included. Some codes well suited for modeling the forward problem (such as EQ3/6, Wolery 1979) automatically include the precipitation of minerals once their saturation indices are exceeded in solution and keep track of masses of minerals formed with the option to redissolve this mass of products if, as the irreversible reaction proceeds, the solution becomes undersaturated. Other codes, such as PHREEQE (Parkhurst et al. 1980), require the user to select the equilibrium constraints in modeling reaction paths. For purposes of locating phase boundaries during irreversible reactions, PHREEQE has the capability of computing the amount of irreversible reaction required for the solution composition to reach the intersection of an assigned phase boundary, with or without the inclusion of other mineral-water apparent equilibria.

Once the forward problem is defined the computed results include definition of the composition of the aqueous fluid and masses of minerals dissolved and precipitated as a function of reaction progress.

Mass transfer calculations were pioneered by H.C. Helgeson and his students and colleagues at Northwestern University (Helgeson 1968; Helgeson et al. 1969, 1970) in developing the reaction path code PATH1 (Helgeson et al. 1970). Reaction paths were



predicted by accumulating small successive increments of irreversible reaction progress and computation of any accompanying mineral mass transfer. Literally hours of computation time were required to achieve meaningful reaction progress. Since development of PATHI, significantly faster codes based on the reaction path concept have been developed such as EQUIL (Fritz 1975), EQ3/6 (Wolery 1979, 1980, 1983, 1984), SOLVEQ (Reed 1982) and FASTPATH (Herrick; as cited in Mercer et al. 1982).

Another school of mass transfer codes is based on REDEQL (Morel and Morgan 1972) and has limited mass transfer capability in computing composition of equilibrium solutions and adsorption equilibria, but is not designed for computing reaction paths as a function of a progress variable. These programs include REDEQL2 (McDuff and Morel 1973), MINEQL (Westall et al. 1976), MICROQL (Westall 1979), GEOCHEM (Mattigod and Sposito 1979), and MINTEQ (Felmy et al. 1983).

A different approach to mass transfer calculation is found in the code PHREEQE (Parkhurst et al. 1980). PHREEQE is capable of computing reaction paths provided the user specifies any accompanying mineral equilibria. The major distinction between the reaction path capability of PHREEQE and true reaction path codes such as EQ3/6 is that PHREEQE solves for the solution composition and mass transfer only at requested points in reaction progress. While this approach is computationally more efficient than the incremental method utilized by EQ3/6, it requires a considerable amount of user manipulation in defining complex reaction paths.

Extensive testing of PHREEQE and EQ3/6 has been conducted in studying the suitability of these codes for nuclear waste performance assessment (INTERA 1983a, 1983b, 1983c). According to these reports PHREEQE and EQ3/6 give identical results when using the same aqueous model and thermodynamic data. This is of interest because the two programs satisfy the required  $J+1$  master equations in different ways. Both programs include the charge balance constraints. EQ6 uses a mass balance equation for each element including hydrogen and oxygen in defining the necessary  $J+1$  equations. PHREEQE includes an electron balance equation and performs all calculations relative to an assumed constant mass of water (1 kg) in satisfying the  $J+1$  equations. By assuming a constant mass of water, an approximation is introduced in PHREEQE that can lead to errors in modeling reactions involving hydration and dehydration of minerals, and redox conditions near or beyond the stability of water. Reactions of these types are usually not important in the geochemical environment and the efficiency in computing gained from the approximation outweighs any loss in accuracy lost by not including mass balance equations for hydrogen and oxygen.

### Logic of Reaction Modeling

There are certain steps that can be performed in

geochemical modeling and these are summarized in Figure 7. The first criteria in constructing a geochemical model concerns the availability of analytical data. If the analytical data are largely incomplete or unavailable, numerous hypothetical reaction models can be constructed for the system via the forward problem. Results of reaction path calculations of these models are unconstrained to the extent that they cannot be tested against direct chemical observations in the system.

If enough chemical data for the system are available, then much of the reaction information may be gained through the combined use of speciation and mass balance calculations—the inverse problem. Beginning with a set of chemical analyses for initial and final water along a flow path, a speciation calculation is performed for each water. This calculation defines the saturation indices of minerals and other information that may be used later, including the total molality of inorganic carbon and the redox state of each solution. The plausible phases that are likely candidates for reactants and products in the system are then selected. Selection of plausible phases is one of the more critical aspects of reaction modeling and requires significant geological and mineralogic insights to the hydrologic system. The logic that follows assumes that all of the true reactant and product phases for the system have been included among the plausible phases.

Having decided upon the total set of plausible phases, a test is made to see if a unique algebraic solution to the problem exists (Figure 7). The test involves three variables defined by the problem: (1) the total number of plausible phases to be considered,  $\Phi$ , (2) the total number of mass balance equations that can be written,  $J-2$ , and (3) the total number of minerals and/or gases allowed in a given model,  $P$ . For non-redox problems  $P=J-2$  and for redox problems  $P=J-1$ . If  $P$  is equal to the total number of plausible phases,  $\Phi$ , a unique reaction model is derived by the mass balance approach and the reaction coefficients,  $\alpha_p$ , define the net masses of the plausible phases that enter or leave the ground water between the initial and final water. If, however, the number of plausible phases is larger than  $P$  (as is usually the case), then there are some number  $N$  ( $N > 1$ ) reaction models for the system consisting of  $N$  subsets of the plausible phases. Next begins a series of tests that may help to eliminate some of the  $N$  reaction models. To eliminate a plausible phase, each reaction model (among the  $N$  reaction models) that contains that particular phase must be shown to be invalid.

Having solved the  $N$  mass balance models and determined the mass transfer coefficients,  $\alpha_p$ , we first check for apparent thermodynamic violations at the initial and final points. For example, if  $\alpha_p$  is positive, indicating dissolution, we would not expect to find supersaturation with respect to the  $p^{\text{th}}$  phase, and for negative  $\alpha_p$  (precipitation), the water should not be undersaturated. Because of the condition of apparent equilibrium discussed previously, saturation indices

near zero are commonly associated with both positive and negative values of  $\alpha_p$ . As we can only check for thermodynamic violations at the initial and final points, apparent thermodynamic contradictions are not always definitive because of possible variations in reaction path. Because the mass balance calculations determine only the net mass transfer, deviations in the true reaction path between the initial and final points from that defined by the net mass transfer could lead to valid thermodynamic conditions at inaccessible intermediate points on the flow path. If, however, monotonic behavior in reaction path is expected between the initial and final points, valid checks for thermodynamic violations can be made by comparing initial and final saturation indices with the computed mass transfer coefficients. Other ways of reducing the number of reaction models include introducing new information such as petrographic evidence or isotopic data.

If through any of these tests the number of reaction models is reduced to one, then a unique reaction has been defined for the system (Figure 7). Commonly, though, the number of remaining reaction models is greater than unity. If at this point the analytical data are saturation-sufficient, i.e., sufficient analytical data exist to define the saturation indices of all plausible phases, then some number  $M$  ( $1 < M \leq N$ ) reaction models remain. None of the  $M$  models may be eliminated without introducing additional data for the system. If, however, the analytical data are saturation insufficient such that one or more saturation indices are undefined, the mass balance reactions may be examined via solubility calculations to see if thermodynamic violations may be identified. Such violations include calculation of significant oversaturation with respect to reactant phases in the final water. If thermodynamic violations reduce the number of reaction models to unity, again, a unique reaction model has been defined for the system.

Although the logic of Figure 7 may serve to eliminate some reaction models and even remove some plausible phases from further consideration, multiple reaction models often remain after all tests have been exhausted. For these cases the problem is non-unique and will remain so until appropriate new data are introduced. Most problems in reaction modeling end in the lower right corner of Figure 7.

We pointed out earlier that the logic of Figure 7 depends on the assumption that the actual reactants and products are included among the plausible phases. We have no assurance that this condition has been met when beginning a problem of reaction modeling. An obvious indication that one has failed to include one or more of the actual reactants or products among the plausible phases is demonstrated if all reaction models are shown to be invalid. In general though, multiple reaction hypotheses remain and we may never know if the true (unique) reaction model is included among the remaining models.

