

Development of reaction models for ground-water systems

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Abstract—Methods are described for developing geochemical reaction models from the observed chemical compositions of ground water along a hydrologic flow path. The roles of thermodynamic speciation programs, mass balance calculations, and reaction-path simulations in developing and testing reaction models are contrasted. Electron transfer is included in the mass balance equations to properly account for redox reactions in ground water. The mass balance calculations determine net mass transfer models which must be checked against the thermodynamic calculations of speciation and reaction-path programs. Although reaction-path simulations of ground-water chemistry are thermodynamically valid, they must be checked against the net mass transfer defined by the mass balance calculations. An example is given testing multiple reaction hypotheses along a flow path in the Floridan aquifer where several reaction models are eliminated. Use of carbon and sulfur isotopic data with mass balance calculations indicates a net reaction of incongruent dissolution of dolomite (dolomite dissolution with calcite precipitation) driven irreversibly by gypsum dissolution, accompanied by minor sulfate reduction, ferric hydroxide dissolution, and pyrite precipitation in central Florida. Along the flow path, the aquifer appears to be open to CO_2 initially, and open to organic carbon at more distant points down gradient.

NOTATION

a_i	Activity of the i^{th} aqueous species.
A	Measured ^{14}C activity in percent modern.
A_{nd}	Calculated ^{14}C activity in the final water corrected for reaction effects but ignoring radioactive decay.
$b_{p,k}$	Stoichiometric coefficient of the k^{th} element in the p^{th} mineral or gas.
E	Total number of linearly independent equations in a mass balance problem.
f_{ps}	Isotope fractionation between a mineral (p) and solution (s).
G	Gibbs free energy.
I	Number of aqueous species.
IAP	Ion activity product for a mineral in solution.
dI_p	Incremental input of carbon from the p^{th} mineral.
J	Number of elements required to define the stoichiometry of the P plausible phases in a mass balance calculation.
K	Equilibrium constant.
m_i	Molality of the i^{th} aqueous species.
$m_{T,k}$	Total molality of the k^{th} element.
mC	Total molality of inorganic carbon in solution.
mC_0	Total molality of inorganic carbon in the initial solution.
$\Delta m_{T,k}$	Difference in total molality of the k^{th} element between an initial and final ground water.
n	Total number of moles.
N	Total number of subsets of the plausible phases.
dO	Incremental output of carbon from a precipitating mineral.
P	Total number of plausible phases in a particular calculation. A plausible phase is defined as an independent stoichiometry of elements. For example the polymorphs calcite, aragonite, and vaterite, although differing crystallographically, would count as one mineral of stoichiometry CaCO_3 .
P_{CO_2}	Partial pressure of CO_2 gas in atm.
R	Isotope ratio $m^{13}\text{C}/m^{12}\text{C}$ generally applied to the solution as a whole. With T , R refers to the gas constant.
RS	The redox state of an initial or final solution. (Eqn. 2)

ΔRS Difference in redox state (RS) between initial and final ground water.

$$\sum_{i=1}^I v_i m_i(\text{final}) - \sum_{i=1}^I v_i m_i(\text{initial}).$$

SI	Saturation index of a mineral in solution. (Eqn. 1)
T	Temperature in kelvins.
x_i	The proportion of the i^{th} net mass balance model contributing to the overall reaction in a system of excess plausible phases. (Eqn. A1.2)
u_p	Sum of the operational valences of the constituents in the p^{th} plausible phase. (Table A1.1)
v_i	Operational valence of the i^{th} aqueous species. (Table A1.1)
α_p	Stoichiometric coefficient in the p^{th} plausible phase in a mass balance calculation.
β	Parameter defined by eqn. A3.5.
Γ_p	Rate of p^{th} carbon input relative to a reference output, dI_p/dO . (Eqn. A3.3)
Γ^T	Total carbon input relative to a reference output. (Eqn. A3.3)
δ	Prefix denoting δ -value (in per mil, ‰) of ^{13}C or ^{34}S concentration relative to a standard.
$\delta^{13}\text{C}^*$	Average ^{13}C content of incoming carbon from multiple sources (see Eqn. A3.4)
Δ	Prefix to define a change between an initial and final solution (defined as final - initial).
$\Delta^{34}\text{S}$	Parameter defined in Eqn. A2.8.
ϵ_{ps}	Additive fractionation factor (Eqn. A3.2).
ϕ	Total number of plausible phases considered in attempting to define reactions in a natural system.
ξ	Reaction progress variable.
μ	Chemical potential.

Subscripts and superscripts

C	Carbon
FM	Refers to ground water from Ft. Meade, Fla. See Example section.
i	Subscript for the i^{th} aqueous species, or i^{th} reaction model.

k	Subscript for the k^{th} element.
N	Subscript for the N^{th} subset of the plausible phases.
0	Denotes initial value. With μ , 0 refers to the standard state.
p	Subscript for p^{th} plausible phase.
PC	Refers to ground water from Polk City, Fla. See Example section.
s	Subscript refers to solution.
S	Sulfur.
T	Denotes total quantity.
W	Refers to ground water from Wauchula, Fla. See Example section.
*	Denotes incoming carbon such as from dissolution.
'	Denotes the final water.
-	Overscript denotes a vector.
^	Superscript denotes per kg H_2O .

INTRODUCTION

THIS paper discusses the philosophy and methodology of chemical reaction modeling that has developed as part of a major research program of the U.S. Geological Survey for evaluating the characteristics, including water quality, of the nation's regional ground-water systems. The modeling principles discussed here were developed to permit evaluation of chemical reactions along ground-water flow paths. The roots of our reaction modeling are found in the works of MACKENZIE and GARRELS (1966); GARRELS and MACKENZIE (1967); HELGESON (1968); HELGESON *et al.* (1969, 1970); and TRUESDELL and JONES (1974). This treatment of reaction modeling is an extension of several recent ground-water modeling studies (PLUMMER, 1977; WIGLEY *et al.*, 1978; THORSTENSON *et al.*, 1979; PLUMMER and BACK, 1980; PARKHURST *et al.*, 1980, 1982).

In chemical reaction modeling, we use the available data to attempt to determine (1) what chemical reactions have occurred, (2) the extent to which the reactions have proceeded, (3) the conditions under which the reactions occurred (such as open vs closed system, equilibrium vs disequilibrium, constant or variable temperature), and (4) how the water quality and mineralogy will change in response to natural processes and perturbations to the system. The available data may include chemical analyses of the aqueous phase, hydrology, mineralogy, gas compositions, isotopic data, and other relevant information. Chemical reaction modeling is largely a mental exercise, but is facilitated by calculations of (1) equilibrium speciation, (2) mass balance, and (3) reaction-path.

The equilibrium speciation calculations determine the saturation state of the water with respect to various minerals and gases of interest based on a thermodynamic model and observed water quality data. From these calculations we learn whether a particular mineral would tend to dissolve or precipitate in a given aqueous environment.

Mass balance calculations determine the amounts of assumed mineral reactants and products that must

dissolve and/or precipitate between selected initial and final points in a system in order to account for the observed water quality. Mass balance calculations can also be used to solve problems of mixing waters, with or without reaction. The calculations are based on observed net changes in the total concentration of elements in solution and (in the case of redox reactions) an accounting of electron transfer between the initial and final points. 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 waters located along a flow path.

Reaction-path calculations tell us what the chemical composition of an aqueous solution should be and the amounts of minerals dissolved and precipitated, if a particular set of hypothetical reactions and thermodynamic constraints are operative. The reaction-path calculations depend on a thermodynamic model, definition of an observed or hypothetical starting water composition and an assumed set of irreversible reactions and/or mineral-water equilibrium constraints. Some of the more important uses of reaction-path calculations are in testing the thermodynamic feasibility of reaction models derived from (non-thermodynamic) mass balance calculations, estimating the mass transfer and water composition along flow paths intermediate to wells of known composition, and predicting the path and outcome of assumed, hypothetical reactions.

It is important to recognize the differences between mass balance and reaction-path simulation methods. The mass balance method is regarded as an inverse problem that begins with the observed chemical data for a ground-water system and attempts to evaluate the uniqueness of hypothetical reaction models within the constraints of the observed data. Reaction-path simulation methods are regarded as a forward problem in which observed data and/or hydrochemical assumptions are used to specify the initial model conditions and, using a hypothetical set of reaction criteria, the resulting reaction path of aqueous solution composition and mass transfer is calculated. In a general way, the value of the mass balance calculations is directly proportional to the amount of analytical data available. The value of the reaction-path calculations tends to be greater in situations where fewer data are available and a greater hypothetical element is present in the modeling process. Speciation calculations form an integral part of both the mass balance and reaction-path calculations.

Our object in this paper is to present methods for finding reaction models that are consistent with all of the available data and satisfy the constraints of chemical thermodynamics. For any system, more than one reaction model can usually be found that satisfies these criteria and rarely, if ever, will the *unique* reaction which corresponds with reality be isolated.

METHODOLOGY

Any reaction model is essentially a combination of chemical reactions and so must satisfy the same constraints required in writing balanced reactions. Charge and the masses of each element must be conserved. The same number of constraints is sufficient to completely specify any aqueous solution; that is, it is necessary to fix the total mass of each element and the net charge in the solution, usually, but not always assumed to be zero. Thus, if J is the number of elements in the system, specifying masses and charge balance results in $J + 1$ equations that must be satisfied. All three types of calculations, speciation, reaction-path simulation and mass balance involve this same number of equations either explicitly or implicitly.

Aqueous models (for either speciation or reaction-path calculations) have many more than $J + 1$ unknowns including all ion pairs and redox species. In practice, it is possible to choose $J + 1$ "master variables" and write chemical reactions for the formation of all other aqueous species ("derived species") in terms of only the master variables. The mass action equations for these reactions provide one equation for each derived species. (In this discussion, it is assumed that the relation between molality and activity is known, for example through the Debye-Hückel theory of activity coefficients.) Thus, it is possible to simplify the discussion by ignoring the derived species, because a mass action equation exists for each of them, and to consider aqueous models only in terms of the set of $J + 1$ master variables and the $J + 1$ equations they require.

Most aqueous models include a master variable and a mass balance equation for each element other than H and O. This leaves three equations which we refer to as mass balance on hydrogen, mass balance on oxygen and charge balance. However, the need for these last three equations can be satisfied in a number of ways. Other equations can be used, and at least one simplifying assumption can be made to replace one equation. The choice of these three remaining equations for the master variables that are associated with them distinguish the various aqueous models.

Speciation calculations

In speciation calculations, the three remaining master variables chosen are usually pH, redox potential (expressed as p_e , Eh, oxygen fugacity, the SO_4^{2-}/S^{2-} ratio, etc.) and mass of H_2O . Two equations thus fix pH and p_e at the observed values. The numerical value used for the mass of water is dependent on the concentration units of the analyses, but these are usually adjusted to molality. This fixes the mass of water at one kilogram and eliminates a corresponding equation. If a charge balance equation is included in the calculations, then one equation is redundant and pH, redox potential, or the total molality of an element could be computed (MERINO, 1979).

The data usually required for speciation calculations are a chemical analysis of the water, including pH, Eh, and temperature, and thermodynamic data for all reactions considered. The distribution of species in solution is solved by the aqueous model using mass action and mass balance equations. From the calculated distribution of species (corrected to individual ion activities) equilibrium partial pressures of gases may be calculated, as well as the saturation state of the solution with respect to appropriate mineral phases. Saturation state is usually defined in terms of the saturation index, SI ,

$$SI = \log \frac{IAP}{K} \quad (1)$$

where IAP is the ion activity product for the mineral-water reaction and K is the equilibrium constant (the value of IAP

which is observed at equilibrium). SI is zero if the mineral is in equilibrium with an aqueous solution, less than zero if the solution is subsaturated and greater than zero for supersaturated solutions. The speciation calculation tells us whether a particular mineral would tend to dissolve or precipitate in this particular aqueous environment.

Some caution is required in interpreting the results of aqueous model and SI calculations because these calculations are dependent on a theoretical model of the aqueous solution and selected thermodynamic data. The accuracy and completeness of ion pairing constants, the validity of the activity coefficient theory, and the uncertainties of equilibrium constants must be considered in order to evaluate speciation calculations.

For speciation calculations, our experience has shown that, although a particular mineral may actually be dissolving or precipitating in a ground-water system, the SI calculation frequently indicates that the water is at or near equilibrium with the mineral (within the uncertainties of the analytical and thermodynamic data). Ground-water systems are often demonstrated to be systems in partial equilibrium. Partial equilibrium occurs when one or possibly several slow mineral-water reactions drive a larger set of faster reactions, the latter of which may continually shift to maintain equilibrium (HELGESON, 1968).

In addition to providing information on saturation indices, speciation calculations can define the masses of elements that may not have been directly analyzed. For example, total inorganic carbon is usually calculated from the field pH and alkalinity using an aqueous model. This information on the total masses of the elements in solution is required in the mass balance method.

The speciation calculation also defines the "redox state" of the solution which is essential to mass balance calculations involving redox reactions. The redox state of the solution provides a means of keeping track of electron transfer during redox reactions. This particular scheme is used in the computer program PHREEQE (PARKHURST *et al.*, 1980).

The redox state, RS , of a solution is defined by

$$RS = \sum_{i=1}^I v_i m_i \quad (2)$$

where I is the total number of species in solution, m_i is the molality of the i^{th} species in solution, and v_i is the "operational valence" which we assign to the species (see Appendix 1).

Speciation calculations provide the following data which are useful to the mass balance method: saturation indices of appropriate minerals in the system, estimates of total masses of elements not directly determined analytically, and the redox state of the solution.

There are a number of computer programs for making speciation calculations on natural waters (such as SOLMNEQ—KHARAKA and BARNES, 1973; WATEQ—TRUESDELL and JONES, 1974; WATEQF—PLUMMER *et al.*, 1976; WATSPEC—WIGLEY, 1977; WATEQ2—BALL *et al.*, 1979; EQ3—WOLERY, 1979; see also the recent review of computer programs for speciation calculations given by NORDSTROM *et al.*, 1979).

Mass balance method

The mass balance method consists of balancing a net chemical reaction of the form

Initial solution composition + "Reactant Phases" \rightarrow

Final solution composition + "Product Phases". (3)

The terms "Reactant Phases" and "Product Phases" refer to constituents that enter or leave the aqueous phase during

the course of the reaction.¹ For example, if the mass balance method defines 2.0 mmol/kg H₂O of CO₂ as a "Product Phase," this means that 2.0 mmol/kg H₂O of CO₂ must physically leave the aqueous phase during the reaction. Similarly, "Reactant Phases" represent chemical constituents that must physically enter the aqueous phase during the reaction.

The masses of "Reactant Phases" and "Product Phases" calculated for a given reaction are derived from a set of "Plausible Phases." "Plausible Phases" is a purposely vague term chosen to represent the set of chemical constituents that are reasonable choices as possible reactants or products in a given hydrologic system. The selection of "Plausible Phases" may be based on mineralogic data, results from speciation calculations, geologic data, or any other reasonable source of information.

