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THE MASS BALANCE APPROACH: APPLICATION TO INTERPRETING THE CHEMICAL EVOLUTION OF HYDROLOGIC SYSTEMS*

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ABSTRACT. Mass balance calculations are applied to observed chemical and isotopic data of three natural water systems involving carbonate reactions in order to define mineral stoichiometry of reactants and products, relative rates of reactions, and mass transfer. One study evaluates reactions in a lagoon on the east coast of the Yucatan Peninsula, Mexico, into which groundwater discharges and mixes with seawater. Calculations test the extent to which conservative mixing reactions, variable fluxes of CO_2 gas, and dissolution and precipitation of $CaCO_3$ influence the observed water chemistry. Two other examples deal with identification of reactions, mass transfer, and apparent rates of reactions in part of the Tertiary limestone aquifer of Florida (Floridan aquifer) and the Mississippian limestone (Madison) aquifer near the Black Hills, S. Dak. Our calculations show that chemical reactions in both groundwater systems are driven irreversibly by solution of gypsum or anhydrite, which causes additional solution of dolomite and precipitation of $CaCO_3$ (de-dolomitization). ^{14}C ages corrected for the derived mass transfer permit comparison of apparent rates of reactions among hydrologic systems.

INTRODUCTION

Predictive models for the chemistry of water in hydrologic systems require information on the rates of reactions occurring in the systems. Reaction rate data can be obtained through at least two approaches: (1) theoretical and experimental study of the kinetics of all possible reactions for the system, and (2) application of mass balance calculations to observed chemical and isotopic data from natural water systems. While the first approach is fundamental and ultimately must prevail, the results of most laboratory kinetic studies for mineral-water reactions are, unfortunately, years from direct application to field situations. For purposes of modeling chemical reactions in regional aquifers, application of mass balance calculations to field data is, for the present, the necessary choice for obtaining reaction rate information.

An important philosophical distinction exists between the two approaches to model reaction in natural water systems: the first uses fundamental thermodynamic and kinetic information to determine which reactions can occur in the system, whereas the second uses mass balance calculations to identify reactions that cannot occur in the system. Proof of reaction is never positive with the mass balance approach, but through a series of elimination processes, there often remains a single reaction model that is consistent with the observed chemical and isotopic data. Rates of reaction are then calculated from the mass transfer implied by the reaction model combined with consideration of total reaction time in the system. In the context of this paper, mass transfer is the *net* amount (in moles per kg H_2O) of each mineral (or gas) transferred from one phase to another (such as, for dissolution, from the solid to aqueous phase). Total reaction time can be estimated from knowledge of the

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hydrology of the system or, as used here, from ^{14}C ages of waters corrected for the implied mass transfer.

Mass balance calculations are a familiar tool of geochemists studying the chemical evolution of water and rock (see, for example, Mackenzie and Garrels, 1966; Garrels and Mackenzie, 1967; Garrels, 1967; Cleaves, Godfrey, and Bricker, 1970). The possibility of deriving information on rates of reactions from field hydrochemical data was recognized by Mercado and Billings (1975). Palciauskas and Domenico (1976) and Domenico (1977) have considered theoretical aspects of incorporating empirical rate equations with hydrodynamic transport in groundwater systems. Current problems affecting the development of geochemical models in groundwater systems are reviewed by Back and Cherry (1976). The present study combines geochemical mass balances with thermodynamically rigorous reaction simulation methods to predict the mass transfer that is consistent with the observed stable-carbon isotopic composition. As our examples demonstrate, this approach can be extremely useful in improving our understanding of the geochemical processes in hydrologic systems and in providing information on rates of reactions.

This paper summarizes the methodology of the mass balance approach and applies this method to three natural water systems involving carbonate reactions. The first study evaluates reactions in a lagoon on the east coast of the Yucatan Peninsula, Mexico, into which groundwater discharges and mixes with seawater (Back and others, 1979). Calculations test the extent to which homogeneous mixing reactions, variable fluxes of CO_2 gas, and dissolution and precipitation of $CaCO_3$ influence the observed water chemistry. The other two examples deal with reactions in groundwater flowing through lithologies dominated by calcite and dolomite and containing lesser amounts of gypsum or anhydrite. Two groundwater systems are studied: the Tertiary limestone aquifer in Florida (Floridan aquifer) (Plummer, 1977) and the Mississippian Madison Limestone aquifer near the Black Hills, S. Dak. (Back and others, 1980). Whereas the Florida system is virtually isothermal ($\cong$25°C), the water in the Madison system increases from 5° to approx 70°C downgradient in the area studied. Parallel calculations for Florida and the Black Hills allow comparison between the two flow systems of (1) mass transfer, (2) age of ground water, (3) mean flow velocity, and (4) apparent rates of reaction.