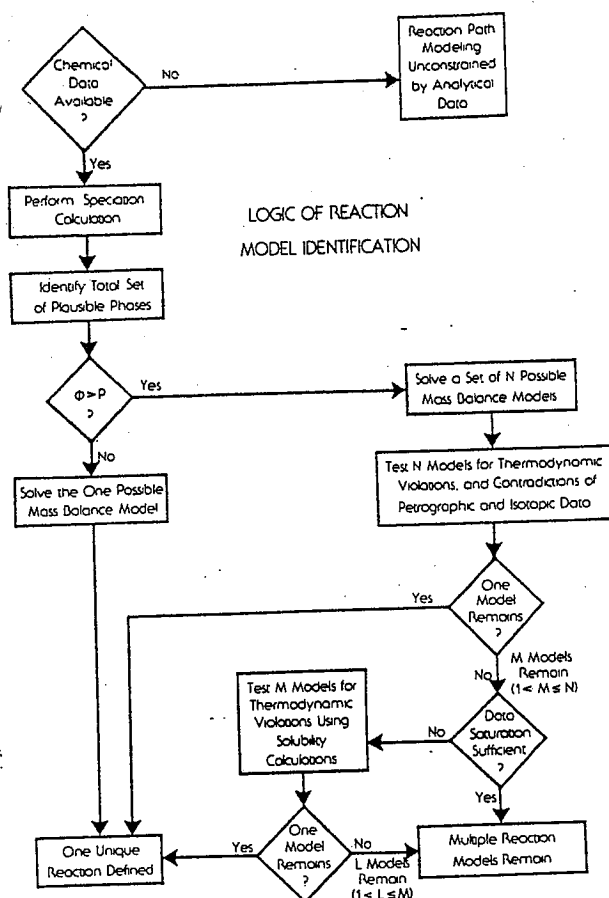


Figure 7. Schematic diagram of the logic of geochemical reaction modeling. The forward problem applies to the condition of no analytical data. Where analytical data exist for initial and final water, reaction modeling follows the inverse method.

## A Modeling Example Comparing Forward and Inverse Methods

Having recently completed an extensive modeling study of the Mississippian Madison Limestone Aquifer of Montana, Wyoming and South Dakota in which the inverse problem was utilized almost exclusively (Busby et al. unpublished) it is of interest to examine a limited portion of the Madison system using both the forward and inverse methods to demonstrate advantages and disadvantages of the two modeling approaches.

### The Inverse Problem

We begin with the observed analytical data for an initial and final water in the Madison Limestone Aquifer of Wyoming and Montana. An average recharge water was selected east of the Bighorn Mountains in north central Wyoming. The final water (Mysse Well) was selected based on hydrologic modeling of Downey (1983) and is some 130 miles to the north-northeast in east central Montana. The Mysse Well has a reported depth of 5,103 feet. The temperature of the flowing



water measured at the surface is 63 C. Table 1 lists the chemical and isotopic composition of the recharge and final water as given by Busby et al. (1983) and unpublished USGS data.

Three lithologic units are recognized in the Madison Limestone (Group); a lower unit consisting of thin-to-medium-bedded argillaceous-to-shaly or silty, and in places cherty limestone (Lodgepole Limestone), a middle unit of thick-to-massive-bedded fossiliferous-to-oolite carbonate rock (Mission Canyon Limestone), and an upper unit of anhydrite and halite interbedded with carbonate rock and shale. These units intertongue somewhat, but the section contains numerous cyclic shaly interlayers (marker-beds) that are regionally pervasive and used for correlation purposes.

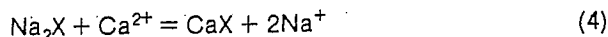
The petrology of a portion of the Madison Group has been reported by Thayer (1983) in core from three USGS test wells located in northeastern Wyoming (Test Well #1), southeastern Montana (Test Well #2), and south-central Montana (Test Well #3). Deike (1984) offers many details of the petrology and mineralogy of Madison Group core from Test Well #1.

Thayer (1983) recognized six major rock types in cores from the three test wells. Dolomite forms two-thirds of the total rock type and limestone about one-fifth. The rest consists of anhydrite, carbonate breccia, carbonate mudstone and chert. The mineralogy is predominantly a mixture of calcite and dolomite but contains 3 to 4 percent anhydrite and a variety of accessory minerals including illite, mixed-layer illite/smectite, kaolinite, quartz, feldspar, chalcedony, hematite and talc (Deike 1984). Halite was not reported in core from the three test wells but becomes more important to the north in the Central Montana Trough and to the northeast toward the Williston Basin. Deike found little evidence of dedolomitization (calcite replacing dolomite) in core from Test Well #1, but there was abundant secondary calcite, particularly in zones of subsurface slumping. Subsurface slumping is presumably caused by solution of anhydrite.

Based on these mineralogic data, analysis of trends in the water composition, and computed saturation indices throughout the Madison Limestone Aquifer, (Busby et al. in preparation), it is reasonable to include calcite ( $\text{CaCO}_3$ ), dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), gypsum/anhydrite ( $\text{CaSO}_4$ ), organic matter ( $\text{CH}_2\text{O}$ ), carbon dioxide ( $\text{CO}_2$ ), ferric hydroxide ( $\text{FeOOH}$ ), pyrite ( $\text{FeS}_2$ ), Ca-Na ion exchange, halite ( $\text{NaCl}$ ) and sylvite ( $\text{KCl}$ ) among the plausible phases.

Organic matter is included as the most likely electron donor for bacterially mediated sulfate reduction. The formula  $\text{CH}_2\text{O}$  is used only to denote carbon of valence zero. Sulfate reduction is known to occur because of the presence of dissolved sulfide species in many wells. Sulfate reduction need not be associated with high concentrations of dissolved sulfide species, if sufficient sources of dissolved iron are available for precipitation of pyrite. Therefore, we have included ferric hydroxide and pyrite in the mass balance models. Dolomite, calcite and gypsum are included to quantify the dedolomitization reaction. Dis-

solution of halite and sylvite were indicated by analysis of trends, although it is not possible to identify the true source of the  $\text{KCl}$ . Excess Na is attributed to Na-Ca ion exchange according to the reaction



$\text{CO}_2$  gas is included to account for the possibility of exchange of  $\text{CO}_2$  gas with other reservoirs such as the atmosphere or other formations. Near zero values for the  $\text{CO}_2$  gas mass transfer indicate that ground water conditions approximate a closed system. As we expect the deep ground water system to be essentially closed, non-zero values of the  $\text{CO}_2$  gas mass transfer are probably indicative of errors in the analytical data and/or choice of mineral phases.

The gypsum and pyrite mass transfers can be estimated accurately by the sulfur mass balance equation and an isotope dilution for  $^{34}\text{S}$  (Plummer et al. 1983).

The sulfur isotope balance equation is

$$\sum_{p=1}^P \alpha_p b_{p,s} \delta^{34}\text{S}_p = \Delta m_T^{34}\text{S} \quad (5)$$

where

$$\Delta m_T^{34}\text{S} = (m_{T,s} \delta^{34}\text{S}_T)_{\text{final}} - (m_{T,s} \delta^{34}\text{S}_T)_{\text{initial}}$$

In Equation 5,  $b_{p,s}$  is the stoichiometric coefficient of sulfur in the  $p^{\text{th}}$  phase and  $\delta^{34}\text{S}_p$  is the sulfur isotopic composition (per mil) of the  $p^{\text{th}}$  phase. The terms  $m_{T,s}$  and  $\delta^{34}\text{S}_T$  denote the total molality of sulfur in solution (sulfate plus sulfide species) and the average isotopic composition (per mil) of total dissolved sulfur. The apparent values of  $\delta^{34}\text{S}$  gypsum was found iteratively through the mass balance modeling as described below. The derived value of  $\delta^{34}\text{S}$  gypsum is  $+15.5\text{‰} \pm 0.5\text{‰}$ . The sulfur isotopic composition of pyrite was assumed to be that of the dissolved sulfide in the Mysse Well (Table 1).

For the 10 plausible phases listed above, 10 equations of the form of Equations 1; 2 and 5 are needed to calculate the mass transfer coefficients,  $\alpha_p$ . These equations are:

#### 1. Mass balance (Equation 1)

$$\alpha_{\text{calcite}} + 2\alpha_{\text{dolomite}} + \alpha_{\text{CH}_2\text{O}} + \alpha_{\text{CO}_2} = \Delta m_{T,C} \quad (6)$$

$$\alpha_{\text{gypsum}} + 2\alpha_{\text{pyrite}} = \Delta m_{T,S} \quad (7)$$

$$\alpha_{\text{calcite}} + \alpha_{\text{dolomite}} + \alpha_{\text{gypsum}} - \alpha_{\text{exchange}} = \Delta m_{T,\text{Ca}} \quad (8)$$

$$\alpha_{\text{dolomite}} = \Delta m_{T,\text{Mg}} \quad (9)$$

$$\alpha_{\text{halite}} + 2\alpha_{\text{exchange}} = \Delta m_{T,\text{Na}} \quad (10)$$

$$\alpha_{\text{sylvite}} = \Delta m_{T,K} \quad (11)$$

$$\alpha_{\text{halite}} + \alpha_{\text{sylvite}} = \Delta m_{T,\text{Cl}} \quad (12)$$

$$\alpha_{\text{FeOOH}} + \alpha_{\text{pyrite}} = \Delta m_{T,\text{Fe}} \quad (13)$$

## 2. Conservation of electrons (Equation 2)

$$4\alpha_{\text{calcite}} + 8\alpha_{\text{dolomite}} + 6\alpha_{\text{gypsum}} + 4\alpha_{\text{CO}_2} + 3\alpha_{\text{FeOOH}} = \Delta\text{RS} \quad (14)$$

Note that terms for  $\text{CH}_2\text{O}$  and  $\text{FeS}_2$  do not appear in Equation 14 because their operational valence is zero.