In our approach to balancing the net chemical reaction between initial and final solution composition, we account for conservation of mass and conservation of electrons. Conservation of mass means that the masses of the *chemical elements* are balanced in chemical reactions. We emphasize elements because in balancing a reaction the number of atoms of each element present are counted, independent of the particular species or valence of the atom as it appears in the reaction. The analytical data (and, if necessary, the speciation calculation) provide the masses of the elements in the initial and final solution. A mass balance equation may be written for each element; however, as discussed below, we usually do not include mass balance equations for hydrogen and oxygen.

In addition to mass balance equations for the elements, one additional equation is provided by accounting for the conservation of electrons in redox reactions. Electrons do not exist under natural conditions as hydrated aqueous species. For every atom that loses an electron through oxidation, some other atom must gain an electron through reduction. The technique used to maintain electron balance is to equate the change in redox state, defined above, between the initial and final solution with the number of electrons transferred between the reactant and product phases. The number of electrons transferred between phases is a function of the masses of the reactants and products and the oxidation state of each element in the reactants and products. This technique requires that we define the same electron transfer convention (operational valence) for phases as we used for the calculation of the redox state of the aqueous solution (Appendix 1).

The constraints of mass balance and conservation of electrons in chemical reactions are formalized by Eqns. (4) and (5)

$$\left\{ \sum_{p=1}^P \alpha_p b_{p,k} = \Delta m_{T,k} \right\}_{k=1,J} \quad (4)$$

$$\sum_{p=1}^P u_p \alpha_p = \Delta RS \quad (5)$$

where the notations are defined as follows: α_p is the net mass transfer, in moles, of the p^{th} plausible phase among the P total reactant and product phases in the reaction (similar to (3)), $b_{p,k}$ denotes the stoichiometric coefficient of the k^{th} element (excluding H and O) in the p^{th} phase, Δ indicates a difference (final value minus initial value), $m_{T,k}$ is the total

molality of the k^{th} element in solution, u_p is the operational valence of the p^{th} phase (Table A1.1) and RS denotes the redox state of the solution (Eqn. 2). See Appendix 2 for an example using Eqns. (4) and (5).

In solving mass balance problems, we do not include mass balance equations for hydrogen and oxygen because of the impracticality of analytically determining the *total* masses of these elements in the initial and final solutions.

As discussed earlier, $J + 1$ independent equations are required to completely define a balanced chemical reaction. Because we do not write mass balance equations on H and O, only $J - 2$ mass balance equations (Eqn. 4) may be written, and thus, three additional constraints must be specified to define the system. We have already seen one of these constraints in the form of the electron conservation equation (Eqn. 5). The second constraint we employ is related to charge balance. Because all phases are electrically neutral, the sum of the charge in any mass transfer is necessarily zero. By assuming that these phases can account for all reaction in the ground water, this also implies that there is no net change in charge between the initial and final solution. In fact, it is generally assumed that any charge imbalance in solution reflects analytical errors and that every solution is effectively charge balanced. Thus, a charge balance equation is satisfied regardless of mass transfer of neutral phases.

The third constraint implied by the mass balance approach is that the mass of water is constant. Again, this is an assumption which must be evaluated when comparing model results to the ground water system. In general, for small mass transfers of phases (less than 1 mole) the error is negligible. Note again that if the total masses of O and H could be determined with sufficient accuracy (impossible with present analytical techniques), the mass balance method could alternatively be solved by incorporating mass balance equations on H and O.

Although we do not use mass balance equations on H and O, H₂ and O₂ may be considered as plausible phases that act as sources or sinks for electrons. Dissolved H₂ and O₂ gases will contribute to the redox state of the solution and analytical concentrations of these gases should be included in the redox state calculation.

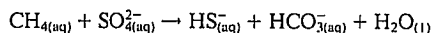
The parameters pH and pe appear only implicitly in Eqns. (4) and (5) in that they have been used in speciation calculations to define the total molality of inorganic carbon and/or the equilibrium concentrations of several oxidation states of an element for which only the total concentration was analytically determined.

In most mass balance applications, there are more plausible phases, ϕ , to be considered than there are linear independent equations, E , that can be written. One way of treating problems of excess plausible phases is to consider selected subsets that contain E plausible phases for which the stoichiometric coefficients, \bar{b}_p , (the bar indicating a vector notation; $\bar{b}_p = (b_{p,1}, b_{p,2}, \dots, b_{p,E})$) are linearly independent. In practice, it is usually not difficult to find several subsets of the plausible phases that satisfy this criterion and lead to mathematical solutions that satisfy the mass balance equations. (See Appendix 1 for an example of treating problems of excess plausible phases.)

Although problems of excess plausible phases may be defined mathematically, they are often impractical to solve due to difficulties in defining the proportions, x_i , of the linearly independent subsets of the plausible phases (Appendix 1). Definition of x_i requires mineralogic and kinetic information as well as data on the spatial distribution of varying compositions of plausible phases which are not always available. Clearly, without knowledge of x_i , an infinite number of mass balance models can be generated, all of which are possible until eliminated on the basis of thermodynamic kinetic, petrographic or isotopic criteria.

The problem of excess plausible phases is increased by the fact that a given mineral in the system may vary in its

¹ If the reaction is homogeneous, that is, occurring only in the aqueous phase, the analytical data define the reaction. For example, if sulfate is reduced by dissolved methane to yield bisulfide and bicarbonate ions



the net chemical reaction is entirely defined by analytical data from the aqueous phase. In this case, there are no "Reactant Phases" or "Product Phases" as in reaction (3).

stoichiometry from an idealized composition. When using the mass balance method, it is usually necessary to work with normalized mineral compositions that represent the known range of mineral stoichiometry in the system. Conclusions regarding the significance of the derived mass transfer must reflect the fact that many other minerals (of perhaps slightly different compositions) may be reacting as well. (A more detailed description of the total set of solutions to a mass balance problem is provided in Appendix 1.)

In solving mass balance problems, the values of $\Delta m_{T,k}$ and ΔRS (Eqns. 4–5) are defined by chemical analyses and speciation calculations performed on the initial and final waters. Values of $b_{p,k}$ and u_p depend on the plausible phases being considered in the reaction. The total number of equations, E , in a given mass balance problem is $J + 1$: one mass balance equation for each element, J , (excluding H and O) required to define the stoichiometry of the plausible phases (Eqn. 4) plus one equation to account for electron transfer (Eqn. 5). If the problem is not a redox problem, Eqn. (5) is not independent and cannot be included. Equations of the form of (4) and (5) are linear and can be solved for the unknown quantities, α_p , the number of moles of reactant and product minerals in the net chemical reaction if the stoichiometries of the selected minerals are linearly independent. We may also extend the mass balance approach to include problems of mixing of ground waters or, in some cases, isotope mass balance. Because the hand solution of multiple linear equations becomes tedious, a computer routine (BALANCE) has been written specifically to accommodate mass balance problems in ground-water systems (PARKHURST *et al.*, 1982).

Reaction-path simulations

Given a starting water composition and an assumed set of irreversible reactions and/or equilibrium constraints, reaction-path calculations can predict the evolution of water and rock as a function of reaction progress. Reaction progress is measured in terms of a progress variable, such as the total number of moles of a particular reactant dissolved in an overall irreversible reaction. Or, alternatively, if sufficient kinetic data are available, time may be chosen as the progress variable. Because reaction progress and flow downgradient both proceed directly as functions of time, the progress variable tends to increase with distance of flow along hydrologic gradients. But, without details of the reaction kinetics and flow velocity, it is not possible to quantitatively relate reaction progress to position in hydrologic systems.

Depending on the types of reactions assumed to occur among the plausible phases, the reaction path simulation will require definition of irreversible reaction(s)² and/or a set of thermodynamic controls on solution composition. Irreversible reactions in ground-water systems typically involve the slow dissolution of one or more host minerals that do not reach equilibrium (or apparent thermodynamic control) within the time scale of the hydrologic system. In general, any chemical or physical process that irreversibly changes the masses of components in solution may be included. If two or more reactions occur simultaneously, the relative rates of reaction must be defined. These relative rates are usually assumed to be constant and are poorly known because of the lack of information on the relative surface areas of the reactive phases and the dearth of knowledge of mineral-water reaction kinetics.

As in the mass balance approach, the phases considered in reaction-path simulations should be limited to a set of

plausible phases. Thermodynamic controls of either equilibrium or "apparent equilibrium" can be applied to plausible phases that react rapidly on the time scale of the hydrologic system. Apparent equilibrium includes non-equilibrium processes that lead to constant (steady-state) levels of supersaturation (or undersaturation) with respect to plausible phases in the system.

If more than one irreversible reaction occurs simultaneously, the number of possible reaction paths that may be computed is unlimited because an unlimited number of perturbations on the relative rates may be considered. A distinct advantage of reaction-path calculations is the possibility of treating mineral phases of variable composition, which in the mass balance calculations only increases the number of excess plausible phases.

There is no guarantee that an arbitrary reaction-path simulation will predict the observed composition of the final water. Although the total mass transfer may vary considerably in a reaction-path simulation, the final computed water composition will match the observed ground water only when the computed *net* mass transfer is identical to that given by the mass balance method. One way then to constrain a reaction-path simulation to reproduce the final water is to begin with the *exact* composition of the initial solution, and then use the irreversible reaction to add and remove the *exact* net masses of phases calculated by the mass balance approach. However, this ignores any thermodynamic criteria and provides no new information beyond that gained by the mass balance and speciation calculations.

Alternatively, reaction-path simulations may incorporate appropriate equilibrium or apparent equilibrium conditions in conjunction with one or more irreversible reactions. Once a particular saturation state (based on field observation) is reached in simulation, that apparent thermodynamic criteria is maintained while the irreversible reaction(s) proceed. A reaction path calculated in this way, specifying zero and/or non-zero saturation indices for plausible phases, may or may not reproduce the observed final water. If it does, *then one thermodynamically valid path has been found*. Inability to simulate the composition of the final water does not necessarily imply that no thermodynamically feasible path exists; it may be that the particular choice of relative reaction rates and/or temperature path are inconsistent with observations.

Because of the complexity of the calculations required in simulating the chemical evolution of a reacting water-rock system, reaction-path simulations are usually performed using computer codes such as PATH1 (HELGESON, 1968; HELGESON *et al.*, 1970), EQ6 (WOLERY, 1979), PHREEQE (PARKHURST *et al.*, 1980), or SOLVEQ (REED, 1982). These programs show considerable variety in the choices of equations and master variables used. For example, EQ6 (WOLERY, 1979) includes mass balance equations on H and O and a charge balance equation. Oxygen fugacity, pH, and the mass of water are the master variables. PHREEQE (PARKHURST *et al.*, 1980) includes equations for charge balance and conservation of electrons, but assumes a constant mass of water. This assumption is valid as long as the mass of water involved in heterogeneous and homogeneous reactions is small relative to one kilogram of water (~55.5 moles). REED (1982) always includes sulfur in the chemical system and uses H_2O , H^+ , and S^{2-} (in addition to SO_4^{2-} to calculate redox potential) as master variables. A general review and comparison of the various attributes of these programs is beyond the scope of this paper. Hereafter, reference to reaction-path simulations implies calculations made by the computer program PHREEQE.

DISCUSSION

In constructing reaction models from a given set of chemical observations in a ground-water system,

² This is true in most applications of reaction path modeling. However, calculations can be envisioned in which a system initially at equilibrium might change, maintaining equilibrium in response to temperature and/or pressure changes.

two related problems arise: (1) Can we identify a single set of phases that accounts for the observed water chemistry? and (2) Is there a unique description of the relative rates of reaction of these phases (*i.e.* reaction path) along the flow path? In general the answer to both questions is almost always no. Usually, the best that can be done is to find at least one set of relative reaction rates for each of several sets of phases. This results in several feasible *net* mass transfer models. As more data become available from more closely-spaced observation wells, the modeling exercise leads to an improved definition of the actual reaction path. We are trying to determine, given the available data, to what extent we can use mass balance and/or reaction path methods in defining feasible net reaction models and the advantages and disadvantages of each method.

Before comparing modeling scenarios, we need to define two types of chemical modeling problems—those in which the analytical data are “saturation-sufficient,” and those in which the analytical data are “saturation-insufficient.” We use the term “saturation-sufficient” to define a set of chemical analyses of initial and final waters that are sufficient to define saturation indices for a given set of plausible phases in the system. The term “saturation-sufficient” does not imply that the set of chemical analyses is necessarily complete; for example, analytical data for fluoride may be missing, yet the available data could define saturation indices for plausible phases involving carbonate and sulfate minerals. In this case, the analytical data are “saturation-sufficient,” provided fluoride minerals are not included among the plausible phases deemed necessary to define the chemical system. If the analytical data are “saturation-insufficient,” values of Δm_T for one or more of the elements required by the plausible phases are not defined and the mass balance method cannot be solved uniquely.

The two most common examples of saturation insufficient data are the absence, or unsatisfactory nature, of analyses of dissolved iron or aluminum. In these cases, the saturation state of the aqueous phase with respect to the aluminosilicate or iron-containing phases cannot be specified even with complete analytical data for other elements in the water. The mass balance method can be extended to these saturation-insufficient cases by making an assumption about the change in concentration of iron and aluminum. Owing to the low solubility of ferric hydroxide and aluminosilicate minerals, it may be satisfactory to assume that $m_{T,Fe}$ and $m_{T,Al} = 0$ in initial and final waters and that the change in concentrations is thus zero. Alternatively, in the reaction-path approach the iron and aluminum could be constrained to be in equilibrium with one or more phases.

There are various degrees of “saturation-insufficient” data, the most extreme case being that no chemical data are available at all. For this case, the reaction-path calculation is the only applicable

method. This kind of modeling is extremely useful in *a priori* prediction of the outcome of hypothetical reactions, prediction of reaction paths and calculation of the theoretical equilibrium composition of mineral-water systems. Reaction-path simulations may also estimate the chemical composition of ground water located along flow lines in an aquifer at positions intermediate or beyond wells of known composition. *It should be kept in mind that in the absence of analytical data, predictions of solution composition at any points along the path other than the observed initial and final solutions are both hypothetical and likely non-unique.* If the intermediate analytical data are available, we have simply defined a new “final” water for a shorter reaction step which may then be evaluated *via* mass balance or reaction path computations. As more intermediate data are available, both methods will be able to more closely approximate the actual reaction path.

Both the mass balance and reaction-path methods require considerable insight into the problem in selecting appropriate plausible phases. An advantage of the mass balance method is that, given the set of plausible phases, all the possible reactions that might be occurring between two points on a flow path are defined mathematically (see Appendix 1). It is relatively simple, in practice, to substitute one set of phases for another set and derive a new mass balance reaction model.

In contrast, reaction-path simulations are much more complex and computationally more difficult to perform. Constructing a reaction-path simulation requires care in evaluating irreversible reaction(s), relative rates, thermodynamic criteria and plausible phases allowed to participate in the reaction. If, through trial and error, a reaction path is found for a particular set of plausible phases that matches exactly the initial and final solution compositions, the calculated *net* mass transfer will always be identical to the net mass transfer defined by the mass balance method for the same set of plausible phases. A distinct advantage of the reaction-path method, however, is that if a reaction is found that satisfies the net mass transfer constraint, the calculated path is thermodynamically valid.