THE MASS BALANCE APPROACH

If the change in water composition between arbitrary starting and ending points in a ground-water system can be attributed only to effects of reactions, the net chemical reactions accounting for the change can be quantified by means of mass balance relations. Furthermore, if the system is at steady state, that is, the solution composition remains constant with time at a given position, knowledge of mass transfer and flow times between starting and ending points can be used to compute average rates of net reactions. We have selected field examples that,

based on our knowledge of the hydrology of these systems, meet the above prerequisite conditions for use of chemical mass balances. (For a formal justification for the use of chemical mass balances in hydrologic systems, see Wigley, Plummer, and Pearson, 1978, app A). In the field examples considered, we have applied mass balance relations to regional aquifer systems in which three chemical processes are important: (1) mixing two end-member waters, (2) variable fluxes of carbon dioxide gas, and (3) mineral dissolution or precipitation.

In the case of mixing two end-member waters, mass balance can be applied to a particular constituent, such as chloride used here, that is conserved in the mixing process; this then defines the fraction of each end-member water in the resulting mixture. For example, if $m_{i,mix}$ is the molality of a conservative constituent, i, in a mixture of two end-member waters, and $m_{i,1}$ and $m_{i,2}$ are the molalities of i in the end-members 1 and 2, mass balance on i gives

$$m_{i,mix} = xm_{i,1} + (1\text{-}x)m_{i,2}, \tag{1}$$

where x is the mixing fraction of water 1 in the mixture. The fraction of water 1 in the mixture is then given by

$$x = \frac{m_{i,mix} - m_{i,2}}{m_{i,1} - m_{i,2}}. \tag{2}$$

The mixing fraction for this conservative constituent can then be applied to all other constituents in the end-member waters to estimate what their total concentrations would be in the mixture, if they too were conserved during mixing. Application of mass balance relations to the differences in composition between the computed conservative mixture and the observed water allows estimation of the magnitude of non-conservative processes, such as CO_2 outgassing, photosynthesis, and mineral dissolution or precipitation, affecting the chemical evolution of the mixture.

In general, we are concerned with using mass balance relations to define the mass transfer involved in the chemical evolution of one water to another. In our study of a lagoon on the east coast of the Yucatan Peninsula, Mexico, the observed water chemistry is assumed to have evolved by conservative mixing and by non-conservative processes of CO_2 outgassing (or photosynthesis) and dissolution or precipitation of calcium carbonate. In our examples dealing with the chemical evolution of groundwater, it is assumed that water originating in the recharge areas of regional carbonate rock aquifers evolves by reaction with the host rock, as it flows down gradient to distant points in the systems.

Knowing the composition of the initial and final water and having defined a net geochemical reaction (that is, having selected a hypothetical set of reactants and products), a mass balance can be made on the change

in total molality of the c^{th} constituent along the reaction path. The mass balance consists of n equations, one for each constituent, similar to

$$\left.\sum_{j=1}^{\phi} \alpha_j \beta_{c,j} = \Delta m_c \right| \quad c = 1,n \tag{3}$$

where ϕ is the total number of minerals and gases (reactants or products) in the mass balance reaction, n is the minimum number of constituents necessary to define the composition of the chosen minerals and gases, α_j is the stoichiometric (reaction) coefficient of the j^{th} mineral or gas in the mass balance reaction in moles per kg H_2O (with positive sign for reactants and negative sign for products), $\beta_{c,j}$ is the stoichiometric coefficient of the c^{th} constituent in the j^{th} mineral or gas, and Δm_c is the change in moles per kg H_2O of the c^{th} constituent in the aqueous phase along the reaction path (final solution minus initial solution). When the values of Δm_c are known (from chemical analysis) and $n = \phi$, a mass balance reaction for the chosen minerals and gases can be obtained by simultaneous solution of the n equations (similar to eq 3) which then defines the n values of the reaction coefficients, α_j, in the reaction.

Obviously there are limitations to the mass balance approach. The maximum number of minerals that can be considered in the mass balance is n, even though a particular mineral may be known to vary in its stoichiometry for several of the n constituents. In order to obtain the mass balance, it is necessary to consider only a few idealized mineral compositions that represent the known range of the mineral stoichiometry in the system. Conclusions regarding the significance of the implied mass transfer must reflect the fact that many other minerals (of perhaps slightly different compositions) may also be involved.

In addition to problems of mineral stoichiometry, the validity of the derived reaction coefficients, α_j, depends significantly on the analytical accuracy of Δm_c. Any errors in the analyses of the initial and final waters used to compute values of Δm_c introduce uncertainties in the calculated values of α_j.