## 3. Sulfur isotope balance (Equation 5)

$$\alpha_{\text{gypsum}} \delta^{34}\text{S}_{\text{gypsum}} + 2\alpha_{\text{pyrite}} \delta^{34}\text{S}_{\text{pyrite}} = \Delta m_{\text{T}}^{34}\text{S} \quad (15)$$

Equations 6 through 15 provide the 10 independent equations required to solve for the unknown mass transfer coefficients,  $\alpha_p$ . The algebraic solution to Equations 6 through 15 defines the mass transfers of gypsum, pyrite, KCl, NaCl,  $\text{Ca}^{2+}/\text{Na}^+$  ion exchange, dolomite, FeOOH, calcite,  $\text{CO}_2$  gas and  $\text{CH}_2\text{O}$  as follows:

$$\alpha_{\text{gypsum}} = \frac{\Delta m_{\text{T}}^{34}\text{S} - \delta^{34}\text{S}_{\text{pyrite}} \Delta m_{\text{T,S}}}{(\delta^{34}\text{S}_{\text{gypsum}} - \delta^{34}\text{S}_{\text{pyrite}})} \quad (16)$$

$$\alpha_{\text{pyrite}} = (\Delta m_{\text{T,S}} - \alpha_{\text{gypsum}})/2 \quad (17)$$

$$\alpha_{\text{KCl}} = \Delta m_{\text{T,K}} \quad (18)$$

$$\alpha_{\text{NaCl}} = \Delta m_{\text{T,Cl}} - \alpha_{\text{KCl}} \quad (19)$$

$$\alpha_{\text{exchange}} = (\Delta m_{\text{T,Na}} - \alpha_{\text{NaCl}})/2 \quad (20)$$

$$\alpha_{\text{dolomite}} = \Delta m_{\text{T,Mg}} \quad (21)$$

$$\alpha_{\text{FeOOH}} = \Delta m_{\text{T,Fe}} - \alpha_{\text{pyrite}} \quad (22)$$

$$\alpha_{\text{calcite}} = \Delta m_{\text{T,Ca}} + \alpha_{\text{exchange}} - \alpha_{\text{gypsum}} - \alpha_{\text{dolomite}} \quad (23)$$

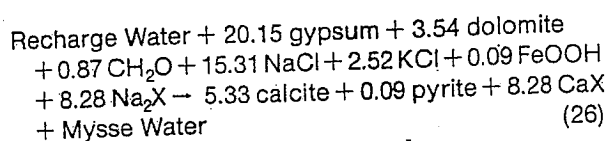
$$\alpha_{\text{CO}_2\text{gas}} = \frac{(\Delta\text{RS} - 3\alpha_{\text{FeOOH}} - 4\alpha_{\text{calcite}} - 8\alpha_{\text{dolomite}} - 6\alpha_{\text{gypsum}})}{4} \quad (24)$$

$$\alpha_{\text{CH}_2\text{O}} = \Delta m_{\text{T,C}} - \alpha_{\text{CO}_2\text{gas}} - 2\alpha_{\text{dolomite}} - \alpha_{\text{calcite}} \quad (25)$$

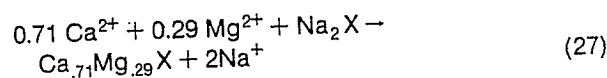
To facilitate the calculations, Equations 6 to 15 were solved using the computer program BALANCE (Parkhurst et al. 1982).

There are only two reported sulfur isotopic analyses of gypsum/anhydrite in the Madison System (Deike, personal communication 1983). The samples are located approximately 100 miles east of the recharge area in northeast Wyoming and are +12.8 and +13.9‰. These values of  $\delta^{34}\text{S}_{\text{gypsum}}$  are considerably lighter than that expected for Mississippian-age marine evaporites (Claypool et al. 1980), and may suggest either a partially terrestrial source of sulfur now found in gypsum of the Madison Limestone or a more complex diagenetic and depositional environment influenced by pyritization, subsequent oxidation, mixing with marine sulfur sources and evaporation. As a consequence,  $\delta^{34}\text{S}_{\text{gypsum}}$  may be variable in the Madison System. In modeling the mass balance reactions,  $\delta^{34}\text{S}_{\text{gypsum}}$  was treated as an adjustable parameter as

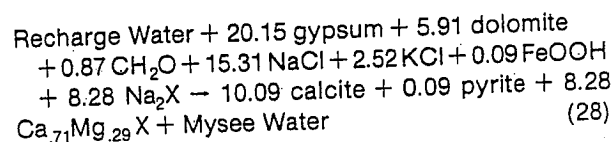
required to define a system closed to  $\text{CO}_2$  gas ( $\alpha_{\text{CO}_2} \equiv \text{gas} \equiv 0$ ). For this condition the solution to Equations 6 through 15 indicates  $\delta^{34}\text{S}_{\text{gypsum}} = 15.5\text{‰} \pm 0.5\text{‰}$ . The solution to Equations 1, 2 and 5 indicates the following net mass transfer reaction between the recharge water and the Mysee Well:



where the reaction coefficients are in mmol per kg  $\text{H}_2\text{O}$  and X denotes an ion exchange site. This is but one of many reactions we could write depending on other possible choices of plausible phases. For example, we might consider the possibility of both calcium and magnesium exchanging for sodium. Assuming that the selectivities of calcium and magnesium for exchange with sodium are approximately equal, the exchange of calcium and magnesium for sodium should be in proportion to the calcium/magnesium ratio in solution. Using the calcium/magnesium ratio at the Mysee Well and resolving the mass balance problem with the exchange reaction



indicates the following net mass transfer reaction:



By considering  $(\text{Ca} + \text{Mg})/\text{Na}$  exchange, the modeled dolomite mass transfer increased by 67 percent and the computed net amount of calcite precipitated increased by 89 percent. Both Models 26 and 28 assume  $\delta^{34}\text{S}_{\text{gypsum}}$  is +15.5‰ corresponding to a nearly zero  $\text{CO}_2$  gas mass transfer ( $\alpha_{\text{CO}_2\text{gas}} = -0.04$ ). If, however,  $\delta^{34}\text{S}_{\text{gypsum}}$  is near 14‰, outgassing of 0.78 mmol of  $\text{CO}_2$  gas per kg  $\text{H}_2\text{O}$  is indicated (independent of nature of ion exchange reaction). No gas separation was evident in the flowing well.

Other uncertainties enter into the mass balance modeling exercises including uncertainties in the analytical data (note that the data of Table 1 indicates a charge imbalance for the Mysee water of 2.8 percent). Uncertainties in the analytical data transfer to the derived mass transfer coefficients. Inspection of Equations 16 to 25 shows how analytical uncertainties are distributed among the mass transfer coefficients. The largest uncertainty is probably in the  $\Delta m_{\text{T,C}}$  term, which affects the  $\text{CO}_2$  gas and  $\text{CH}_2\text{O}$  mass transfers. Although the field pH and alkalinity measurements accurately define  $m_{\text{T,C}}$  in the recharge and Mysee

water, the flow path is not well-defined and large variations in  $m_{T,C}$  of recharge water (as much as 2 mmol/kg  $H_2O$ ) are recognized throughout the Madison Limestone Aquifer. Although the two recharge wells averaged to define the recharge water for the Mysse Well have nearly identical alkalinities (240 and 250 mg/L  $HCO_3^-$ ) (Busby et al. 1983), the question still remains as to whether this water is typical of those along the true flow path to the Mysse Well. Unfortunately, no other potential recharge wells are close enough to resolve this uncertainty.