The mass balance method can only be partially checked for thermodynamic consistency. For a reaction to proceed at any point along a reaction path, the derivative of the free energy of reaction for the p^{th} phase with respect to reaction progress, ξ , must be less than zero, $dG/d\xi_{(p)} < 0$ for each dissolving phase. Using our previous definition of SI , it follows that for a precipitation reaction to proceed at any point along the flow path, $dG/d\xi_{(p)}$ must be greater than zero for that reaction. The change in free energy of the reaction of the p^{th} phase is related to the saturation index of the p^{th} phase by:

$$\frac{dG}{d\xi_{(p)}} = 2.303RT(SI_p). \quad (6)$$

At constant temperature and pressure, the term $-(dG/d\xi_{(p)})$ is known as the chemical affinity of the reaction (PRIGOGINE and DEFAY, 1954).

If the analytical data are saturation sufficient with respect to the p^{th} phase, we can evaluate $dG/d\xi_{(p)}$ at observed points on the flow path. For all thermodynamically valid reactions, as we have defined the problem, the sign of α_p must be opposite the sign of SI_p (within the uncertainties of the analytical and thermodynamic data). That is, a plausible phase will not dissolve (α_p positive) in a water supersaturated with the p^{th} phase (SI_p positive), nor precipitate (α_p negative) from an undersaturated solution (SI_p negative).

Since we define only *net* mass transfer via the mass balance method, a contradiction in the sign of $dG/d\xi_{(p)}$ does not necessarily invalidate a reaction because, in this case, the p^{th} phase may have both dissolved and precipitated at different points between the initial and final waters leading to the calculated *net* mass transfer. Therefore, the thermodynamic criterion, $dG/d\xi_{(p)} < 0$ for dissolution and $dG/d\xi_{(p)} > 0$ for precipitation of the p^{th} phase, can be used only to identify reactions that are thermodynamically feasible. However, if it can be proven (such as petrographically) that the mass transfer of a particular phase varies monotonically with reaction progress, that is, the phase does not *both* dissolve and precipitate at different points along the flow path, it is possible to use the observed contradictions in the sign of $dG/d\xi_{(p)}$ to eliminate a particular reaction model.

In testing a mass balance model for thermodynamic contradictions, it is necessary to examine the sign of $dG/d\xi_{(p)}$ for each mineral in the overall reaction. A model is thermodynamically feasible if no contradictions are found among *all* phases in the model.

Alternatively, if the analytical data are again saturation-sufficient, we may compute the total Gibbs free energy change per kg H_2O in the system, $\Delta\hat{G}$, between the initial and final points on the flow path ("final" minus "initial"), and draw conclusions regarding the change in *total* free energy of the system as a function of reaction progress, $dG/d\xi$, for a particular mass balance model. Calculation of $\Delta\hat{G}$ requires details of the distribution of species in the initial and final waters (including a_{H_2O}), the saturation indices of the P phases in the final water (SI_p), and the appropriate mass transfer coefficients (α_p) defined by the mass balance method (Appendix 1). If $\Delta\hat{G}$ is positive, then at some point in reaction progress $dG/d\xi$ must be positive which implies a non-spontaneous reaction. Thus, a positive value of $\Delta\hat{G}$ would indicate the model is thermodynamically invalid. Although thermodynamically valid reactions will have negative values of $\Delta\hat{G}$, a calculated negative value of $\Delta\hat{G}$ does not always prove the existence of a spontaneous reaction. For example, even though there may be a net decrease in Gibbs free energy from the initial to the final water, a particular path of the net reaction would

be thermodynamically invalid if there were a free energy minimum (or maximum) at an intermediate point in reaction progress such that $dG/d\xi$ is positive over a portion of the reaction path. In the limiting case, as wells become more closely spaced, the sign of $\Delta\hat{G}$ approaches the sign of $dG/d\xi$ of the actual reaction path. Thus, with more closely spaced data, $\Delta\hat{G}$ becomes a more reliable criterion for spontaneity. Usually, in order to show that a mass balance reaction is thermodynamically feasible, it is necessary to find a reaction-path simulation that reproduces the final water.

Mass balance models based on saturation-insufficient data are more difficult to check for thermodynamic violations. However, with careful analysis, solubility calculations may provide some information on the thermodynamic feasibility of a particular saturation-insufficient reaction defined by the mass balance method.

Consider, for example, a problem in reaction identification between initial and final waters where aluminosilicates are included among the plausible phases, but for which no dissolved aluminum data are available. These waters are saturation-insufficient with respect to all aluminum-bearing minerals. Assuming that the unknown total aluminum concentration is low (owing to the low solubility of most aluminosilicate minerals in ground water), we may solve the mass balance equations using the value $\Delta m_{T,Al} = 0$, and appropriate sets of plausible phases. For simplicity, consider further that a particular set of plausible phases contains a single aluminum-bearing reactant and a single aluminum-bearing product.

Having determined the values of α_p for each phase in the particular mass balance model, we may turn to solubility calculations to test for thermodynamic violations in the defined net reaction. One way of checking for thermodynamic violations is to constrain the final water to be in equilibrium with the aluminum-bearing product mineral defined by the mass balance. This procedure is accomplished in PHREEQE by adjusting the total concentration of aluminum in the final water and changing pH to satisfy charge balance for the whole solution. The total aluminum added to reach equilibrium with the aluminum-bearing product is usually so small as to cause negligible changes in pH. This procedure estimates the minimum value of the unknown dissolved aluminum in solution, since only higher values of dissolved aluminum are expected if the product phase forms at supersaturation.

The particular reaction model is thermodynamically invalid if (1) the minimum aluminum concentration results in supersaturation at the end point with respect to the reactant phase defined by the mass balance method, and (2) the mass transfer is known to vary monotonically between the initial and final points on the flow path. The test is indeterminate if non-monotonic behavior is expected since it is possible that the aluminum-bearing reactant may have

dissolved initially and later precipitated along the flow path leading to the calculated *net* mass transfer. Thus with non-monotonic reaction paths, *apparent* thermodynamic contradictions to the *net* mass balance model may be observed which do not invalidate the model. Of course, this criterion for testing reaction models for saturation-insufficient data must be used within the limits of uncertainty of the thermodynamic and analytical data. Cases involving more than one reactant and product phase for the unknown element, or cases where the waters are saturation-insufficient with more than one element, are more difficult to treat in general.

Aside from elimination by testing against thermodynamic criteria, the only way to reduce the number of feasible reaction models is by introducing new data on the chemistry of the system.

New data can include detailed mineralogic and petrographic information identifying which of the plausible phases are present, and visual evidence as to which minerals are reactants and products in the system. Other new data may include isotope data for the ground water and the reactant and product minerals of the system. Simulation of the isotopic composition of the ground water is a significant step in reducing the number of possible reaction models because the isotopic composition of the solution and product minerals are functions of the mass transfer. The correct reaction model, while predicting the ob-

served ground-water chemistry, must be consistent with both the speciation calculation and the observed isotopic data for the system.

If the feasibility of mass balance models is to be checked with isotopic data, reaction-path modeling may be necessary, regardless of whether the data are saturation-sufficient or saturation-insufficient. If a continuously fractionating input or output is postulated for a particular model, a calculated reaction path between the initial and final waters may be necessary to define the intermediate mass transfers and solution compositions used to compute the isotopic evolution. Reaction-path modeling may also be used to investigate sensitivity of the computed isotopic composition of a final water to deviations of the reaction path from the net linear path defined by the mass balance. In other cases, as in our example (Appendix 3), the integrated equation (WIGLEY *et al.*, 1978) provides sufficient accuracy for realistic deviations in reaction path. In cases where the isotopic fractionation between solution and precipitate can be ignored, it is possible to include a linear isotope balance equation in the mass balance calculations (see Appendix 2). In this case, models that satisfy all the mass balance criteria and the isotopic composition can be found immediately.

A similar problem to isotopic fractionating systems exists if solid solutions must be considered. In this case, the aqueous phase composition at any point is

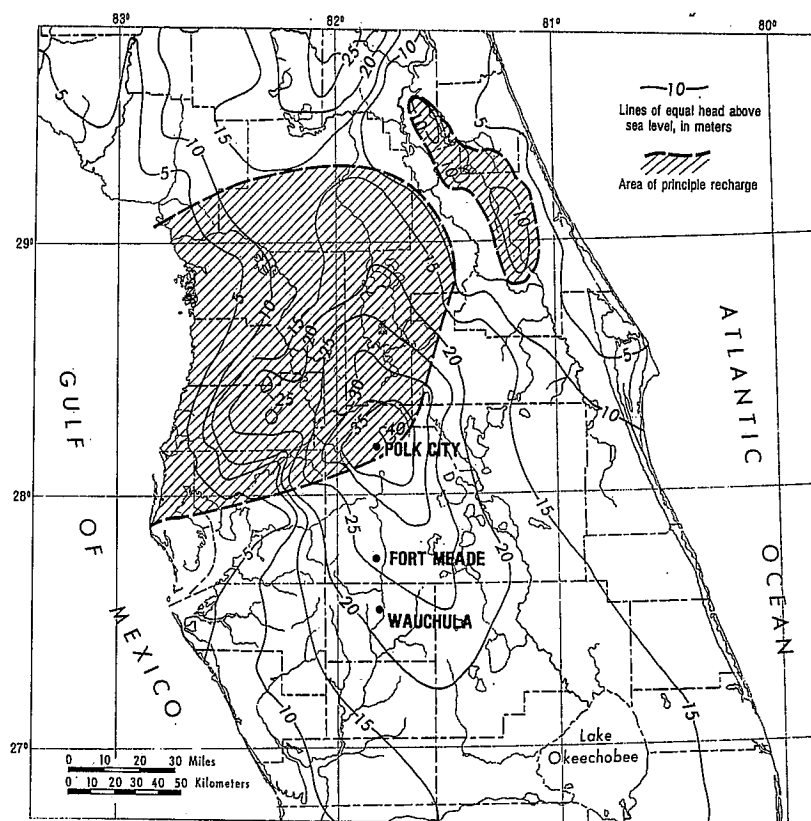


FIG. 1. Potentiometric map of the principal artesian aquifer in central Florida showing location of the three wells studied (after STRINGFIELD, 1936).

also path dependent and can be accurately simulated only by reaction-path methods. This problem is more likely to be encountered in high-temperature systems than in the relatively low-temperature ground waters that are the basis for most of this paper.

EXAMPLE

For purposes of illustrating the principles discussed above, we now consider the problem of identifying a unique reaction model in a limited portion of the Floridan aquifer. In this example we have analytical data from three wells in central Florida located along an approximate flow line from Polk City southward 68 km to Wauchula (Fig. 1). In the Polk City well, the potentiometric head is 40 meters above sea level; in the Wauchula well, the head is 20 meters. Data from an intermediate well (Ft. Meade) located approximately 47 km south of Polk City are included for later testing of reaction path. The area north of, and including, Polk City is one of recharge (BACK and HANSHAW, 1970). To the south recharge is probably less owing to cover by the relatively impermeable Hawthorn formation of Miocene age (PRIDE *et al.*, 1961; LEGRAND and STRINGFIELD, 1966; STEWART, 1980). This particular example of reaction modeling was chosen in part because earlier mass balance studies of this system (PLUMMER, 1977; PLUMMER and BACK, 1980) did not model redox reactions.

We assume that we are dealing with an initial ground water (Polk City) that changes composition *only via* reaction as it moves downgradient to Wauchula, that is, other effects such as dispersion are assumed unimportant. The hydrologic validity of this assumption is *not* the subject of this paper. Our purpose here is—given this assumption—to evaluate the chemical models that can be applied in this system.

The chemical data for the initial (Polk City), intermediate (Ft. Meade) and final water (Wauchula) are given in Table 1 (largely from BACK and HANSHAW (1970)). Carbon and sulfur isotopic data are also included in Table 1 for testing reaction hypotheses. The results of the speciation calculations are given in Table 2. These results include the total molality of inorganic carbon which was calculated from the field alkalinity and pH, the redox state of the waters (Eqn. 2), an estimation of the p_e of Wauchula water based on the $\text{SO}_4^{2-}/\text{S}^{2-}$ couple, selected saturation indices and P_{CO_2} . Also included in Table 2 are the Δ terms (final water minus initial water) for $\Delta m_{T,k}$, and ΔRS between Polk City and Wauchula. Several of the analyzed species (notably silica) are not included in Table 2 because we do not require them to define the stoichiometry of the plausible phases defined below.

Some details of the mineralogy of the Oligocene to middle Eocene limestones and dolostones penetrated by the wells are given by BACK and HANSHAW (1970); HANSHAW *et al.* (1971); HANSHAW and BACK (1972); RANDAZZO and HICKEY (1978); and R. G. DEIKE (unpublished data, 1972). From these studies and for the purposes of this example, it is reasonable to include among the plausible phases:

- (1) gypsum (or anhydrite),
- (2) calcite (ranging in composition from CaCO_3 to $\text{Ca}_{.98}\text{Mg}_{.02}\text{CO}_3$),
- (3) magnesian calcite ($\text{Ca}_{.95}\text{Mg}_{.05}\text{CO}_3$),

Table 1: Analytical Data¹

Constituent	Initial Water (Polk City) mg/l	Inter- mediate Water (Ft. Meade) mg/l	Final Water (Wauchula) mg/l
SiO_2	12.0	16.0	18.0
Ca	34.0	58.0	66.0
Mg	5.6	17.0	29.0
Na	3.2	6.1	8.3
K	0.5	0.7	2.0
HCO_3^-	124.0	163.0	168.0
SO_4^{2-}	2.4	71.0	155.0
Cl	4.5	9.0	10.0
F^-	0.1	0.4	0.7
NO_3^-	0.1	0.1	0.0
H_2S	0.0	—	1.2 ⁷
pH	8.00	7.75	7.69
p_e	—	—	-4.26 ²
$\delta^{13}\text{C}$	23.8	26.6	25.4
$\delta^{13}\text{C}$	-11.4 ³	-10.8 ⁸	-8.5 ⁴
$\delta^{34}\text{S}$ % modern ⁵	34.3	17.3	4.4 ⁵
$\delta^{34}\text{S}(\text{SO}_4)^{6/00}$	-14.7	—	+24.9 ⁶
$\delta^{34}\text{S}(\text{H}_2\text{S})^{6/00}$	—	—	-32.9 ⁷

¹ Back and Hanshaw (1970); ² Calculated using $\text{SO}_4^{2-}/\text{S}^{2-}$ couple. ³ Rightmire and Hanshaw (1973); ⁴ Pearson and Hanshaw (1970). ⁵ Hanshaw *et al.* (1965), $\pm 2\%$ modern; ⁶ Rightmire *et al.* (1974). ⁷ Pearson and Rightmire (1980); Rye *et al.* (1981); ⁸ Back and Hanshaw (unpublished data, 1967) as given in Plummer (1977).