Having determined possible reaction stoichiometry using mass balance relations, the thermodynamic realism of the mass balance can be demonstrated by performing a more detailed reaction simulation. If the starting and/or ending water is not balanced in charge (that is, if there are significant errors in the measured pH or total molalities of the dissolved constituents), the pH predicted by the detailed reaction simulation will differ from the measured value.

In the examples considered below, detailed reaction simulations have been made using a modified version of the computer program MIX2 (Plummer, Parkhurst, and Kosiur, 1975). The program uses an aqueous model and the constraints of mass and charge balance in solution to predict the pH and equilibrium distribution of inorganic species in solution as a function of net reaction progress in the system CaO–MgO–K_2O–Na_2O–CO_2–H_2SO_4–HCl–H_2O. In addition, the simulation scheme

predicts the amounts of minerals dissolved or precipitated in maintaining their equilibrium in solution. The aqueous model used is similar to that of WATEQ (Truesdell and Jones, 1974; see, also, Plummer, Jones, and Truesdell, 1976), except that fewer species are considered.

There is a subtle difference between the mass balance reactions, as given by eq (3), and detailed simulation of mass balance reactions. Whereas mass balance reactions require prior knowledge of Δm_c and $\beta_{c,j}$ to derive the mineral reaction coefficients, (α_j), detailed reaction simulation begins with knowledge of α_j for all reactants (derived from the mass balance) and $\beta_{c,j}$ for all reactant and product minerals. The reaction simulation then predicts values of α_j for product minerals, values of Δm_c, and the solution pH which are consistent with thermodynamic constraints placed on the reactions. For example, in reaction simulation, we might impose the thermodynamic constraint that a given mineral will precipitate if a water has attained a pre-defined level of saturation (or supersaturation). Detailed reaction simulation then predicts the final solution composition, pH, and mass transfer that is consistent with this constraint.

A check on the validity of a mass balance reaction is provided by theoretical evaluation of the carbon isotopic composition of the final solution. Simulation of isotopic composition of water is significant in checking the mass balance approach, because the isotopes link mass transfer with solution composition. Predicted values of the isotopic composition of the final solution depend on the mass transfer, and the mass transfer depends, in turn, on the assumed reactant and product mineral stoichiometries. In some cases, multiple reactant and (or) product stoichiometries are possible; the result being that each reaction simulation predicts an identical solution composition, while the masses of minerals dissolved and (or) precipitated change depending on the mineral stoichiometries. As the reactant and product stoichiometry changes, the predicted isotopic composition of the final solution also changes. Our calculations rely on the fact that the correct mass balance reaction must predict both the observed chemical *and* isotopic composition of the final solution. The isotopic composition of water has been simulated using a finite difference solution for the predicted mass transfer, as described by Wigley, Plummer, and Pearson (1978).

GEOMORPHIC STUDY OF A COASTAL LAGOON

The lagoon on the east coast of the Yucatan Peninsula, Mexico, consists of two major arms (fig. 1) which are hydrologically dissimilar. The water in each arm is divided into two distinct layers, an upper layer approximately a meter thick, which, based on chlorinity, ranges from 27 to 40 percent seawater, and a lower layer which is essentially seawater.

In order to determine the amount of mixing and extent of CO_2 outgassing, dissolution, and precipitation of calcium carbonate, three models were developed: (1) a conservative closed system mixing of two end-member waters, (2) mixing of two end-member waters in a system open

to CO_2 gas, and (3) mixing in a system open to CO_2 in which $CaCO_3$ may dissolve or precipitate. End-member waters used in the calculations (table 1) occur naturally in the lagoon; one water that occurs in the lower depths is similar to seawater, and the other is water of lower salinity from the upper layer of each separate arm of the lagoon. The lower salinity water is further characterized by having the highest total dissolved carbon.

Figure 2 compares the results of the calculations with the observed values of the water enclosed in each arm. For the south arm, the final chemical evolution of the water is at its mouth (sta. 1); for the north arm, the final evolution is in the restricted reaches of the upper part (sta. 7).

With the exception of total inorganic carbon, the major cation and anion composition of the waters is controlled primarily by the mixing process. For model 1, in which only conservative closed-system mixing is considered, the total inorganic carbon is higher and the pH is lower than the observed values. Model 2, which incorporates the process of CO_2 outgassing (or photosynthesis) with mixing (model 1), shows that the computed values for pH and total carbon are similar to the observed values when the predicted P_{CO_2} is equal to that observed. Model 2 accounts for all the observed properties of the water elsewhere in the lagoon, except for water at one station in the south arm (fig. 2), where computed calcium and alkalinity in the mixtures are less than the observed. When calcite dissolution is combined with the processes of mixing and CO_2 outgassing (model 3), we obtain excellent agreement in the south arm as well.