There is no indication of the source of the 2.8 percent charge imbalance for the Mysse water. This value is atypical of most analyses of Madison water (Busby et al. 1983), which have charge imbalances of less than 1 percent. If all the charge imbalances were attributed to the sodium analysis, for example, the ion-exchange mass transfer would be decreased from 8.3 to 6.5 mmol/kg  $H_2O$ . Equation 23 shows that this decrease in ion exchange corresponds to an increase of 1.8 mmol in the amount of calcite precipitated and similar changes in the  $CO_2$  gas and  $CH_2O$  mass transfers.

A check on the reliability of the mass transfer models of Equations 26 and 28 is provided by a calculation of the carbon isotopic composition of water at the Mysse Well. The  $\delta^{13}C$  at the Mysse Well was calculated beginning with that measured for the average recharge water (Table 1) and Raleigh distillation equations of Wigley et al. (1978, 1979). A detailed example of these calculations is given in Plummer et al. (1983). Using -25‰ for  $\delta^{13}C$  of organic matter, Equation 26 predicts the observed  $\delta^{13}C$  at the Mysse Well if  $\delta^{13}C$  of reactant dolomite is near  $3.8 \pm 0.1$ ‰. A similar calculation for  $^{14}C$  leads to a corrected  $^{14}C$  age of 22,600 years. When the possibility of both Ca and Mg ion exchange for Na is considered (Equation 28),  $\delta^{13}C$  of the Mysse Well is predicted if  $\delta^{13}C$  of reacting dolomite is near 2.0‰, corresponding to a corrected  $^{14}C$  age of 15,400 years. Using the model of Equation 28, it was found that an uncertainty of  $\pm 5$ ‰ in  $\delta^{13}C$   $CH_2O$  corresponds to an uncertainty in the predicted  $^{13}C$  at the Mysse Well of  $\pm 0.3$ ‰. An uncertainty of  $\pm 2.0$ ‰ in  $\delta^{13}C$  of dolomite leads to  $\pm 1.7$ ‰ in the predicted  $\delta^{13}C$  of the Mysse Well. An average of six  $\delta^{13}C$  analyses of dolomites from the Madison Limestone Aquifer averages  $1.8 \pm 1.5$ ‰ (Deike, personal communication). Considering this range of  $^{13}C$  uncertainties, both reaction Models 26 and 28 are acceptable even though only the results of Model 28 agree with the median of the  $\delta^{13}C$  data from Madison dolomites.

As required by mass balance modeling, both Models 26 and 28 exactly account for the change in mass between the initial and final water. This condition holds for any other choices of plausible phase we might choose to solve via the inverse problem. Thus, if treated as a forward problem beginning with the initial water, the mass balance model should precisely predict the observed final water composition. In actual practice, though, other criteria must be considered in treating a mass balance problem as a forward problem. First, since we are dealing with real water analyses, it

must be recognized that the initial and final water probably do not balance perfectly in charge. The modeler has the choice of either adjusting the totals on the initial and final water to achieve charge balance and then resolving the mass balance problem prior to forward simulation, or including the  $\Delta$  charge imbalance (final minus initial) as a "reactant" in the forward simulation. One final point in forward simulation of mass balance models concerns use of equilibrium conditions to determine mass transfer in partial equilibrium systems. As mentioned earlier, few natural waters are in equilibrium. If, for example, the final water is oversaturated with a mineral shown to be a product in the mass balance model, forward problem simulation will not predict the observed final water unless the simulation utilizes the observed oversaturation in defining the phase boundary.

Modeling of the Mysse Well (and many other of the higher temperature Madison waters) poses an additional problem because the speciation calculation shows it to be significantly oversaturated with dolomite (Figure 3, Table 1), under conditions of the dedolomitization reaction, which requires dissolution of dolomite. In this case the problem is probably due to faulty thermodynamic data for the dolomite equilibrium constant at higher temperatures as discussed by Busby et al. (unpublished).

Assuming we have selected water on a flow path unaffected by mixing or dispersive effects and have chosen the correct reactant and product stoichiometry, the inverse problem has defined the net mass transfer between the initial and final wells that exactly accounts for the changes in chemical and isotopic composition. The net mass transfer between the recharge water and Mysse Well is probably similar to that of Equations 26 and 28 but will vary somewhat with changes in mineral stoichiometry, other possible choices of plausible phases (such as associated with clay diagenetic reactions, methanogenesis, etc.) and possible corrections for charge imbalance. The predominant reaction (dedolomitization) is not likely to vary outside of the range shown in Equations 26 and 28. Having solved for the net mass transfer and corrected  $^{14}C$  ages, the inverse problem leads to an independent estimate of flow velocity and reaction rate. The flow velocity may be used to check the hydrologic model. Although we have applied the inverse modeling to a regional flow system of assumed negligible dispersive effects, mass transfer coefficients derived by the inverse problem, in general, combine effects of both reaction and fluid flow and are, in one sense, results of a combined reaction-flow model.

### The Forward Problem

In modeling the chemical evolution of the Madison water via the forward problem, it is assumed that we have very limited knowledge of the chemistry of the ground water system. The goal of this exercise is to see how closely we can predict the known composition of Madison water via the forward problem from (1)

knowledge of the starting recharge water composition (Table 1), (2) pertinent mineralogy, (3) reasonable estimates of relative rates of reactions, and (4) expected temperature variation.

From the work of Busby et al. (1983) and Back et al. (1983) we expect temperatures to reach at least 80 C and we expect the dedolomitization reaction (dolomite dissolution accompanying calcite precipitation driven irreversibly by dissolution of gypsum/anhydrite) to predominate. The dissolution of dolomite and precipitation of calcite are assumed to follow apparent equi-

librium as gypsum dissolves. For modeling purposes, we will assume that during sulfate reduction, apparent equilibrium is maintained among FeOOH and pyrite. This, then, defines a partial equilibrium system where equilibrium is maintained for all aqueous speciation reactions and apparent equilibrium is maintained for calcite, dolomite, pyrite and FeOOH. The modeling includes the possibility of four simultaneous irreversible reactions: (1) temperature variation from (starting temperature) to 80 C, (2) gypsum/anhydrite dissolution, (3) sulfate reduction via organic matter oxidation,

**Table 1**  
**Average Composition of Recharge Water\* and Selected Well (Mysee)\*\***

Constituent	Recharge Water			Mysee Well	
	mg/l	mmol/kg H <sub>2</sub> O	mmol/kg H <sub>2</sub> O***	mg/l	mmol/kg H <sub>2</sub> O
Calcium	48.0	1.20	1.01	450.	11.28
Magnesium	24.5	1.01	1.27	110.	4.54
Sodium	0.5	0.02	0.02	730.	31.89
Potassium	0.85	0.02	0.02	99.	2.54
Iron	0.06	0.001	0.001	0.02	.0004
Chloride	0.6	0.02	0.02	630.	17.85
Sulfate	15.0	0.16	0.16	1900.	19.86
Alkalinity	245.	—	—	320.	—
Total inorganic carbon	—	4.30	4.37	—	6.87****
Redox state	—	18.14	—	—	146.13
H <sub>2</sub> S	—	—	—	8.8	.259
Tritium (TU)	27.6	—	27.6	—	—
$\delta^{34}\text{S}_{\text{SO}_4^{2-}}$ (‰)	9.73	—	9.73	16.30	16.30
$\delta^{34}\text{S}_{\text{H}_2\text{S}}$ (‰)	—	—	—	-22.09	-22.09
$\delta^{13}\text{C}$ (‰)	-6.99	—	-6.99	-2.34	-2.34
$^{14}\text{C}$ (‰)	33.1	—	33.1	0.8	0.8
T°C	9.9	—	9.9	63.	63.
pH	7.55	—	7.67	6.61	6.61
SI calcite	- .05	—	0.0	—	.29
SI dolomite	- .27	—	0.0	—	.51
SI gypsum	- 2.47	—	- 2.55	—	.15
log P <sub>CO2</sub>	- 2.26	—	- 2.36	—	.94
Charge balance (meq/kg H <sub>2</sub> O)	—	0.11	0.11	—	3.38

\*Flow path 3 of Busby et al. (unpub.). Average of Mock Ranch, Wyo. 1 and Denius #1, Wyo. 2 of Busby et al. (1983).

\*\*Flow path 3 of Busby et al. (unpub.).

\*\*\*Adjusted for equilibrium with calcite and dolomite as starting water for modeling via forward problem, maintaining initial charge imbalance as inert charge.

\*\*\*\*Calculated from alkalinity adjusted for non-carbonate alkalinity.

and (4) sodium-calcium ion exchange. Because there is more than one irreversible reaction, an unlimited number of reaction paths, water compositions and mass transfers could be calculated.