(4) dolomite (ranging in composition from $\text{CaMg}(\text{CO}_3)_2$ to $\text{Ca}_{1.05}\text{Mg}_{.90}\text{Fe}_{.05}(\text{CO}_3)_2$),

(5) additional carbon sources including CO_2 , organic matter (CH_2O , *i.e.*, carbon of valence zero), and possibly methane,

(6) ferric hydroxide (FeOOH),

(7) iron sulfides (FeS_2 , FeS).

Notice that, for this problem, the original analytical data of Table 1 are saturation-insufficient in that no data for total dissolved iron are known although iron minerals have been included among the plausible phases. The concentration of iron in both waters is very low owing to the low solubility of ferric hydroxide minerals, and for mass balance purposes, we are safe within the limits of the data of assuming $\Delta m_{T,\text{Fe}} = 0$. Even though total iron is very low in these waters, its inclusion in the mass balance, as $\Delta m_{T,\text{Fe}} = 0$, is an important and valid constraint; that is, if iron is involved in reactions, it is conserved among the reactant and product phases.

Because sulfide species are below detection in the Polk City water, and present in the Wauchula water, we are necessarily dealing with a redox problem. Although much of the mass transfer between Polk City and Wauchula was accounted for by non-redox reactions (PLUMMER, 1977), appropriate plausible phases must be selected in developing reaction models that include redox processes. Several of the reaction models of PLUMMER (1977) are expanded in our treatment below to take into account the presence of dissolved sulfide species in central Florida. In order to form reduced sulfur species, a source of reduced carbon such as organic matter or methane is required.

The number of linearly independent sets of the plausible phases is large. For this example, we will only consider six sets of the plausible phases for mass balance calculations (Table 3). As a first approximation in solving possible mass balance reactions, we have considered only reduced carbon sources such as organic matter and methane (Table 3) in the car-

Table 2 - Results of the Speciation Calculation.

	mmols/kg H ₂ O			
	Initial Water (Polk City)	Intermediate Water (Ft. Meade)	Final Water (Wauchula)	Ammol/kg H ₂ O (Final - Initial)
Ca _T	0.848	1.448	1.647	0.799
Mg _T	0.230	0.699	1.193	0.963
ST	0.025	0.739	1.649 ¹	1.624
CT	2.054	2.743	2.843	0.789
Fe _T	~0.0	~0.0	~0.0	~0.0
RS	8.366	15.406	20.986	12.620
SI _C ³	0.22 ± 0.04	0.28 ± 0.04	0.22 ± 0.04	---
SI _G ³	-3.35 ± 0.02	-1.78 ± 0.02	-1.46 ± 0.02	---
SI _D ³	-0.29 ± 0.2	0.06 ± 0.2	0.14 ± 0.2	---
log P _{CO₂}	-2.92	-2.55	-2.49	---
Charge	0.07213	---	-0.33230	-0.40443
Balance				

¹ Includes sulfate (1.614 mmols/kg H₂O) and sulfide (0.035 mmol/kg H₂O) species.

² Equation (6).

³ Subscripts are C-calcite (log K_C = -8.483 ± .02; Plummer and Busenberg, 1982), G-gypsum (log K_G = -4.602 ± 0.02; based on data Lilley and Briggs, 1976), D-dolomite (CaMg(CO₃)₂) (log K_D = -16.8 ± 0.2, large uncertainty in log K_D is given to reflect possible differences in free energy of dolomites of low temperature origin, Busenberg and Plummer, 1982). Saturation indices of Ca₉₈Mg₀₂CO₃ and Ca₉₅Mg₀₅CO₃ are within 0.04 SI units of calcite (Thorstenson and Plummer, 1977) and thus within the uncertainty of SI_C. As no data are available for total dissolved iron and pe is poorly known, the analytical data are saturation insufficient with respect to the iron sulfide and hydroxide minerals that may be included among the plausible phases.

bon balance. That is, the sets of plausible phases of Table 3 assume a ground-water system closed to CO₂.

Each reaction model includes gypsum, FeOOH, and the possibility of formation and/or dissolution of iron sulfides. In addition to the carbonate minerals each reaction model allows for a source of carbon of reduced valence: 0 (organic carbon, models 1-4), and -4 (methane, models 5-6). The stoichiometry of the magnesium source mineral is varied from stoichiometric dolomite (model 1), to magnesian calcite (model 2) to non-stoichiometric dolomite (models 3-6). Models 4 and 6 compare differences in mass transfer resulting from inclusion of FeS rather than FeS₂ in the reactions. All models include redox reactions and require inclusion of Eqn. (5) to account for conservation of electrons. As a matter of convenience, Eqns. (4) and (5) were solved by the computer program BALANCE (PARKHURST *et al.*, 1982). Table 4 lists the calculated values of α_p (in mmol/kg H₂O) for each model from Table 3. Each set of α_p values in Table 4 satisfies the constraints of conservation of mass and conservation of electrons in a net reaction similar to Eqn. (3).

Having solved the mass transfer implied by each of the six sets of plausible phases, we check to see if a unique reaction may be defined. From Table 4 the number of plausible phases, ϕ , is equal to 12 while the maximum value of P is only 6, therefore we are

far from obtaining a unique solution to the mass balance problem. The next test is to determine if any of the mass balance reactions are inconsistent with known values of the saturation indices of the P phases used in each reaction. Comparison of values of α_p with the saturation indices of Table 2 shows that all but one of the mass balance reactions are consistent within the uncertainty of the observed saturation state of the waters. Reaction 5 may be eliminated however, because it requires the precipitation of a large amount of gypsum from waters that are certainly subsaturated with the mineral in a ground-water system of demonstrated monotonic variation on a regional scale (BACK and HANSHAW, 1970).

At this point five of the original six models remain, and it is necessary to resort to additional data in order to further eliminate reaction possibilities.

The sulfur isotope data offer relevant information for examining the uniqueness of the remaining models of Table 4. RIGHTMIRE *et al.* (1974) noted a systematic shift in $\delta^{34}\text{S}$ of dissolved sulfate to higher values with the amount of gypsum dissolved in the Floridan aquifer. The sulfur isotopic composition of gypsum in central Florida varies from 19 to 22‰ (RIGHTMIRE *et al.*, 1974). The dissolved sulfate of the Wauchula water is then shifted at least 2.9‰ heavier than gypsum (Table 2) and is indicative of sulfate reduction, since reduced sulfur species formed *via* preferential reduction of isotopically lighter SO₄²⁻. Reactions 1-4 involve sulfate reduction accompanying (the assumed bacterially me-

Table 3: Selected Sets of Plausible Phases for Mass Balance Calculations Assuming a Reaction System Closed to CO₂.

Model	Plausible Phases
1	Calcite, dolomite, gypsum, CH ₂ O, FeOOH, FeS ₂
2	Ca(.95)Mg(.05)CO ₃ (Mg-calcite), calcite, gypsum, CH ₂ O, FeOOH, FeS ₂
3	Ca(1.05)Mg(.90)Fe(.05)(CO ₃) ₂ , Ca(.98)Mg(.02)CO ₃ , gypsum, CH ₂ O, FeOOH, FeS ₂
4	Ca(1.05)Mg(.90)Fe(.05)(CO ₃) ₂ , Ca(.98)Mg(.02)CO ₃ , gypsum, CH ₂ O, FeOOH, FeS
5	Ca(1.05)Mg(.90)Fe(.05)(CO ₃) ₂ , Ca(.98)Mg(.02)CO ₃ , gypsum, CH ₄ , FeOOH, FeS ₂
6	Ca(1.05)Mg(.90)Fe(.05)(CO ₃) ₂ , Ca(.98)Mg(.02)CO ₃ , gypsum, CH ₄ , FeOOH, FeS

Table 4: Results of the Mass Balance Calculation for a Reaction System Closed to CO₂. Values of α_p in mmols/kg H₂O¹

Plausible Phases	Reaction Model					
	1	2	3	4	5	6
CaCO ₃	-2.45	-19.79	---	---	---	---
CaMg(CO ₃) ₂	0.96	---	---	---	---	---
CaSO ₄ ·2H ₂ O	2.29	2.29	2.24	2.06	-7.60	6.13
CO ₂	---	---	---	---	---	---
CH ₂ O	1.32	1.32	1.21	1.03	---	---
FeOOH	0.33	0.33	0.25	0.37	-4.66	4.44
FeS ₂	-0.33	-0.33	-0.31	---	4.61	---
Ca _{0.95} Mg _{0.05} CO ₃	---	19.26	---	---	---	---
Ca _{0.98} Mg _{0.02} CO ₃	---	---	-2.68	-2.49	7.61	-6.74
Ca _{1.05} Mg _{0.95} Fe _{0.05} (CO ₃) ₂	---	---	1.13	1.13	0.90	1.22
FeS	---	---	---	-0.43	---	-4.50
CH ₄	---	---	---	---	-8.62	5.09

¹ Negative values of α_p indicate the phase leaves the aqueous solution (such as through precipitation) and positive values indicate the phase enters the aqueous solution such as through dissolution.

diated) oxidation of organic matter. Reaction 6 requires a larger amount of sulfate reduction to accompany the oxidation of methane (source unspecified).

Model feasibility may be tested by comparing the measured $\delta^{34}\text{S}$ at Wauchula (+24.9‰) with the calculated isotopic composition of dissolved sulfate at Wauchula implied by the mass transfer in the remaining models (Table 4). The calculated $\delta^{34}\text{S}$ of dissolved sulfate in the Wauchula water ($\delta^{34}\text{S}_{\text{W}}$) can be approximated by the following linear isotope balance equation (ignoring the small fractionation in the precipitation of sulfide minerals from dissolved sulfide species):

$$\delta^{34}\text{S}_{\text{W}} = [\alpha_{\text{gypsum}} (22\%) + 2\alpha_{\text{pyrite}} (-32.9\%) - \text{H}_2\text{S}_{\text{T(W)}} (-32.9\%) + \text{SO}_{4\text{T(PC)}} (14\%)] / \text{SO}_{4\text{T(W)}} \quad (7)$$

where values of α_{gypsum} and α_{pyrite} (or α_{FeS} , in which case the stoichiometric coefficient of sulfur must be changed from 2 to 1) are given in Table 4, $\text{SO}_{4\text{T(PC)}}$ and $\text{SO}_{4\text{T(W)}}$ denote the total concentrations of SO_4^{2-} in the Polk City and Wauchula waters, respectively, and $\text{H}_2\text{S}_{\text{T(W)}}$ is the total concentration of sulfide species in the Wauchula water. The numbers in parentheses in Eqn. (7) denote the $\delta^{34}\text{S}$ value of the respective sulfur species or mineral, and are taken from RIGHTMIRE *et al.* (1974), PEARSON and RIGHTMIRE (1980), and RYE *et al.* (1981) (Table 1). Using Eqn. (7) and the calculated mass transfer of Table 4, the calculated values of $\delta^{34}\text{S}$ at Wauchula are +45.6‰, +45.6‰, +44.0‰, and +37.8‰ for models 1-4, and +176.4‰ for model 6. (Model 5 has already been eliminated using saturation indices.) The calculated values of $\delta^{34}\text{S}$ at Wauchula are not very sensitive to uncertainties in $\delta^{34}\text{S}$ of gypsum. For example using +19‰ rather than +22‰ for $\delta^{34}\text{S}$ of gypsum Eqn. (7) predicts +41.3‰ at Wauchula rather than +45.6‰ for reaction 1. The calculated values of $\delta^{34}\text{S}$ at Wauchula are all significantly larger than the observed (+24.9‰) and indicate that all the remaining models of Table 4 are incorrect.

At this point we clearly need to re-examine our statement of the problem, because the combined use of mass balance calculations and the sulfur isotope data have eliminated all of the reaction models listed in Table 3. Excluding the possibility of other less obvious and/or exotic sets of plausible phases, the discrepancy in the reaction models may be due to our original assumption that the ground-water system is closed to CO₂. The use of carbon at valence 0 as the only carbon source in the mass balance models requires too much sulfate reduction to produce the observed total carbon concentrations. This "excess" sulfate reduction implies too large an enrichment of ^{34}S in the dissolved sulfate at Wauchula. The

significance of the sulfur isotope data should not be underestimated in our example because the mass balance calculations alone did not reveal the problem of "excess" sulfate reduction.

By combining the sulfur isotope balance equation (Eqn. 7) with a mass balance equation on sulfur (Eqn. 8)

$$\text{S}_{\text{T(W)}} - \text{S}_{\text{T(PC)}} = \alpha_{\text{gyp}} + 2\alpha_{\text{pyrite}} \quad (8)$$

we may solve directly for the net mass transfer of gypsum and pyrite (or FeS). Using data of Tables 1 and 2 and +22‰ for the isotopic composition of gypsum, we calculate that approximately 1.68 mmols of gypsum should dissolve and 0.03 mmols of pyrite should precipitate between Polk City and Wauchula per kg H₂O.

The calculated pyrite and gypsum mass transfers are not particularly sensitive to even exaggerated uncertainties in $\delta^{34}\text{S}_{\text{H}_2\text{S}}$. For example, using +22‰ for dissolving gypsum and assigning $\pm 5\%$ to the observed $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ at Wauchula ($-32.9 \pm 5\%$), the pyrite mass transfer is -0.027 ± 0.003 mmol per kg H₂O with 1.678 ± 0.005 mmol of gypsum dissolved per kg H₂O. The calculated pyrite and gypsum mass transfers are significantly more sensitive to the value of $\delta^{34}\text{S}$ of dissolving gypsum. Our choice of $\pm 22\%$ is based on the value found by RIGHTMIRE *et al.* (1974) to be most consistent with the isotopic evolutionary path of waters in the Floridan aquifer (see their Fig. 3). The reported range of sulfur isotopic composition of evaporite minerals in Florida is +19 to +22‰ (PEARSON and RIGHTMIRE, 1980). If gypsum of +19‰ were dissolving rather than +22‰, nearly 3 times more pyrite (0.075 mmols/kg H₂O) could be precipitated between Polk City and Wauchula. To maintain consistency with other wells in the Floridan aquifer on a regional scale, the calculations that follow assume dissolution of gypsum at +22‰. The calculated net mass transfer of pyrite from (7) and (8) is approximately one-tenth that calculated when the ground-water system was assumed closed to CO₂ (Table 4). Alternatively, if the ground-water system were open only to an oxidized carbon source (CO₂), no sulfate reduction would occur and there would be no enrichment in $\delta^{34}\text{S}_{\text{SO}_4}$. In order to satisfy the sulfur isotope data, it is necessary to consider reaction models using carbon sources of average valence greater than zero, that is, sources of both CO₂ and organic matter.

The six sets of plausible phases listed in Table 3 have been revised to include CO₂ (Table 5). Each reaction model of Table 5 now contains seven phases and thus one additional constraint must be added to the mass balance equations (Eqn. 4) and the Aredox state equation (Eqn. 5) in order to achieve a solution for each model. This final constraint is the sulfur isotope balance equation (Eqn. 7) which (ignoring the small fractionation between H₂S and pyrite) is linear in the values of α_p and may be represented as

Table 5: Selected sets of Plausible Phases for Mass Balance Calculations Assuming a Reaction System Partially Open to CO₂.