In order to examine the various effects contributed by the four irreversible reactions, the forward problem was evaluated using PHREEQE (Parkhurst et al. 1980) in seven separate models of increasing number of irreversible reactions. Each model begins at the selected recharge water composition (Table 1). As all reaction paths follow calcite-dolomite equilibrium, the first step, before any irreversible reaction was initiated, was to recompute the composition of the recharge water to define equilibrium with calcite and dolomite in a closed system. This initial step caused dissolution of 0.26 mmol of dolomite and precipitation of 0.45 mmol of calcite at the initial temperature of 9.9 C. The adjusted starting point is shown in Table 1. Choice of initial estimates of relative rates of irreversible reaction for the Madison System have been guided by the previous inverse modeling to the Mysse Well.

In the first model only the temperature variation was considered while maintaining the adjusted recharge water in equilibrium with calcite and dolomite between 9.9 and 80 C. Figure 8 shows calculated variations in calcium, magnesium and total carbon concentrations along with predicted values of pH and  $\log P_{CO_2}$  as the starting water is heated to 80 C maintaining calcite and dolomite equilibrium. The temperature path causes net dissolution of calcite and precipitation of dolomite, which is opposite that expected for the dedolomitization reaction (Back et al. 1983). The predicted mass transfer is small, near 0.9 mmol of calcite dissolved and 0.6 mmol of dolomite precipitated per kg  $H_2O$  at 60 C. The predicted decrease in pH and total carbon, and increase in  $\log P_{CO_2}$  is not unlike that found in the Madison System, using the Mysse Well (Table 1) as an example, though computed calcium, magnesium and sulfate concentrations are far from the observed.

Model 2 adds gypsum dissolution to Model 1 for three paths of assumed constant relative rates of gypsum dissolution to change in temperature (Figure 9). Path A of Figure 9 corresponds to the net gypsum mass transfer to the Mysse Well (temperature ~63 C) as previously determined via the inverse problem. Paths B and C assume realistic variations from this net path: path B representing 1.5 times more gypsum dissolution at 63 C than path A, and path C corresponding to 0.5 that of path A at 63 C. Paths A to C assume that the relative rates of gypsum dissolution are independent of temperature. Two additional gypsum/temperature paths considered in Model 2 (D and E) are shown in Figure 10. Paths D and E have the identical net gypsum mass transfer at 63 C as does path A, but the gypsum mass transfer to temperature variation is not constant as temperature varies.

Model 2 treats the dedolomitization reaction with simultaneous increasing temperature. Unlike Model 1 where only one reaction path was possible, an infinite number of relative rates of gypsum dissolution to

temperature change are possible in Model 2. Figure 11 shows predicted trends and ranges of values for  $SI_{gypsum}$ ,  $Ca_T$ ,  $Mg_T$ ,  $C_T$ , pH and  $\log P_{CO_2}$  along paths A to E (Figures 9 and 10). The predicted trends in  $SI_{gypsum}$ ,  $Ca_T$ ,  $Mg_T$ , pH and  $\log P_{CO_2}$  are similar to those observed along the flow path to the Mysse Well (Table 1) but the predicted decrease in  $C_T$  is opposite that observed at the Mysse Well. A large range of values for  $SI_{gypsum}$ ,  $Ca_T$ , and  $Mg_T$  is possible between the five reaction paths shown. Variations in  $C_T$ , pH and  $\log P_{CO_2}$  are less sensitive to uncertainty in reaction path.

Model 3 adds sulfate-reduction to the dedolomitization reaction of Model 2. Sulfate reduction is accomplished by the irreversible introduction of carbon of valence zero (organic matter) to the solution. Model 3 treats three simultaneous irreversible reactions (processes): (1) increase in temperature to 80 C, (2) dissolution of gypsum/anhydrite, and (3) oxidation of organic matter via sulfate reduction. Two relative rates of organic matter oxidation to temperature change were considered (Figure 12). Path A (Figure 12) corresponds to the net amount of organic matter oxidized along the flow path to the Mysse Well at 63 C, as determined by the inverse problem (Equation 26) and path B represents a three-fold increase in organic matter oxidation at 63 C, over that of path A. Taking into account the three gypsum dissolution/temperature paths of Model 2, a total of four reaction paths were treated in Model 3: (1) following path A (Figure 12) along paths A and B of Figure 9, and (2) following path B (Figure 12) along paths A and B of Figure 9.

**Note:** The nomenclature used to identify reac-

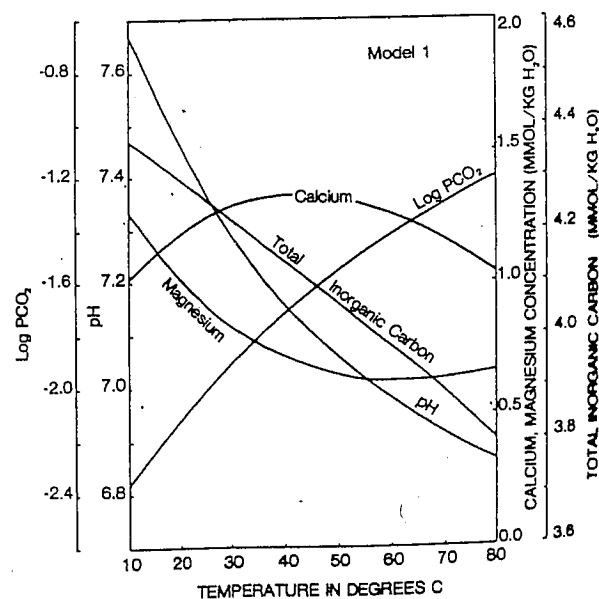


Figure 8. Variation in fluid  $P_{CO_2}$ , pH, dissolved calcium, magnesium and carbon during forward simulation (Model 1) of heating Madison Limestone recharge water maintaining equilibrium with calcite and dolomite.

tion paths is as follows:

1. Single letters A, B, C, D and E refer to paths of Model 2 as shown on Figures 9 and 10
2. Paths of Model 3 use double letters, the first letter corresponding to the path of Model 2 and the second to that of Model 3.

For example, path AB defines a reaction path of Model 3, which follows simultaneously the gypsum/temperature path A of Model 2 (Figure 9) and the organic matter/temperature path B of Model 3 (Figure 12). Triple letter codes are similar but refer to Model 4. Table 2 summarizes the models, paths and relative rates of reaction used.

Figure 13 shows predicted values of  $\text{Ca}_T$ ,  $\text{Mg}_T$ ,  $\text{C}_T$ , pH and  $\log P_{\text{CO}_2}$  along paths A, AA, AB and B, BA, BB for simultaneous dedolomitization and sulfate reduction/reactions. Computed values of  $\text{Ca}_T$ ,  $\text{Mg}_T$ , pH and  $\log P_{\text{CO}_2}$  are not significantly affected by variations in the extent of sulfate reduction over the range of zero to as much as 2.4 mmol of  $\text{CH}_2\text{O}$  oxidized per kg  $\text{H}_2\text{O}$  (path BB at 60 C). For these the results are similar to those obtained for Model 2 (paths A and B). The extent of sulfate reduction has a significant effect, however, on the total inorganic carbon content (Figure 13) and can even reverse the trend in  $\text{C}_T$  with reaction progress. For example, without sulfate reduction, there is a decrease in  $\text{C}_T$  with increasing temperature (path A) while following path AB, we find a significant increase in dissolved inorganic carbon with increasing temperature (Figure 13). This is potentially a useful guide in separating Madison water influenced significantly by sulfate reduction from those of minimal sulfate reduction.

With Model 4 the possibility of Ca-Na ion exchange was added along path AA (only) of Model 3. Two relative rates of ion exchange mass transfer were considered (Figure 14). The first path (AAA) assumes 8.28 mmol of  $\text{Ca}^{2+}$  are exchanged (irreversibly) for 16.56 mmol of  $\text{Na}^+$  per kg  $\text{H}_2\text{O}$ . As before, this starting mass transfer estimate was derived from the inverse modeling to the Mysse Well (Equation 26). The second path of Model 4 (AAB) doubles the amount of ion exchange used in path AAA.

Figure 15 shows that there are large variations in  $\text{C}_T$ , pH and especially  $\text{Ca}_T$  and  $\text{Mg}_T$  concentrations with extent of calcium-sodium ion exchange when added to simultaneous dedolomitization and sulfate reduction. The ion exchange reaction was followed only along path AA of Model 3, which is based on the mass balance estimates of mass transfer to the Mysse Well. Path AA includes the net mass balance mass transfers of  $\text{CaSO}_4$  dissolution, organic matter oxidation and ion exchange as defined by Equation 26 along with simultaneous equilibria with calcite and dolomite. The implied calcite mass transfer for selected reaction paths are summarized in Figure 16.

It is evident that through all the reaction paths considered, including those based of the net mass transfer derived from the inverse problem, none pre-

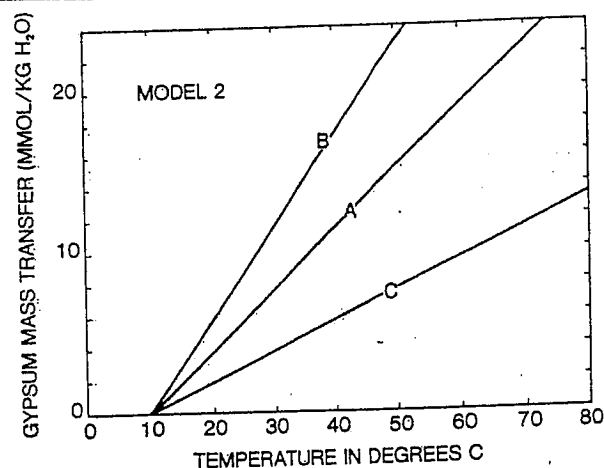


Figure 9. Three constant relative rates of gypsum (anhydrite) dissolution to temperature change used to model paths A-C of Model 2. Path A corresponds to the net  $\text{CaSO}_4$  mass transfer to the Mysse Well as determined by the inverse method.

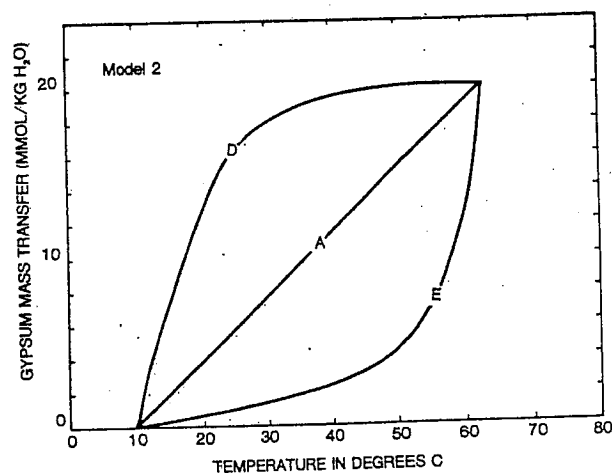


Figure 10. Definition of two non-linear relative rates (Paths D and E) of gypsum (anhydrite) dissolution to temperature variation of Model 2. Paths A, E and D have identical  $\text{CaSO}_4$  mass transfers at 63 C, corresponding to the net  $\text{CaSO}_4$  mass transfer to the Mysse Well obtained via the inverse method at the Mysse Well temperature (63 C).

cisely predicts the observed water composition at the Mysse Well. We then ask what additional modeling criteria need to be considered in order to predict the observed water composition of the Mysse Well. In modeling the reaction path to the Mysse Well several other properties of the Mysse water were not considered. These are (1) apparent oversaturation with calcite and dolomite rather than the modeled equilibrium condition; (2) dissolution of halite and sylvite, and (3) provision for charge imbalance in the Mysse water.

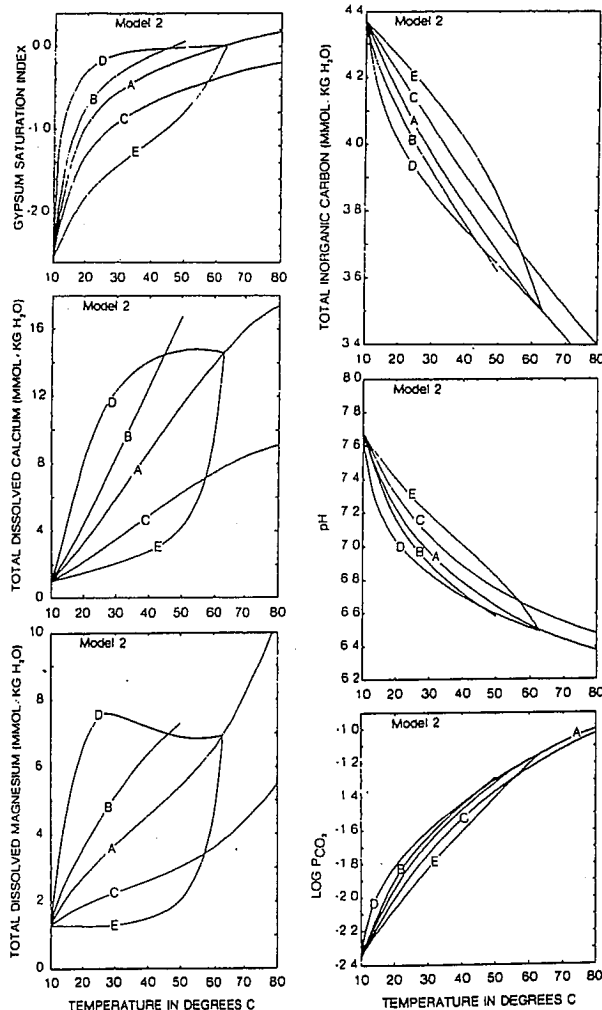


Figure 11. Predicted variation in gypsum saturation index, total dissolved calcium, magnesium, inorganic carbon, pH and  $\log P_{CO_2}$  as a function of temperature during forward simulation along the  $CaSO_4$ -temperature reaction Paths A-E of Model 2 (Figures 9 and 10), as a function of temperature. All water is in equilibrium with calcite and dolomite.

Table 3 summarizes modeling results at 63 C along the net path to the Mysse Well for Models 1 to 4 as discussed above, along with the three additional criteria to be considered. The uncertainty in the calcite and dolomite saturation indices changes the calcite and dolomite mass transfers by 0.9 and 0.3 mmol, respectively (Model 4 to Model 5, Table 3). Inclusion of NaCl and KCl dissolution has no meaningful effect on the modeled  $Ca_T$ ,  $Mg_T$ ,  $C_T$ , pH values or mass transfer (Model 5 to 6, Table 3). By inclusion of the charge imbalance at the Mysse Well, the modeled water composition agrees closely with the observed. The minor differences between the observed and Model 7 (Table 3) are due to round off errors in relative rates of reaction and saturation indices.

Note that when we solve a particular mass balance model via the inverse method, no adjustment is made

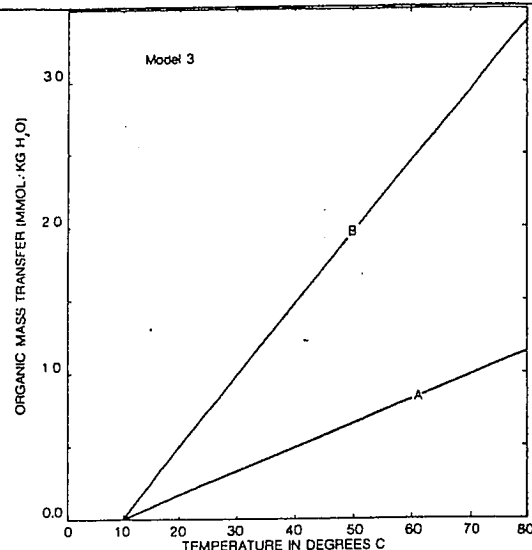


Figure 12. Definition of selected relative rates of organic matter oxidation to temperature change used in Model 3 forward simulations. Path A corresponds to the inverse model result at the Mysse Well (63 C) and Path B represents a three-fold increase in organic matter mass transfer at 63 C.