Model	Plausible Phases
7.	Calcite, dolomite, gypsum, CH ₂ O, FeOOH, FeS ₂ , CO ₂
8.	Ca(.95)Mg(.05)CO ₃ (Mg-calcite), calcite, gypsum, CH ₂ O, FeOOH, FeS ₂ , CO ₂
9.	Ca(1.05)Mg(.90)Fe(.05)(CO ₃) ₂ , Ca(.98)Mg(.02)CO ₃ , gypsum, CH ₂ O, FeOOH, FeS ₂ , CO ₂
10.	Ca(1.05)Mg(.90)Fe(.05)(CO ₃) ₂ , Ca(.98)Mg(.02)CO ₃ , gypsum, CH ₂ O, FeOOH, FeS ₂ , CO ₂
11.	Ca(1.05)Mg(.90)Fe(.05)(CO ₃) ₂ , Ca(.98)Mg(.02)CO ₃ , gypsum, CH ₄ , FeOOH, FeS ₂ , CO ₂
12.	Ca(1.05)Mg(.90)Fe(.05)(CO ₃) ₂ , Ca(.98)Mg(.02)CO ₃ , gypsum, CH ₄ , FeOOH, FeS ₂ , CO ₂

$$\left\{ \sum_{p=1}^P \alpha_p b_{S,p} \delta^{34}S_p = \Delta^{34}S \right\}_{k=\text{sulfur}} \quad (9)$$

where

$$\Delta^{34}S = (m_{T,S} \delta^{34}S_T)_{\text{final}} - (m_{T,S} \delta^{34}S_T)_{\text{initial}} \quad (10)$$

and T denotes total sulfur (sulfide plus sulfate species).

Equations (4), (5) and (9) were again solved by the computer program BALANCE, using the data of Tables 1 and 2 (which give $\Delta^{34}S = 38.687$, $\delta^{34}S$ pyrite = -32.9% and $\delta^{34}S$ gypsum is $+22\%$, based on the data of RIGHTMIRE *et al.*, 1974; PEARSON and RIGHTMIRE, 1980; and RYE *et al.*, 1981). The results of the mass balance calculations for the new six sets of plausible phases (Table 5) are given in Table 6. (See Appendix 2 for a detailed example of the mass balance calculations of Table 6.)

The mass transfers of gypsum and pyrite (or FeS) are identical to those calculated from Eqns. (7)–(8) as required by inclusion of the sulfur isotope balance equation. All the new models require more CO₂ than reduced carbon (CH₂O or CH₄). When included, relatively small amounts of methane are required in the models. As found previously for a system closed to CO₂, a large mass transfer is implied among the carbonate minerals if magnesium is derived from dissolution of magnesian calcite (5 mole percent MgCO₃).

The calculations given in Table 6 indicate that if the ground-water system is partially open to CO₂, none of the new reaction models (7–12) may be eliminated using known saturation indices (Table 2). Therefore, without additional information, none of the models of Table 6 may be eliminated.

The last remaining information we have in the given data set (Table 1) which we may use for testing reaction hypotheses are the carbon isotope data. In the case of the sulfur isotope data we were able to ignore the small fractionation in the precipitation of sulfide minerals because of the very large (measured) fractionation that occurs during reduction of sulfate. No such large fractionations of carbon isotopes exist, and thus the carbon isotope evolution implied by each mass balance model is sensitive to the fractionation factor between solution and solid. The calculation of carbon isotopic evolution from Polk City

to Wauchula combines isotope dilution as described by isotope balance equations (similar to Eqn. 9 for sulfur) and the process of Rayleigh distillation. The carbon isotope evolution equation used to test reaction models 7–12 is summarized in Appendix 3, where a detailed example for model 7 is given.

In making calculations similar to those of Appendix 3, it is important to determine if the calculated value of $\delta^{13}C$ of the final water is sensitive to reaction path. Dependence on reaction path is tested by assuming different relative rates of dissolution of reactants along the path, but maintaining the same net mass transfer for each model. This is equivalent to assuming, for example, the rate of gypsum dissolution relative to that of dolomite differs along the flow path owing to possible heterogeneity of the mineralogy and/or differences in reaction kinetics for the same net mass transfer as in Table 6.

Figure 2A shows four hypothetical reaction paths computed between Polk City and Wauchula by varying the relative gypsum to dolomite solution rates for reaction model 7 of Table 6. In simulating the reaction paths, the irreversible net mass transfers of CO₂, CH₂O and FeOOH were computed in linear proportions to the net gypsum mass transfer. This assumption is justified since most of the mass transfer is determined by the dissolution of dolomite and gypsum. Thermodynamic constraints were used to determine the amounts of pyrite and calcite precipitated. We have chosen total dissolved sulfate as our progress variable which is nearly equal to the amount of gypsum dissolved.

Path 1 (Fig. 2A) assumes that gypsum is less abundant near the recharge area such that most of the dolomite dissolution occurs prior to contact of the ground water with gypsum. In simulating this reaction path in PHREEQE, it was found that the saturation index of dolomite (observed at Wauchula) was significantly exceeded early along reaction path 1. Thus, reaction path 1 as defined is thermodynamically impossible. A second reaction path (Path 1a) was then constructed to dissolve the maximum amount of dolomite relative to gypsum without exceeding the observed end point saturation index of dolomite as a function of reaction prog-

Table 6: Results of the Mass Balance Calculation for a System Partially Open to CO₂. Values of α_p in mmols/kg H₂O

Plausible Phases	Reaction Models					
	7	8	9	10	11	12
CaCO ₃	-1.84	-19.18	---	---	---	---
CaMg(CO ₃) ₂	0.96	---	---	---	---	---
CaSO ₄ ·2H ₂ O	1.68	1.68	1.68	1.68	1.68	1.68
CO ₂	0.53	0.53	0.49	0.47	0.57	0.56
CH ₂ O	0.17	0.17	0.16	0.18	---	---
FeOOH	0.03	0.03	-0.03	-0.002	-0.03	-0.002
FeS ₂	-0.03	-0.03	-0.03	---	-0.03	---
Ca _{.95} Mg _{.05} CO ₃	---	19.26	---	---	---	---
Ca _{1.05} Mg _{.90} Fe _{.05} (CO ₃) ₂	---	---	1.12	1.12	1.12	1.12
FeS	---	---	---	-0.05	---	-0.05
CH ₄	---	---	---	---	0.08	0.09
Ca _{.98} Mg _{.02} CO ₃	---	---	-2.09	-2.09	-2.09	-2.09

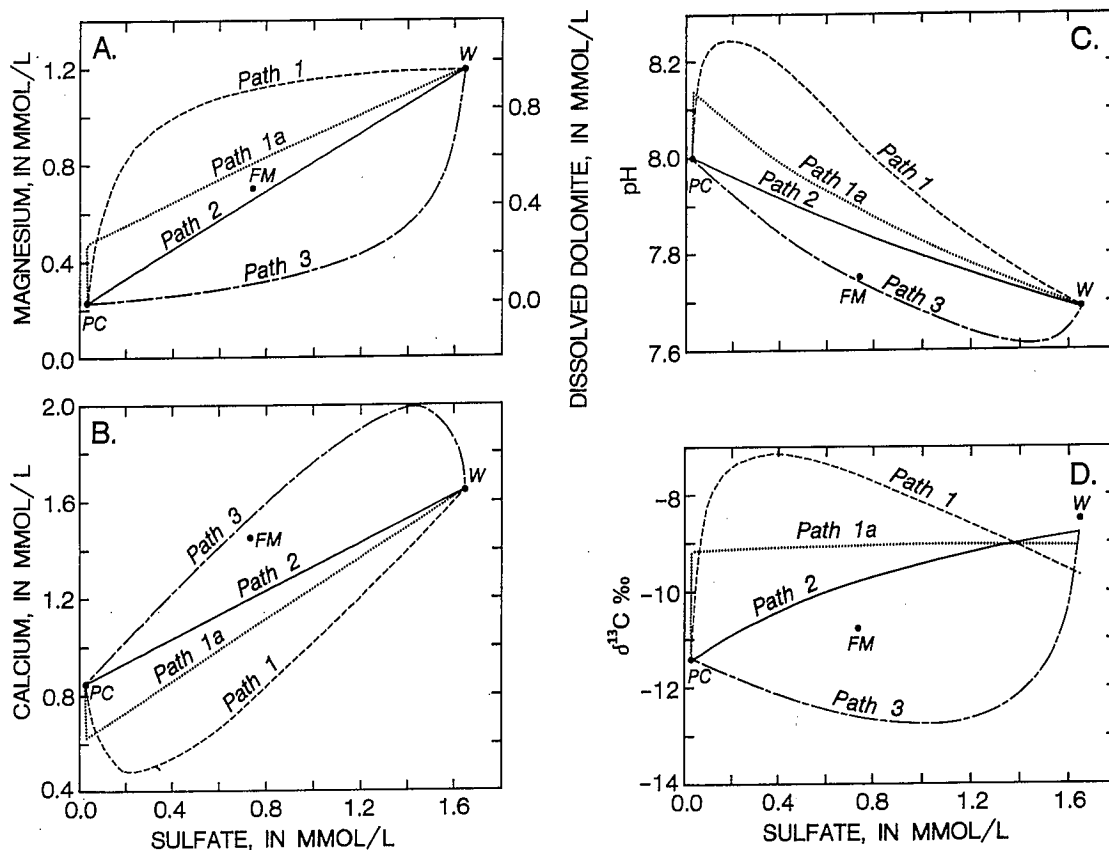


FIG. 2. Predicted variation of magnesium, calcium, pH and $\delta^{13}\text{C}$ in ground water between Polk City (PC) and Wauchula (W) assuming the relative rates of dolomite to gypsum dissolution defined in A.

ress. Path 1a then defines the thermodynamic upper bound of the dolomite mass transfer rate relative to gypsum. Path 2 is the net path, that is, the dolomite to gypsum solution rate is constant as a function of reaction progress as defined by the net mass transfer (Table 6). In the final path (Path 3) we assume that the kinetics of dolomite dissolution are slow relative to gypsum such that most of the gypsum dissolves before dolomite (Fig. 2A).

Figures 2B and 2C show the predicted variation of total calcium and pH as a function of the assumed reaction paths between Polk City (PC) and Wauchula (W). Notice that in Figs. 2A–2C the computed values of Mg_T , Ca_T and pH at Wauchula are identical to the observed. This is required since each path obeys the same net mass transfer as defined by the mass balance method, and since in our simulation, we accounted for the charge imbalances of the initial and final waters (Table 2) and the observed end point saturation index of calcite in determining the amount precipitated.

Contrary to the computed water composition which agrees perfectly with the observed end point value, the calculated end point value of $\delta^{13}\text{C}$ depends on the isotopic composition of incoming carbon and reaction path. Figure 2D shows the computed evolution of $\delta^{13}\text{C}$ between Polk City and Wauchula assuming $\delta^{13}\text{C}$ of incoming CO_2 and CH_2O is -25‰ and $\delta^{13}\text{C}$ of dolomite is 0‰ (see Appendix 3 for further details). The computed endpoint values of $\delta^{13}\text{C}$ for paths 1, 1a, 2 and 3 are -9.65 , -9.07 , -8.81 , and -8.87‰ , respectively. Excluding path 1 (-9.65‰) which is thermodynamically invalid, Figure 2D shows that for a wide range of reaction paths, the predicted value of $\delta^{13}\text{C}$ at Wauchula (for reaction model 7) is nearly insensitive to reaction path within the uncertainty of the observed $\delta^{13}\text{C}$

value ($\pm 0.1\text{‰}$). Reaction paths 1a, 2, and 3 all predict values of $\delta^{13}\text{C}$ at Wauchula slightly lighter than the observed (-8.5‰), and will closely match the observed value if, for example $\delta^{13}\text{C}$ of dolomite is near 0.7‰ rather than the assumed 0.0‰ .

Although variations in reaction path have no effect on the computed end point water composition when constrained by the observed net mass transfer, and have little effect on the computed final carbon isotopic composition, large differences in computed chemical and isotopic compositions are predicted at intermediate points depending on choice of reaction path. Included on Figure 2 are the observed values of Mg_T , Ca_T , pH and $\delta^{13}\text{C}$ at the intermediate well, Ft. Meade (FM). Figure 2 shows that the net path (path 2) closely approximates the dolomite and gypsum mass transfers at the intermediate well, but since total calcium, pH and $\delta^{13}\text{C}$ are not accounted for at the intermediate well by the net path, it is suggested that other irreversible mass transfers such as CO_2 and/or CH_2O do not vary linearly with the gypsum mass transfer. We will examine this question more closely later.

Since we have shown that the calculated endpoint $\delta^{13}\text{C}$ is nearly independent of reaction path, we have calculated $\delta^{13}\text{C}$ at Wauchula for reaction models 7–12 using the net path (Table 6). The isotopic calculations assume the carbon isotopic composition of organic matter and CO_2 is $-25.0\text{‰} \pm 5.0\text{‰}$, and methane was taken as -40.0 and -80.0‰ . Using these values for the additional carbon sources, $\delta^{13}\text{C}$ at Wauchula was calculated from Eqn. (A3.1) for a range of values of $\delta^{13}\text{C}$ of the magnesium source mineral. Table 7 summarizes values of the average $\delta^{13}\text{C}$ of incoming carbon, $\delta^{13}\text{C}^*$, and $\delta^{13}\text{C}$ of the magnesium source mineral,

Table 7: Results of Stable Carbon Isotope Calculations¹

Model	$\delta^{13}\text{C}^*_{\text{CH}_4}$	$\delta^{13}\text{C}^*_{\text{CO}_2}$	$\delta^{13}\text{C}^*_{\text{CH}_4}$
7	—	-6.18	0.7 ± 1.8
8	—	-7.36	-6.7 ± 0.2
9	—	-6.36	-0.9 ± 1.4
10	—	-6.36	-0.9 ± 1.4
11	-40.0	-6.36	-0.4 ± 1.3
11	-80.0	-6.36	1.0 ± 1.3
12	-40.0	-6.36	-0.3 ± 1.3
12	-80.0	-6.36	1.2 ± 1.3

¹ $\delta^{13}\text{C}_{\text{CH}_4\text{O}}$ and $\delta^{13}\text{C}_{\text{CO}_2}$ assumed to be

$-25.0 \pm 5.0\text{‰}$, $\delta^{13}\text{C}_0 = -11.4$
(Table 2), $m\text{C} = 2.843$, $m\text{CO} = 2.054$
(Table 2), $\epsilon_{\text{PS}} = 1.2\text{‰}$, calculations made at 25°C, results reported in ‰.

² Average carbon isotopic composition of incoming carbon required for each model to predict the observed $\delta^{13}\text{C}$ at Wauchula. See eqn. A3.4.

³ Carbon isotopic composition of the magnesium source mineral (see Table 5) required for each model to predict the observed $\delta^{13}\text{C}$ at Wauchula.

$\delta^{13}\text{C}^*$, that are required for each reaction model of Table 6 to predict the observed $\delta^{13}\text{C}$ at Wauchula (-8.5‰). (See Appendix 3.)

Two distinct stable carbon isotopic groupings of dolomite are observed in the Floridan aquifer: heavy dolomites which range from $+0.1$ to $+1.0\text{‰}$ and a lighter group which range from -3.1 to -7.5‰ $\delta^{13}\text{C}$ (HANSHAW and BACK, 1972). Although no isotopic data are available for the magnesian calcites in the Floridan aquifer, they are expected to be of biogenic marine origin and similar to marine calcites in the Floridan aquifer which range between -0.4 to $+0.6\text{‰}$ $\delta^{13}\text{C}$.

Comparison of the expected isotopic composition of magnesium source minerals in central Florida with the value required for each model to predict the observed $\delta^{13}\text{C}$ of Wauchula water (Table 7) indicates that model 8 (Table 6) may be eliminated from further consideration. Model 8 is insensitive to $\delta^{13}\text{C}^*$ of CH_4O and CO_2 because of the large implied mass transfer of carbon from Mg-calcite. Because we do not find or expect large masses of isotopically light magnesian calcites in central Florida, we may rule out magnesian calcites as the source of magnesium along the flow path.

All of the remaining models of Table 6 (7 and 9–12) predict the observed $\delta^{13}\text{C}$ at Wauchula if $\delta^{13}\text{C}$ of dolomite is assumed to be between -0.9 and 1.2‰ ($\pm \sim 1\text{‰}$). Thus, within the uncertainty of the isotopic data, only model 8 may be eliminated using carbon isotopic data. If the system is open to a source of methane (models 11 and 12), so little

methane is required in the mass balance (Table 6) that we would be unable to detect a significant shift in $\delta^{13}\text{C}$ at Wauchula even if $\delta^{13}\text{C}_{\text{CH}_4}$ varied between -40.0 and -80.0‰ .

We have now exhausted our available data in testing reaction models, yet multiple reactions remain. As the analytical data are saturation-insufficient with respect to all iron-bearing minerals, we may use the solubility calculations discussed earlier to test for thermodynamic inconsistencies in the calculated mass balance reactions.

Reaction model 7 shows a ferric hydroxide mineral as reactant and a ferrous sulfide mineral as product. Since we expect monotonic variations in reaction path, reaction model 7 will be thermodynamically invalid for a particular set of ferric hydroxide–ferrous sulfide minerals, if the final water is oversaturated with the ferric hydroxide reactant while just saturated with the ferrous sulfide product.

The remaining models 9–12 derive all reactant iron from dolomite. For these models, there are two product phases, a ferric hydroxide and ferrous sulfide mineral and no separate iron-bearing reactant. As it is likely that both of these products grow from significant oversaturation, there is no test, in the absence of analytical data for dissolved iron, for identifying thermodynamic violations of models 9–12. The solubility calculations can give us insights, however, into the non-equilibrium requirements of models 9–12.

Because the thermodynamic data for ferric hydroxide and ferrous sulfide minerals show a great deal of variability depending on crystallinity, we have considered a range of phases using thermodynamic data tabulated by BALL *et al.* (1980).

Using PHREEQE, ferrous iron in Wauchula water was constrained to satisfy saturation for a particular ferrous sulfide mineral (pyrite, mackinawite, or FeS-precipitate). The saturation indices of ferric hydroxide minerals (hematite, goethite, and amorphous ferric hydroxide) in the modified Wauchula water were then examined. The results are summarized in Table 8. These calculations show that the iron-mineral mass transfers in reaction model 7 are thermodynamically valid if the reactant ferric hydroxide is similar in stability to goethite or amorphous ferric hydroxide. Reaction model 7 is thermodynamically invalid if FeS and hematite are substituted for pyrite and FeOOH, respectively. Hematite, however, can be excluded from the plausible phases on the basis of petrographic evidence.

For models 9–12, the calculations of Table 8 show the final water at equilibrium with ferrous sulfide minerals is

Table 8: Testing Saturation-insufficient Data at Wauchula for Thermodynamic Violations¹

Iron Sulfide	Log K	Calculated	Predicted Saturation Indices		
		$m\text{T,Fe at Wauchula}$ ²	Hematite ³	Goethite ⁴	FeOOH ⁵
Pyrite ⁶	-18.469	1.27×10^{-16}	-16.90	-10.95	-15.36
Mackinawite ⁷	-4.361	3.76×10^{-8}	+0.05	-2.48	-6.89
FeS-precipitate ⁷	-3.915	1.95×10^{-7}	+1.48	-1.76	-6.17

¹ Calculations made using the computer code PHREEQE at the temperature of Wauchula ground water (25.4°C). Thermodynamic data from Ball *et al.* (1980).

² These amounts of ferrous iron added to Wauchula water cause changes in pH and pe of Wauchula water (Table 1) of less than 0.0012.

³ Hematite: $\text{Fe}_2\text{O}_3 + 6\text{H}^+ = 2\text{Fe}^{3+} + 3\text{H}_2\text{O}$, Log K = -4.038

⁴ Goethite: $\text{FeOOH} + 3\text{H}^+ = \text{Fe}^{3+} + 2\text{H}_2\text{O}$, Log K = 0.486

⁵ Amorphous FeOOH: $\text{FeOOH} + 3\text{H}^+ = \text{Fe}^{3+} + 2\text{H}_2\text{O}$, Log K = 4.891

⁶ Pyrite: $\text{FeS}_2 + 2\text{H}^+ + 2\text{e}^- = \text{Fe}^{2+} + 2\text{HS}^-$

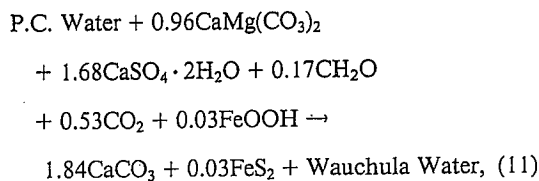
⁷ FeS: $\text{FeS} + \text{H}^+ = \text{Fe}^{2+} + \text{HS}^-$

significantly undersaturated with goethite and amorphous FeOOH, the likely *product* minerals. These calculations show that if the iron-mineral mass transfers of models 9–12 are thermodynamically valid, the ferrous sulfide mineral must be precipitating from significant oversaturation in order to account for the oversaturation required to precipitate FeOOH. As the Wauchula water is likely oversaturated with both ferrous sulfide and ferric hydroxide minerals, we have no basis for excluding reaction models 9–12 without obtaining reliable analytical data on dissolved ferrous and ferric iron.

In the above analysis we have considered 12 sets of plausible phases (Tables 3 and 5) and at this point five of these sets remain in consideration (7, 9–12). Many more reaction models are possible if we consider differing stoichiometries of calcite and dolomite and the choice of sulfide mineral stoichiometry. The carbon isotope calculations are not sensitive enough to make subtle distinctions in mineral stoichiometry within the uncertainty of the known isotopic data. As originally defined, our problem has led to multiple reaction models.

The elimination process has been successful in showing that (1) the reaction system must include a carbon source of valence greater than zero, otherwise the carbon balance would require much larger enrichments of $\delta^{34}\text{S}_{\text{SO}_4}$ at Wauchula, (2) the sulfur isotope data combined with a sulfur mass balance show that accompanying sulfate reduction, 1.68 mmols of gypsum should dissolve and 0.03 mmols of pyrite (or 0.06 mmol of FeS) should precipitate from each kg of water between Polk City and Wauchula, and (3) carbon isotopic calculations eliminate magnesian calcites as important reactants.

The average valence of carbon in the carbon source(s) is 3.0, as given by the reaction coefficients (α_p) of Table 6. We have tentatively included CO_2 (+4.0) with organic matter (0.0) or methane (−4.0) in our reaction models (Table 6). Data are not available to support or exclude an argument of a single (organic) carbon source of valence near 3.0. The reaction model that remains is one of incongruent dissolution of dolomite (dolomite dissolution accompanying calcite precipitation) driven irreversibly by gypsum dissolution. Accompanying the incongruent reaction is the oxidation of a small amount of organic carbon and sulfate reduction. Iron and sulfide concentrations are kept low by ferric hydroxide and probably pyrite solubilities. Along the flow path, the system is probably open to a source of CO_2 . The net reaction between Polk City and Wauchula is similar to:



where the reaction coefficients (in mmols per kg H_2O) are from reaction (7), Table 6.

Although we have gained considerable insight into the reactions in the Floridan aquifer through our modeling effort, the elimination process is far from complete. The most serious concern is the suggestion that the ground-water system is partially open to CO_2 , particularly since the deeper parts of the aquifer approximate a closed system. If the ground water were freely exchanging with the soil atmosphere, we would expect modern ^{14}C concentrations in the ground water, which is not the case. However, we cannot exclude the possibility of a very slow transport of soil or unsaturated zone CO_2 into the aquifer along the flow path (on the time scale of approximately one mmol CO_2 per l of ground water per 20,000 years), or alternatively, the possibilities of a deep source of CO_2 beneath the Floridan aquifer, or CO_2 production within the aquifer *via* fermentation (FOSTER, 1950). The carbon isotopic data and reaction models appear to be consistent with an isotopically light CO_2 source such as $-25.0 \pm 5.0\%$.

In Fig. 2, we showed that the magnesium concentration (and thus dolomite mass transfer) at the intermediate well (Ft. Meade) was accounted for by the net reaction path between Polk City and Wauchula. But, since the total calcium, pH, $\delta^{13}\text{C}$ (and total carbon) are not predicted by the net path (at Ft. Meade), it was suggested that the CO_2 and/or CH_2O irreversible mass transfers do not vary linearly with the amount of gypsum dissolved. As a means of demonstrating one of the uses of reaction-path calculations, we have considered the hypothesis that the source of CO_2 is the unsaturated zone associated with the recharge area near Polk City and that this CO_2 enters the ground water early along the flow path. We further assume that organic matter is more common in the deeper parts of the aquifer and is thus oxidized in the more distant points along the flow path.

In modeling the reaction path with PHREEQE, the overall reaction of model 7 (Table 6) was divided equally into early and later parts based on the net gypsum mass transfer. In both halves of the overall reaction, dolomite was dissolved in linear proportion to the net gypsum mass transfer while a constant supersaturation of calcite, at the observed value of Wauchula, was used to determine the mass of calcite precipitated. All of the net CO_2 mass transfer computed by the mass balance method between Polk City and Wauchula was entered linearly in the first half of reaction. In the second half of reaction, all of the CH_2O and FeOOH mass transfers computed between Polk City and Wauchula were entered linearly while maintaining equilibrium with pyrite.

Figure 3 shows agreement within the uncertainty of the analytical data in the computed Mg_T , Ca_T , C_T and pH at Ft. Meade supporting our assumption that CO_2 enters the aquifer early and CH_2O is oxidized late. Using 0‰ for $\delta^{13}\text{C}$ of dissolving dolomite, the *net* path (Fig. 2D) predicted a value of $\delta^{13}\text{C}$ at Ft. Meade that was more than 1‰ heavier than the observed, but by entering the CO_2 mass transfer early, the value of $\delta^{13}\text{C}$ predicted at Ft. Meade is within 0.2‰ of the observed.

Certainly one of the more important applications of reaction path calculations is the prediction of water composition at intermediate points along flow paths. Such modeling can define areas where additional data are needed to resolve reaction uncertainties. In our problem, we actually had analytical and isotopic data at an intermediate well and, therefore, most of the reaction information could have been gained by solv-

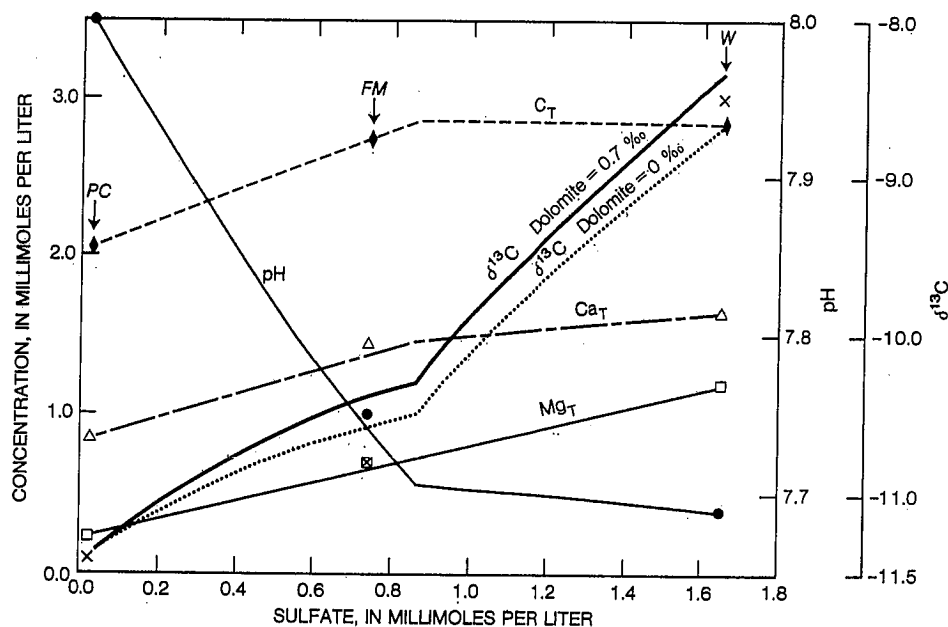


FIG. 3. Predicted reaction path between Polk City (PC) and Wauchula (W) assuming the net CO_2 mass transfer enters the ground water in the first half of reaction and organic matter is oxidized in the last half of reaction.

ing mass balance calculations for the paths Polk City to Ft. Meade and Ft. Meade to Wauchula, without the necessity of performing reaction-path calculations. The reaction path calculations demonstrate, though, that for reaction model 7, there is at least one thermodynamically valid reaction path that is consistent with the observations.

The reaction path calculations do not support the suggestion of a fermentation source of CO_2 , unless it can be reasoned that fermentation is important only along the initial parts of the flow path. The possibility of introducing methane to the Floridan aquifer (from presumably deep ground-water systems beneath the aquifer) cannot be excluded, but if methane is being introduced to the aquifer, our calculations show that less than 0.1 mmols of CH_4 per liter could react in the system between Polk City and Wauchula.