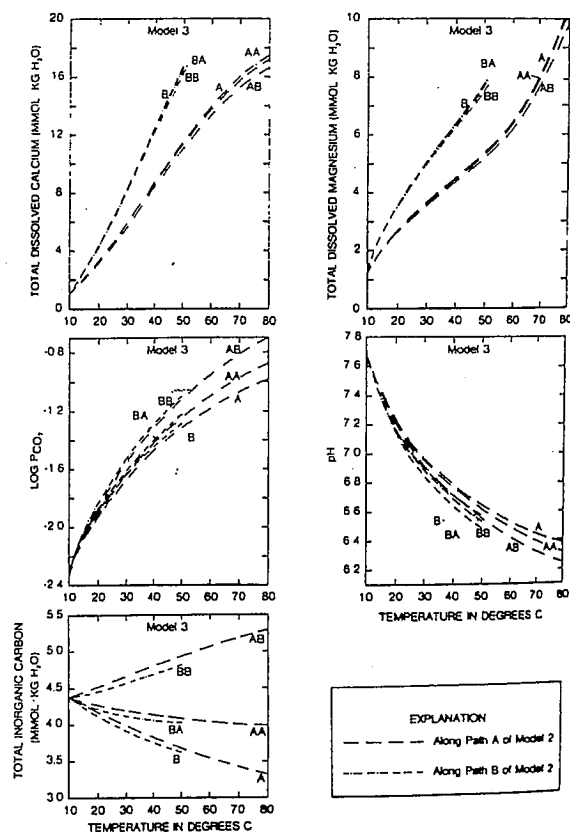


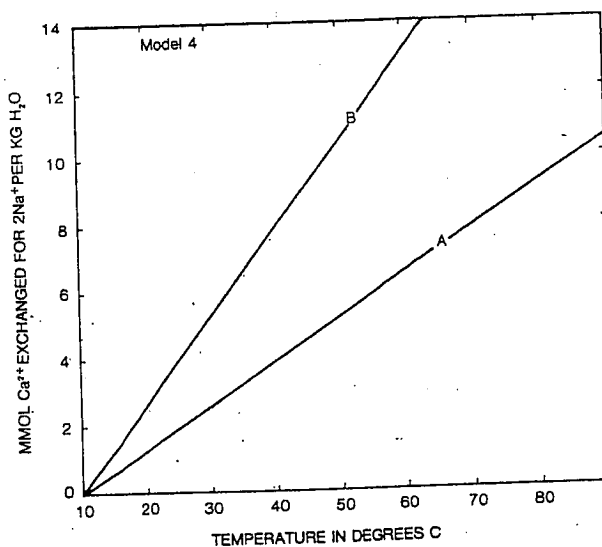
Figure 13. Predicted Model 3 variation in total dissolved calcium, magnesium, inorganic carbon, pH and  $\log P_{CO_2}$  along Paths A and B of Model 2. Path AB corresponds, for example, to simultaneous irreversible  $CaSO_4 \cdot CH_2O$  temperature variation along Path A of Model 2 (Figure 9) and Path B of Model 3 (Figure 12). All water is in equilibrium with calcite, dolomite, pyrite and geothite.

**Table 2**  
**Summary of Reaction Paths and Relative Rates of Reaction Modeled**

Model	Path	Temperature Range °C	$\frac{d(\text{Gypsum})}{d(\text{Temp.})}$	$\frac{d \text{CH}_2\text{O}}{d \text{Temp}}$	$\frac{d(\text{Ca Exch.})}{d(\text{Temp.})}$	Comment
1	—	0 - 80	0	0	0	
2	A	0 - 80	0.38	0	0	
2	B	0 - 60	0.56	0	0	Oversaturated with gypsum at temp > ~ 50 C
2	C	0 - 80	0.19	0	0	
2	D	0 - 63	1.67-0.004	0	0	Variable relative rate of gypsum dissolution
2	E	0 - 63	0.06-2.88	0	0	Variable relative rate of gypsum dissolution
3	AA	0 - 80	0.38	0.016	0	
3	AB	0 - 80	0.38	0.049	0	
3	BA	0 - 80	0.56	-0.016	0	
3	BB	0 - 80	0.56	0.049	0	
4	AAA	0 - 80	0.38	0.016	0.156	
4	AAB	0 - 80	0.38	0.016	0.312	
5	AAA	0 - 80	0.38	0.016	0.312	Model 4 AAA with SI calcite and SI dolomite at 0.29 and 0.51, respect.
6	AAA	0 - 80	0.38	0.016	0.312	Model 5 plus 15.31 mmol NaCl plus 2.52 mmol KCl at 63 C.
7	AAA	0 - 80	0.38	0.016	0.312	Model 6 plus 3.38 meq/kgH <sub>2</sub> O $\Delta$ charge imbalance.

for the fact that the raw chemical analyses may not balance perfectly in charge, or that a particular element, important in accounting for charge balance in the water may not have been included in the mass balance problem. Because we are computing the net mass transfers of charge balanced minerals, the charge imbalance of the initial and final water is distributed among the calculated mineral transfers. If the initial and final water balance perfectly in charge for those elements included in the mass balance problem, there will be no charge error translated to the mass transfer coefficients, and in the case of Mysse Well; had there been no charge error, the results of Models 5 and 6 (Table 3) would match the observed.

Without reason to suspect any of the analytics, it is difficult to define a strategy for accounting for the charge imbalance when solving the inverse problem. Several possibilities can be suggested such as attributing the total charge error to a single element, or distributing the error in proportion to the measured concentrations, or in proportion to the uncertainties in the analytical procedures. None of these procedures are judged satisfactory. The most reasonable approach



*Figure 14. Definition of selected relative rates of Ca<sup>2+</sup>-Na<sup>+</sup> ion exchange for Model 4 forward simulation. Path A corresponds to the net ion exchange mass transfer computed by the inverse method in the Mysse Well. Path B doubles the ion exchange mass transfer of Path A.*



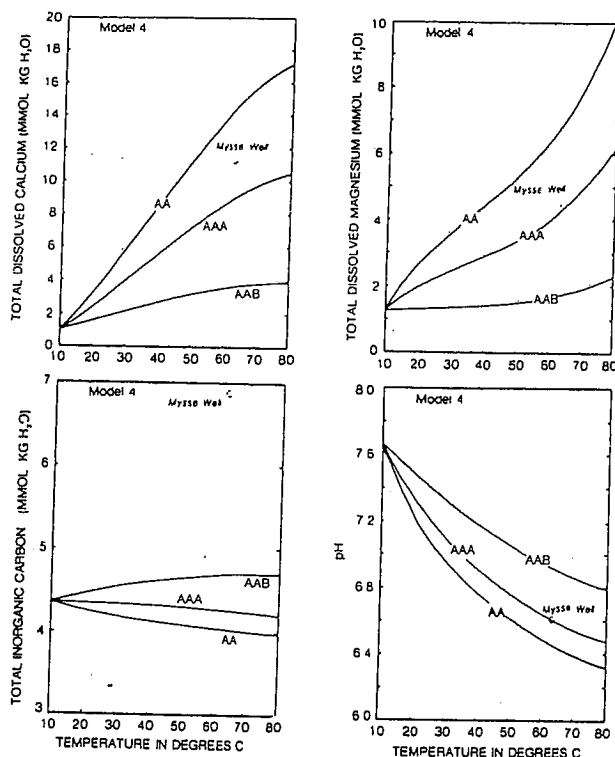


Figure 15. Predicted Model 4 variation in total dissolved calcium, magnesium, inorganic carbon and pH as a function of irreversible exchange of  $\text{Ca}^{2+}$  for  $2\text{Na}^+$ . Path AA is the Model 3 result (Figure 13) for no ion exchange. Path AAA follows Path A of Models 2, 3 and 4 and Path AAB follows Path A of Models 2 and 3, and Path B of Model 4. If all reactions were accounted for, Path AAA would pass through the corresponding value for the Mysee Well.

is to work with reliable analytical data, i.e., water that at least balances closely in charge. But accepting these uncertainties, it is better to leave the analytical data unadjusted and simply recognize that charge imbalances will be distributed among the computed mass transfer coefficients. The possible magnitude of uncertainties can be estimated by performing a sensitivity analysis via the inverse problem with variously adjusted (charged balanced) water. Of the Madison Limestone water studied by Busby et al. (1984), the Mysee Well analysis has the poorest charge imbalance (2.8 percent) compared to an average of about 0.9 percent for all other water of similar total dissolved solids.

In the forward simulation of the mass balance model, the results of Table 3 show the importance of accounting for charge imbalance of the initial and final water. In the modeling of Table 3, the charge imbalance was accounted for by the following procedure in computing the result for Model 7: (1) the charge imbalance of the initial recharge water (0.11 meq/kg) was retained as "inert charge" using an option available in PHREEQE. The change in charge balance

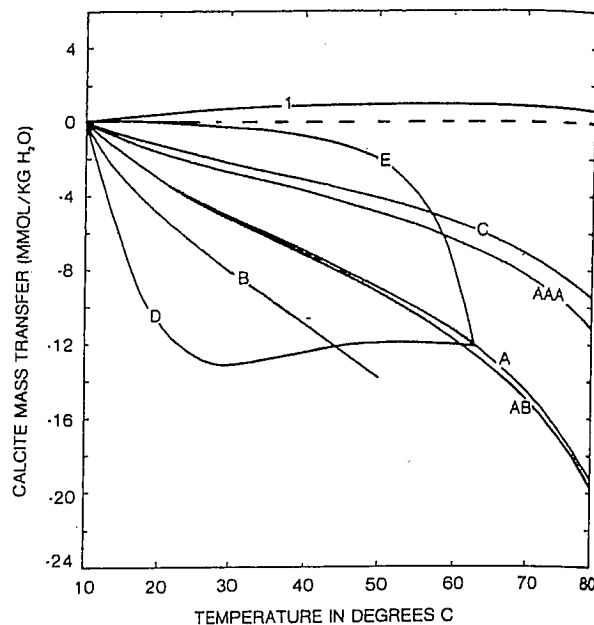


Figure 16. Summary of calcite mass transfer for Model 1, Model 2 (Paths A to E), Model 3 Path AB and Model 4 Path AAA. Starting point is at calcite-dolomite equilibrium (Model 0 of Table 3).