One of the important applications of reaction identification is in carbon-14 dating of ground water (WIGLEY *et al.*, 1978). In this case, a reaction model could be used to predict A_{nd} , the value of ^{14}C activity in the ground water at Wauchula if there were no radioactive decay. The value of A_{nd} is calculated in a manner similar to $\delta^{13}\text{C}$ (Appendix 3) (note that $\delta^{14}\text{C} = 10A - 1000$, where A is in ‰ modern). In calculating values of A_{nd} , all carbon sources other than CO_2 were assumed to be "old," with no ^{14}C content. The

CO_2 source was assumed to be either very old, such as from a deep source ($A_{\text{CO}_2} = 0.0\%$), or 50% modern, a reasonable value for unsaturated zone CO_2 . Thus, depending on our choice for the ^{14}C content of the CO_2 source, two values of A_{nd} were calculated. The time in years required for flow between Polk City and Wauchula, Δt , is calculated from the ^{14}C activity observed at Wauchula ($A = 4.4\%$, Table 1) and the calculated value of A_{nd} (using the known ^{14}C half-life)

$$\Delta t \text{ years} = \frac{5730}{\ln 2} \ln \left(\frac{A_{\text{nd}}}{A} \right). \quad (12)$$

It is of interest to calculate the uncertainty in age of Wauchula water resulting from differences in reaction stoichiometry and our alternative hypotheses in the nature of the CO_2 source. Table 9 gives calculated values of A_{nd} for models 7, and 9–12 (Table 6), flow times between Polk City and Wauchula, and the implied average flow velocity over the 68 km distance. The calculations of Table 9 demonstrate that the different stoichiometries of reaction models 7 and 9–12 lend only minor uncertainties to carbon-14 dating of Wauchula water. Larger uncertainties, on the order of 30%, remain if the CO_2 source is 0% modern rather than 50% modern. Accepting these uncertainties, the reaction modeling effort indicates flow velocities of 6 to 9 m/yr along the flow path. This estimate of velocity compares well with estimates based on hydrologic models of the Floridan aquifer between Polk City and Wauchula (7 to 10 m/yr, HANSHAW *et al.*, 1965).

SUMMARY AND CONCLUSIONS

Given the observed chemistry of a ground-water system, the number of plausible phases that might be reacting in the system is almost always larger than the number of elements required to define the composition of the plausible phases. As a result, multiple reaction hypotheses are generated. Reaction identification is a process of eliminating sets of plausible phases from further consideration. The elimination

Table 9: Flow Times and Velocities Based On Corrected ^{14}C .

Model	CO_2 source = 50% modern			CO_2 source = 0.0% modern		
	$A_{\text{nd}} (\%)$	Δt years	velocity m/yr	$A_{\text{nd}} (\%)$	Δt years	velocity m/yr
7	18.33	11,800	5.8	11.61	8,000	8.5
9	16.39	10,900	6.2	10.45	7,200	9.4
10	16.15	10,800	6.3	10.45	7,200	9.4
11	17.34	11,300	6.0	10.45	7,200	9.4
12	17.21	11,300	6.0	10.45	7,200	9.4

process utilizes both mass balance and reaction path calculations.

Mass balance calculations are regarded as an inverse problem in which a reaction model is constrained to satisfy the elemental composition of "initial" and "final" waters. Thermodynamic constraints are not an explicit part of the mass balance methodology. Reaction-path calculations, on the other hand, specify an initial composition of an aqueous phase and a variety of assumptions involving processes, such as irreversible reactions, assumed equilibrium with specified phases, etc., and then predict the evolution of water and rock as a function of reaction progress. The reaction path calculations are not explicitly constrained to satisfy chemical composition of the "final" water. Thus, we can compute mass balance models and attempt to find those that are thermodynamically rigorous, or we can calculate reaction paths and hope to find the appropriate process assumptions that calculate observed water compositions.

Our study of the reaction identification process indicates that mass balance calculations accounting for conservation of mass and electrons in net chemical reactions, when combined with the speciation calculation, are extremely useful in defining possible reactions from the observed data.

Since mass balance models are not constrained by thermodynamic criteria, it is usually necessary to check each model for thermodynamic violations. Several tests for thermodynamic violations in mass balance models are provided by results of the speciation calculations at the endpoints of the flow path. Thermodynamic tests over the entire flow path are provided by reaction-path simulations. If a reaction path is found that reproduces exactly the compositions of the initial and final waters for a particular set of plausible phases, the computed net mass transfer will be identical to that calculated by the mass balance method for the same plausible phases. Gained through the modeling exercise, though, is a demonstration that at least one thermodynamically valid reaction path exists for the net mass balance reaction.

Aside from thermodynamic criteria, further elimination of sets of plausible phases requires additional independent data for the system, such as detailed petrographic, mineralogic and isotopic information.

As an example of the principles of reaction identification, we have included a problem from the Floridan aquifer. Although requiring additional hydrologic, mineralogic, geologic and isotopic data, the reaction identification scheme allows elimination of seven of twelve proposed sets of plausible phases. All remaining reaction models are similar and indicate that between Polk City and Wauchula in central Florida the net reaction is the incongruent dissolution of dolomite (dolomite dissolution with calcite precipitation) driven irreversibly by gypsum dissolution, with accompanying sulfate reduction and conservation of iron and sulfide probably among ferric hydroxide and pyrite. The modeling suggests the ground-water system is open initially to CO_2 and reacts with organic carbon at more distant points along the flow path. The error in carbon-14 dating of the ground water due to uncertainties in the choice of stoichiometry of reactants and products appears to be small, relative to age errors introduced by the uncertainty in the nature and ^{14}C content of the external CO_2 source. Predicted flow velocities based on the corrected ^{14}C data are similar to those derived from hydrologic models.

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Acknowledgments—Many of the modeling concepts presented here resulted from a truly joint effort among the authors. Several sections and/or concepts, however, can be attributed to a single author and deserve such designation. The redox convention employed in PHREEQE, and its role in mass balance problems is due to Thorstenson who also defined the concepts of plausible phases, saturation-sufficient, and saturation-insufficient data. Parkhurst contributed thermodynamic criteria for testing mass balance models and formulated the mathematics defining the total set of mass balance models for a given set of plausible phases. The example section is due to Plummer.

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APPENDIX 1

Definition of operational valance

Our convention for accounting for electron transfer is as follows: 1) use the formal elemental valence for aqueous redox species; 2) use the sum of the formal valences of redox species which associate to form redox complexes; 3) use zero for non-redox species; 4) assign zero to the valence of H and O in aqueous species; 5) use zero for H^+ and OH^- ; 6) use -2.0 for $H_{2(aq)}^0$ and $+4.0$ for $O_{2(aq)}^0$. We define a redox species as a species of a particular element which can occur in more than one oxidation state in the aqueous environment. As examples, $v_{Fe^{2+}} = +2.0$ (Rule 1), $v_{SO_4^{2-}} = +6.0$ (Rules 1 and 4), $v_{FeSO_4} = +8.0$ (Rules 2 and 4), $v_{Na^+} = 0.0$ (Rule 3), $v_{Ca(OH)_2} = 0.0$ (Rules 3 and 4), $v_{H^+} = 0.0$ (Rule 5), $v_{H_{2(aq)}^0} = -2.0$ (Rule 6), $v_{H_2O} = 0.0$ (Rule 3). The operational valence of minerals, u_p , is calculated similar to that of aqueous species. The operational valence system defined here is internally consistent and greatly simplifies our book-keeping of electrons transferred during redox reactions. For further reference, Table A1.1 lists values of v_i for selected species and values of u_p for selected minerals. In non-redox problems the redox state equation degenerates to a linear combination of the mass balance equations and is omitted.

Mass balance problems of excess plausible phases

If $\bar{\alpha}_1, \bar{\alpha}_2, \dots, \bar{\alpha}_N$ are solutions to the N subsets of plausible phases ($\alpha_{i,1}, \alpha_{i,2}, \dots, \alpha_{i,p,\phi}$), then a new solution can be found, $\bar{\alpha}'$, where

$$\bar{\alpha}' = \sum_{i=1}^N x_i \alpha_i \quad (A1.1)$$

and

$$\sum_{i=1}^N x_i = 1. \quad (A1.2)$$

In this way, solutions to the linear equations may be constructed to involve mass transfer of more than E phases. For example, consider reactions in a coal spoils pile open to CO_2 and O_2 and containing pyrite, calcite, goethite and siderite. This problem involves six plausible phases for which we may write only five linear equations (four mass balance equations on Fe, S, C and Ca of the form of Eqn. (4) and one redox state equation similar to Eqn. (5)). We have an indeterminate situation with five equations and six unknowns. If we find two solutions to the mass balance and redox state equations, $\bar{\alpha}_1$ and $\bar{\alpha}_2$ ($\bar{\alpha}_1$ corresponding, for example, to pyrite, calcite, goethite, CO_2 , and O_2 with $\alpha_{siderite} = 0$; and $\bar{\alpha}_2$ corresponding to pyrite, calcite, goethite, siderite and O_2 with $\alpha_{CO_2} = 0$) then, for arbitrary values of x_1 ($x_2 = 1 - x_1$), $\bar{\alpha}'$ is also a solution of the equations where

$$\alpha'_{pyrite} = x_1 \alpha_{1,pyrite} + x_2 \alpha_{2,pyrite} \quad (A1.3)$$

$$\alpha'_{calcite} = x_1 \alpha_{1,calcite} + x_2 \alpha_{2,calcite} \quad (A1.4)$$

$$\alpha'_{CO_2} = x_1 \alpha_{1,CO_2} + x_2 \cdot 0 \quad (A1.5)$$

$$\alpha'_{O_2} = x_1 \alpha_{1,O_2} + x_2 \alpha_{2,O_2} \quad (A1.6)$$

Table A1.1: Definition of v_i and u_p for selected aqueous species and minerals¹

Species	v_i	Mineral	u_p
Ca^{2+}	0.0	$CaCO_3$	4.0
Mg^{2+}	0.0	$CaMg(CO_3)_2$	8.0
Na^+	0.0	5% Fe-Dol.	8.1
K^+	0.0	$NaCl$	0.0
Fe^{2+}	2.0	$CaSO_4$	6.0
Fe^{3+}	3.0	$FeOOH$	3.0
Cl^-	0.0	Fe_2O_3	6.0
SO_4^{2-}	6.0	$FeCO_3$	6.0
H_2S^0	-2.0	FeS	0.0
HS^-	-2.0	FeS_2	0.0
HCO_3^-	4.0	$CaSO_4 \cdot 2H_2O$	6.0
CH_4^0	-4.0	"CH ₄ O"	0.0
$CaHCO_3^+$	4.0	$KAlSi_3O_8$	0.0
$H_2CO_3^0$	4.0	$Al(OH)_3$	0.0
N_2^0	0.0	KOH	0.0
NO_3^-	5.0	H_2S gas	-2.0
NH_4^+	-3.0	CH_4 gas	-4.0
$Fe(OH)_2^+$	3.0	CO_2 gas	4.0
$FeSO_4^0$	8.0	H_2 gas	-2.0
H^+ , OH^-	0.0	O_2 gas	4.0
H_2O^0	-2.0	N_2 gas	0.0
O_2^0	4.0	NH_3 gas	-3.0
H_2O	0.0	CaF_2	0.0

¹ The list is obviously incomplete but should serve as an example for other species and minerals that may be considered.

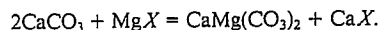
² $Ca_{1.05}Mg_{.90}Fe_{.05}(CO_3)_2$

$$\alpha'_{Goethite} = x_1 \alpha_{1,Goethite} + x_2 \alpha_{2,Goethite} \quad (A1.7)$$

$$\alpha'_{Siderite} = x_1 \cdot 0 + x_2 \alpha_{2,Siderite} \quad (A1.8)$$

Other combinations of plausible phases are possible, and it is necessary to check each model for thermodynamic violations, as discussed in the text.

An indeterminate problem arises when the stoichiometries of the E plausible phases are not linearly independent. An obvious example of non-independent stoichiometries is the inclusion of polymorphs in the mass balance calculation. Other occurrences of non-independent stoichiometries are less obvious. For example, suppose the evolution of a final water from an initial water involves reactions with calcite, dolomite, Na^+/Ca^{2+} ion exchange and Na^+/Mg^{2+} ion exchange. We have four plausible phases for which four mass balance equations could be written (for Ca, Mg, Na, and C). The mass balance cannot be solved, however, because in this case the stoichiometries of the four phases are not independent, that is, we can write the formation of dolomite in terms of the stoichiometries of the other three phases



Definition of the total set of mass balance models for a given set of plausible phases

Let the linear equation be written as follows:

$$\overline{\Delta M} = \sum_{i=1}^{\phi} \alpha_p \bar{b}_p \quad (A1.9)$$

where $\overline{\Delta M}$ is the vector of changes in concentration and \bar{b}_i is the vector of stoichiometric coefficients of the i th plausible phase. $\overline{\Delta M}$ and \bar{b}_i are J -tuples $\overline{\Delta M} = (\Delta M_1, \dots, \Delta M_J)$ and $\bar{b}_i = (b_{i,1}, \dots, b_{i,J})$. Solutions to the equation are ϕ -tuples $\bar{\alpha} = (\alpha_1, \dots, \alpha_p)$ where α_p is the mass transfer of the p th phase. It can be shown (see PAIGE and SWIFT, 1961, p. 60-66) that the solution to the homogeneous equation,

$$0 = \sum_{p=1}^{\phi} \alpha_p \bar{b}_p \quad (A1.10)$$

is a vector space of dimension $\phi - J$. Thus if $\phi - J$ linearly

independent $\bar{\alpha}$, ($\bar{\alpha}_1, \bar{\alpha}_2, \dots, \bar{\alpha}_{\phi-j}$) are found, then all of the solutions to Eqn. (A1.10) are defined by linear combinations of those vectors. Let the set of all solutions to Eqn. (A1.10) be called V . Then if $\bar{\alpha}_s$ is a solution to Eqn. (A1.9) and if v is any element of V , $\alpha_s + v$ is a solution to Eqn. (A1.9). Furthermore, all solutions to Eqn. (A1.9) can be written in this form. In a mathematical sense, one solution to Eqn. (A1.9) and $\phi - J$ linearly independent solutions to Eqn. (A1.10) determine all possible solutions to a mass balance problem.

Calculation of the total Gibbs free energy change for a net mass balance model

If the analytical data are saturation-sufficient, it is also theoretically possible to calculate the total free energy change for a net mass balance reaction model. Following WALL (1965, p. 218–221), the change in Gibbs free energy for a net isothermal reaction is

$$\Delta G = G' - G = \sum_{i=1}^I n'_i \mu'_i - \sum_{i=1}^I n_i \mu_i + \sum_{p=1}^P n_p \mu'_p \quad (\text{A1.11})$$

where n_i is the total number of moles of the i^{th} aqueous species (including water) in solution, μ_i is the chemical potential of the i^{th} species, n_p is the total mass transfer of the p^{th} phase (in moles), and μ_p is the chemical potential of the p^{th} phase. The prime refers to quantities calculated from the final water composition and non-primed quantities are from the initial water. Substituting the definition $\mu_i = \mu_i^0 + RT \ln a_i$ where μ_i^0 is the standard chemical potential and a_i is the activity of the i^{th} species; and performing all calculations relative to one kg H_2O , it can be shown that

$$\Delta \bar{G} = 2.303RT \left[\sum_{i=1}^I m_i \log \frac{a'_i}{a_i} + \sum_{p=1}^P \alpha_p SI'_p \right] \quad (\text{A1.12})$$

where $\Delta \bar{G}$ is the change in Gibbs free energy per kg H_2O , m_i is the molality of the i^{th} species (including water where $m_{\text{H}_2\text{O}} = 55.509$) in the initial solution, and α_p is defined by the mass balance calculation (Eqns. 4–5).

Calculation of the first summation in Eqn. (A1.12) requires definition of the activity of water in mixed electrolyte solutions, plus thermodynamic speciation calculations for the initial and final waters. The importance of the activity of water in Eqn. (A1.12) cannot be overlooked because, even though the term $\log a'_{\text{H}_2\text{O}}/a_{\text{H}_2\text{O}}$ is usually only slightly less than zero, it is multiplied by 55.509 in the summation. In comparison, other dissolved species may have much larger values of the term $\log a'_i/a_i$ but are multiplied by m_i values orders of magnitude smaller than that of water. Using the approximation (GARRELS and CHRIST, 1965) for the activity of water in dilute solutions

$$a_{\text{H}_2\text{O}} \approx 1.0 - 0.017 \sum_{i=1}^I m_i, \quad (\text{A1.13})$$

preliminary calculations indicate that for typical ground waters with total dissolved solids increasing down hydrologic gradient, the first summation in Eqn. (A1.12) is negative.

The second summation in Eqn. (A1.12) involves the mass transfer coefficients, α_p , defined by the mass balance calculation and the saturation indices of all phases in the reaction model. As discussed earlier, the product $\alpha_p SI'_p$ will be negative for thermodynamically valid reactions; thus, if the reaction is thermodynamically feasible, the second summation of Eqn. (A1.12) will be negative.

APPENDIX 2

MASS BALANCE EXAMPLE INCLUDING CONSERVATION OF ELECTRONS AND LINEAR SULFUR ISOTOPE EQUATION

In calculating the net mass transfer in the evolution of Polk City water to water at Wauchula, three types of equa-

tions are solved simultaneously: 1) chemical mass balance (Eqn. 4), 2) conservation of electrons (Eqn. 5), and 3) a linear isotope balance equation (Eqn. 9). These equations are developed below for a reaction model that assumes the following set of seven plausible phases: Calcite (CaCO_3), Dolomite ($\text{CaMg}(\text{CO}_3)_2$), Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), organic matter (CH_2O), Carbon Dioxide (CO_2), Ferric Hydroxide (FeOOH), and Pyrite (FeS_2), (model 7 of Table 5).

Chemical mass balance

Five elements (excluding H and O) are required to define the stoichiometry of the plausible phases (Ca, Mg, C, S, and Fe). Using values of $\Delta m_{T,k}$ (in mmol/kg H_2O) from Table 2, the five mass balance equations (following the form of Eqn. 4) are:

$$\alpha_{\text{calcite}} + \alpha_{\text{dolomite}} + \alpha_{\text{gypsum}} = \Delta m_{T,\text{Ca}} = 0.799 \quad (\text{A2.1})$$

$$\alpha_{\text{dolomite}} = \Delta m_{T,\text{Mg}} = 0.963 \quad (\text{A2.2})$$

$$\alpha_{\text{calcite}} + 2\alpha_{\text{dolomite}}$$

$$+ \alpha_{\text{CH}_2\text{O}} + \alpha_{\text{CO}_2} = \Delta m_{T,\text{C}} = 0.789 \quad (\text{A2.3})$$

$$\alpha_{\text{gypsum}} + 2\alpha_{\text{pyrite}} = \Delta m_{T,\text{S}} = 1.624 \quad (\text{A2.4})$$

$$\alpha_{\text{FeOOH}} + 2\alpha_{\text{pyrite}} = \Delta m_{T,\text{Fe}} = 0.0 \quad (\text{A2.5})$$

Values of α_p are negative for precipitation and positive for dissolution, and have units of mmols/kg H_2O .

Conservation of electrons

Since our problem involves changes in oxidation state, one equation of the form of Eqn. (5) may be included. Using the value of ΔRS defined between final and initial water (Table 2) and the given set of plausible phases, the conservation of electron equation is:

$$4\alpha_{\text{calcite}} + 8\alpha_{\text{dolomite}} + 6\alpha_{\text{gypsum}} + 0\alpha_{\text{CH}_2\text{O}} + 4\alpha_{\text{CO}_2}$$

$$+ 3\alpha_{\text{FeOOH}} + 0\alpha_{\text{pyrite}} = \Delta RS = 12.620. \quad (\text{A2.6})$$

Note that the pyrite and organic matter terms drop out of the electron conservation equation because their operational valence is zero. The coefficient for the dolomite term (=8) is the product of the operational valence of carbon in dolomite (=4) and the stoichiometric coefficient of carbon in dolomite (=2).

Linear isotope equation

Isotope balance equations may be included with the linear mass balance and electron balance equations provided the reaction is either congruent (*i.e.* mineral dissolution only), or, if incongruent, the fractionation between solution and precipitating solid can be neglected. Of the two elements for which we have isotopic data (C and S) both are involved in incongruent reactions (precipitation of calcite and pyrite). Because of the small changes in carbon isotope values along the flow path, the precipitation of calcite must be treated as a (non-linear) Rayleigh distillation process (see Appendix 3) and may not be approximated with a linear isotope equation. On the other hand, the sulfur isotopes are involved in a very large fractionation during sulfate reduction of approximately 55‰ along the flow path between Polk City and Wauchula and we are safe in ignoring the small fractionation between dissolved total sulfide and pyrite (of perhaps 1 to 2‰). Therefore, following the form of Eqn. (9) the linear sulfur isotope balance equation is

$$\alpha_{\text{gyp}} \delta^{34}\text{S}_{\text{gyp}} + 2\alpha_{\text{pyrite}} \delta^{34}\text{S}_{\text{pyrite}} = \Delta^{34}\text{S} \quad (\text{A2.7})$$

where

$$\Delta^{34}\text{S} = [m_{T,\text{S}} \delta^{34}\text{S}_T]_{\text{W}} - [m_{T,\text{S}} \delta^{34}\text{S}_T]_{\text{PC}}. \quad (\text{A2.8})$$

The isotopic composition of total dissolved sulfur $\delta^{34}\text{S}_T$ at Wauchula is

$$\delta^{34}\text{S}_T = \frac{m_{\text{T,SO}_4} \delta^{34}\text{S}_{\text{SO}_4} + m_{\text{T,H}_2\text{S}} \delta^{34}\text{S}_{\text{H}_2\text{S}}}{S_T} \quad (\text{A2.9})$$

The isotopic composition of sulfate and sulfide at Wauchula are given in Table 1 (24.9‰ and -32.9‰, respectively). The total concentrations of sulfate and sulfide at Wauchula are given in Table 2 (1.614 mmol/kg H₂O and 0.035 mmol/kg H₂O, respectively). These two constituents are combined to give S_T (1.649 mmol/kg H₂O). Using these values $\delta^{34}\text{S}_T$ at Wauchula is 23.673‰. Since dissolved sulfides are not present in the Polk City water, $\delta^{34}\text{S}_T$ at Polk City is that of sulfate alone (~14‰, Table 1). Using these values of $\delta^{34}\text{S}_T$ and the total concentrations of sulfur at Wauchula and Polk City (1.649 and 0.025, respectively, Table 2), $\Delta^{34}\text{S}$ from Eqn. (A2.8) is 38.687. Using the $\delta^{34}\text{S}$ values of +22‰ for dissolving gypsum and -32.9‰ for precipitating pyrite (which ignores a small fractionation between solution and solid), the linear sulfur isotope equation (Eqn. A2.7) is

$$22.\alpha_{\text{gyp}} - 65.8\alpha_{\text{pyrite}} = 38.687. \quad (\text{A2.7})$$

Equations (A2.1)–(A2.7) are linear, independent and may be solved simultaneously using linear algebra techniques (see BALANCE, PARKHURST *et al.*, 1982) to yield the unknown values of α_p , and give $\alpha_{\text{calcite}} = -1.842$, $\alpha_{\text{dolomite}} = 0.963$, $\alpha_{\text{gypsum}} = 1.678$, $\alpha_{\text{CH}_2\text{O}} = 0.171$, $\alpha_{\text{CO}_2} = 0.534$, $\alpha_{\text{FeOOH}} = 0.027$, and $\alpha_{\text{pyrite}} = -0.027$ (Table 6). If the chosen set of plausible phases for reaction model 7 correctly includes the true reactant and product phases between Polk City and Wauchula, the net reaction is Polk City water + 1.678 Gypsum + 0.963 Dolomite + 0.171 CH₂O + 0.534 CO₂ + 0.027 FeOOH → Wauchula water + 1.842 Calcite + 0.027 Pyrite.

APPENDIX 3 EVALUATION OF THE STABLE CARBON ISOTOPE DATA

Each reaction model of Table 6 involved input of three separate carbon sources (such as dolomite, CO₂, and CH₂O) and precipitation of calcite. The isotopic composition of carbon precipitated in calcite and the remaining carbon isotopic composition of the ground water depends on the non-linear fractionation between precipitating calcite and solution, and linear isotope dilution from carbon sources. For the case of three carbon inputs and one fractionating output (Table 6), the isotopic evolution equation is (WIGLEY *et al.*, 1978, 1979)

$$\delta^{13}\text{C}_{\text{final}} = \frac{\left[\left(\bar{\beta} \delta^{13}\text{C}_0 - \delta^{13}\text{C}^* + \frac{\epsilon_{\text{ps}}}{\Gamma^T} \right) \left(\frac{m\text{C}}{m\text{C}_0} \right)^{\xi} - \frac{\epsilon_{\text{ps}}}{\Gamma^T} + \delta^{13}\text{C}^* \right]}{\bar{\beta}} \quad (\text{A3.1})$$

where $\delta^{13}\text{C}_{\text{final}}$ is the carbon isotopic composition of the final water (Wauchula) predicted by a particular reaction model. In Eqn. (A3.1), ϵ_{ps} is the (additive) fractionation between precipitating solid (p) and solution (s). ϵ_{ps} is related to the fractionation factor f_{ps} ($f_{\text{ps}} = R_p/R_s$; R_p and R_s being the ¹³C/¹²C ratio of the precipitate and solution) by

$$\epsilon_{\text{ps}} = 1000(f_{\text{ps}} - 1) \approx \delta^{13}\text{C}_p - \delta^{13}\text{C}_s. \quad (\text{A3.2})$$

Values of ϵ_{ps} were calculated from MOOK (1979, written commun.) which gives results at these temperatures similar to calculations based on the compilation of DEINES *et al.* (1974) (see Fig. 3 of WIGLEY *et al.*, 1978). Along the flow path between Polk City and Wauchula ϵ_{ps} is near 1.2‰. The

ratio of total carbon input along the flow path to that precipitated, Γ^T , is given by

$$\Gamma^T = \sum_{p=1}^3 \Gamma_p = \frac{|dI_1|}{|dO|} + \frac{|dI_2|}{|dO|} + \frac{|dI_3|}{|dO|}, \quad (\text{A3.3})$$

for the case of three incremental inputs dI_p and one output dO of carbon. The term $\delta^{13}\text{C}^*$ defines the average carbon isotopic composition of carbon input to the reaction. For the case of 3 inputs

$$\delta^{13}\text{C}^* = \frac{\sum_{p=1}^3 \Gamma_p \delta^{13}\text{C}_p^*}{\Gamma^T} = \frac{\sum_{p=1}^3 b_{p,c} \alpha_p \delta^{13}\text{C}_p^*}{\sum_{p=1}^3 b_{p,c} \alpha_p} \quad (\text{A3.4})$$

where $\delta^{13}\text{C}_p^*$ is the isotopic composition of the p^{th} carbon source, α_p is the number of mmoles of the i^{th} source in the reaction (Table 6), and $b_{p,c}$ is the stoichiometric coefficient of carbon in the p^{th} carbon source. The terms $\bar{\beta}$ and ξ simplify the algebra and are defined by

$$\bar{\beta} = 1 + \left(\frac{10^{-3} \epsilon_{\text{ps}}}{\Gamma^T} \right) \quad (\text{A3.5})$$

and

$$\xi = \frac{\bar{\beta} \Gamma^T}{1 - \Gamma^T} \quad (\text{A3.6})$$

(see WIGLEY *et al.*, 1978). The remaining terms in Eqn. (A3.1), $\delta^{13}\text{C}_0$, $m\text{C}_0$, and $m\text{C}$ are the carbon isotopic composition and total molality of carbon in the initial water (Polk City) and the total molality of carbon in the final water (Wauchula).

As an example of the use of Eqn. (A3.1), we again consider reaction model 7 between Polk City and Wauchula. The combined mass balance, conservation of electrons and sulfur isotope balance equations imply the following carbon mass transfers along the flow path (in mmol/kg H₂O): $\alpha_{\text{dolomite}} = 0.963$, $\alpha_{\text{CO}_2} = 0.534$, $\alpha_{\text{CH}_2\text{O}} = 0.171$ and $\alpha_{\text{calcite}} = -1.842$ (Table 6, and Appendix 2). From Eqn. (A3.3) we find

$$\Gamma^T = \frac{2\alpha_{\text{dolomite}} + \alpha_{\text{CO}_2} + \alpha_{\text{CH}_2\text{O}}}{|\alpha_{\text{calcite}}|} = 1.42834 \quad (\text{A3.7})$$

If the carbon isotopic compositions of dolomite, CO₂ and CH₂O are 0.0‰, -25‰ and -25‰ respectively, the average isotopic composition of incoming carbon, $\delta^{13}\text{C}^*$, is (Eqn. A3.4) -6.70‰. Values of $\bar{\beta}$ and ξ (Eqns. A3.5–A3.6) for this example are 1.000840136 and -3.337395527. Values of the remaining terms in Eqn. (A3.1) come from Tables 1 and 2 ($\delta^{13}\text{C}_0 = -11.4$ ‰; $m\text{C}_0 = 2.054$; $m\text{C} = 2.843$). Using these values for the terms in Eqn. (A3.1), the calculated carbon isotopic composition of water at Wauchula is -8.84‰ which compares well with -8.5‰ measured for Wauchula water (Table 1). In practice it is convenient to find the value of $\delta^{13}\text{C}^*$ that is required for Eqn. (A3.1) to predict the observed $\delta^{13}\text{C}$ in the final water. In this example a value of $\delta^{13}\text{C}^*$ of -6.18‰ will, through Eqn. (A3.1) and the mass transfer coefficients of reaction model (Table 6), predict the observed $\delta^{13}\text{C}$ at Wauchula. From Eqn. (A3.4) we find that if $\delta^{13}\text{C}$ of CH₂O and CO₂ sources are -25‰, then the average isotopic composition of incoming dolomite must be 0.7‰ for the given reaction model to predict the observed $\delta^{13}\text{C}$ at Wauchula. Assigning an uncertainty of ±5‰ to the isotopic compositions of CH₂O and CO₂, we may repeat the calculation and determine the sensitivity of the implied value of $\delta^{13}\text{C}$ for reacting dolomite to uncertainties in the other isotopic data used. Such an analysis leads to 0.7 ± 1.8 ‰ for reaction model 7 (Table 7).