(final minus initial) is  $3.38 - 0.11 = 3.27$  meq/kg  $\text{H}_2\text{O}$  (Table 1). In forward simulation, the change in charge imbalance was added as an irreversible reaction adding 3.27 meq/kg  $\text{H}_2\text{O}$  of "inert charge" to the recharge water. In PHREEQE the inert charge is added to the charge balance condition, which then, of course, affects the computed pH, solution composition, mass transfer, etc. Having accounted for the chemical mass transfer and charge imbalance, the final modeled water (Model 7) possesses all the properties of the original analytical data.

Clearly then, considerable effort is involved in applying a forward simulation to a mass balance model in order to match the known composition of the final water. There are several advantages to be gained, however, from correct application of the forward problem to inverse model results. These include a prediction of reaction path behavior, and thus a prediction of water composition at points intermediate to the initial and final wells, and, in general, an appreciation for trends in water composition that might be expected elsewhere in the system. Forward simulations also allow checks on the thermodynamic validity of net mass balance models. Note, for example, that path B of Model 2 (Figure 11) is thermodynamically invalid beyond about 50 °C where the modeled water becomes oversaturated with the reactant gypsum.

In contrast to the inverse problem, which defined single values for the net mass transfer in a given reaction model, the forward problem is successful in predicting only trends in water quality parameters and ranges of values to be expected for a given range of

**Table 3**  
**Summary of Forward Modeling Results to the Mysse Well**

Summary of Forward Modeling Results								
Results at 63 C								
Model	Path	Solution Composition mmol/kgH <sub>2</sub> O				Net* Mass Transfer mmol/kgH <sub>2</sub> O		Process and reaction per kgH <sub>2</sub> O
		Ca <sub>T</sub>	Mg <sub>T</sub>	C <sub>T</sub>	pH	Calcite	Dolomite	
0	—	1.00	1.26	4.35	7.67	- 0.45	0.25	Equilibrate recharge water with calcite and dolomite at 9.9 C
1	—	1.24	0.62	3.95	6.95	0.42	-0.39	Heat calcite-dolomite equilibria to 63 C
2	A	14.62	6.95	3.50	6.50	-12.67	5.93	Step 1 + 20.15 mmol CaSO <sub>4</sub>
3	AA	14.38	6.84	4.03	6.46	-12.80	5.83	Step 2 + 0.87 mmol CH <sub>2</sub> O
4	AAA	8.94	4.23	4.26	6.61	- 7.36	3.22	Step 3 + 8.28 mmol Ca/Na Exch.
5	AAA	9.60	3.87	4.55	6.80	- 6.51	2.89	Step 4 + changes to SI <sub>C</sub> = .288, SI <sub>D</sub> = .506
6	AAA	9.62	3.88	4.58	6.81	- 6.51	2.90	Step 5 + 15.31 mmol NaCl, + 2.52 mmol KCl
7	AAA**	11.26	4.54	6.89	6.61	- 5.35	3.53	Step 6 + 3.27 meq charge imbalance
Observed		11.28	4.54	6.87	6.61	- 5.33***	3.54***	at the starting point

\*Net mass transfer from the initial recharge water unadjusted for calcite-dolomite equilibrium at the starting point. All final water is at calcite-dolomite equilibrium or as specified. Mass transfer is negative for precipitation, positive for dissolution.

\*\*Differences between Model 7 and observed are due to round off in relative rates of reactions used in simulating the forward problem.

\*\*\*Calc. via inverse method.

possible relative rates of reactions. Unlike the inverse problem, the forward simulation is sensitive to the reliability of the thermodynamic data used to follow phase boundaries. Because the forward simulation considered here was based on initial estimates of relative rates of reaction derived from the inverse problem, we might have some expectation of closely modeling reality. Table 4 shows that the predicted range of calcium, magnesium and total carbon concentrations along with pH and log P<sub>CO2</sub> is reasonably matched by the range of these parameters measured in some 60 Madison Limestone water samples. Although the ranges of values match relatively well, no particular modeled water composition agrees entirely with any observed Madison water. This is a result of the limited number of relative rates of reactions considered and an indication of a large variation in the relative rates of reaction in the actual ground water system.

### Conclusion

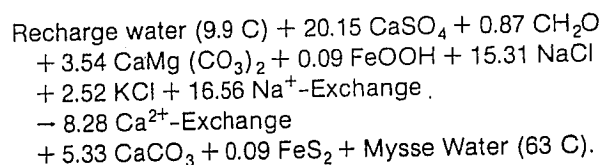
There are advantages and disadvantages to both forward and inverse modeling methods. Generally, as

more chemical, isotopic, mineralogic and hydrologic data became available for a ground water system, most of the reaction information will be gained via the inverse problem. Inverse modeling results, however, are not constrained by thermodynamics, and uncertainties in analytical data are transferred to the computed net mass transfer coefficients. If treated as a forward problem, the inverse modeling results will predict exactly the final water composition and provide a means of estimating water composition along flow lines intermediate to wells of known composition. The inverse modeling results define only the net mass transfer between the initial and final points. Caution must be exercised in discerning the true reaction path from the net path. Furthermore, the inverse modeling requires prior hydrologic information in defining initial and final water on the same flow path.

The forward problem is generally best suited for cases of limited chemical and mineralogic data. Modeled results depend significantly on use of reliable thermodynamic data and detailed knowledge of the relative rates of all quantitatively significant irreversible

reactions. In the modeling example considered here, the forward model was successful in predicting trends and observed ranges of Madison Limestone water compositions. But even though very realistic estimates of relative rates of reactions, derived from inverse modeling were used, there was no close match in computed and observed water composition for any particular well. Much larger uncertainties in forward modeling results could be expected without prior knowledge of reasonable estimates of relative rates of reaction.

Along an average flow path some 130 miles into east-central Montana, inverse modeling to the Mysse Well indicates that the net reaction in the Madison Limestone Aquifer is similar to



Inclusion of the possibility of both calcium and magnesium exchange for sodium significantly alters the dolomite and calcite mass transfers and leads to corrected  $^{14}\text{C}$  ages of 22,600 years (no Mg ion exchange) to 15,400 years (considering both Ca and Mg ion exchange for sodium). Both ion exchange models are consistent with the observed  $^{13}\text{C}$  data. Reasonable estimates of rates of reactions (mmol/kg  $\text{H}_2\text{O}/\text{year}$ ) and flow velocities may be computed using the corrected  $^{14}\text{C}$  ages.

The correspondence of the wide range of water compositions predicted via the forward problem with the observed range in water composition helps to confirm a large variation in relative rates of reactions

for the Madison System, presumably in response to regional variations in mineral abundance.

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Table 4  
Comparison of Range of Madison Water Composition Modeled  
(Models 1 to 4)

Parameter	40 C		60 C		80 C		63 C	Observed* range for Madison water	
	Min.	Max.	Min.	Max.	Min.	Max.	Mysse Well Obs.		
mmol $\text{Ca}_T$	2.8	14.1	7.5	19.9	9.1	17.4	11.3	1.2	13.8
mmol $\text{Mg}_T$	0.7	7.2	0.6	9.2	0.7	10.4	4.5	0.9	5.0
mmol $\text{C}_T$	3.8	4.8	3.5	5.1	3.3	5.3	6.9	1.9	6.9
pH	6.6	7.2	6.4	7.0	6.2	6.9	6.6	6.4	7.6
log $\text{P}_{\text{CO}_2}$	-1.7	-1.3	-1.4	-1.0	-1.2	-0.7	-0.9	-2.6	-0.7
$\alpha_{\text{calcite}}$	-12.5	+0.9	-17.4	+0.9	-19.7	+0.6	-5.3**	-0.2***	-22.5***

\*From Busby et al. (1983)

\*\*Equation 26

\*\*\*From Busby et al. (unpub.)

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