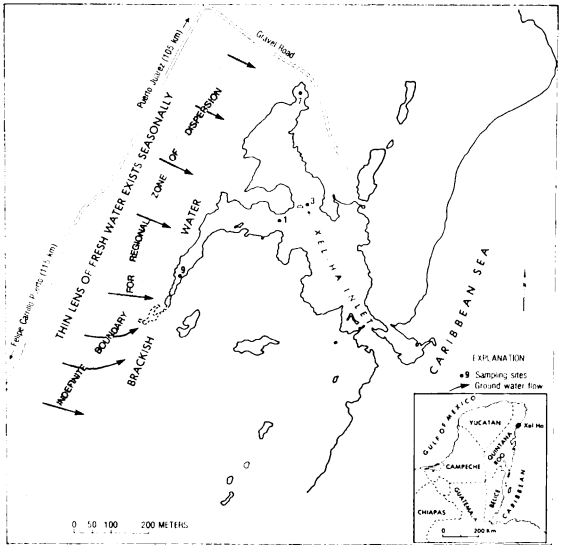

Fig. 1. Sketch map of lagoon showing location of sampling points.

TABLE 1

Description of end-member waters in Lagoon Xel Ha

	Sample	Type	Percent in Mix	Temperature °C	Field pH	mmol/kg H_2O Ca	Mg	Sr	Na	K	Cl	SO_4	Alk*	Total** CO_2	Log P_{CO_2}	SI_c***	$\delta^{13}C$ ‰
North Arm	3	End-member	94.3	27.6	7.60	5.62	21.10	0.029	177.3	4.9	211.6	11.1	5.62	5.69	−2.23	0.50	−11.9
	Avg Bottom Water	End-member	5.7	26.0	8.42	10.08	53.13	0.056	456.3	12.4	541.2	27.0	2.81	2.43	−3.57	0.96	− 3.0
	7	Mixture	100.0	29.0	8.20	5.82	22.42	0.031	189.4	5.4	230.5	11.3	5.44	5.09	−2.89	1.05	−10.7
South Arm	9	End-member	78.7	26.0	6.88	4.84	14.54	0.025	120.8	3.3	146.7	7.4	6.12	7.26	−1.44	−0.19	−13.0
	Avg Bottom Water	End-member	21.3	29.8	8.06	9.54	52.97	0.057	453.0	12.1	533.4	27.1	2.77	2.56	−3.13	0.68	− 3.5
	1	Mixture	100.0	27.0	7.45	6.33	24.38	0.037	196.9	4.9	229.0	10.4	5.76	5.93	−2.05	0.39	—

* Total alkalinity in Meq/kg H_2O.

** Total inorganic carbon in solution.

*** Saturation index of calcite. SI_c = log IAP/K where IAP is the ion activity product of calcite and K is the equilibrium constant (taken from Jacobson and Langmuir, 1974; see footnote to table 2).

TABLE 2

Description of end-member waters from the Floridan and Madison Limestone aquifers

Well	Aquifer	Temperature °C	Field pH	mmol/kg H_2O Ca	Mg	Total CO_2	SO_4	Log P_{CO_2}	Saturation index* SI_c	SI_d	SI_g	$\delta^{13}C$ ‰
Polk City	Floridan	23.8	8.00	0.84	0.23	2.10	0.025	−2.89	0.17	−0.07	−3.10	−11.4
Arcadia	Floridan	26.3	7.44	2.65	2.47	3.63	3.584	−2.15	0.14	0.43	−0.81	− 8.3
Rhoads Fork	Madison	5.7	7.35	1.65	0.95	5.71	0.032	−1.98	−0.08	−0.62	−2.90	−11.0
Midland	Madison	71.1	6.69	6.65	2.72	3.17	8.360	−1.27	0.17	−0.14	−0.43	− 6.2

* Saturation Index, SI, SI = log IAP/K, where IAP is the ion activity product in solution and K is the equilibrium constant. The subscripts c, d, and g denote stoichiometric calcite, dolomite, and gypsum. Thermodynamic data used to calculate K as a function of temperature are as follows: $CaCO_3$ (calcite) = $Ca^{2+} + CO_3^{2-}$, log K = 13.543 −0.0401T −3000./T (Jacobson and Langmuir, 1974); $CaMg(CO_3)_{2\,(dolomite)} = Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$, log $K_{(298.16°K)} = -17.0$ (Berner, 1967), $\Delta H_r°_{(298.16°K)} = -8.290$ kcal mol^{-1} (Helgeson, 1969); $CaSO_4 \cdot 2H_2O$ (gypsum) = $Ca^{2+} + SO_4^{2-} + 2H_2O$, log K = $-4.6535 + 4.545 \times 10^{-3}T - 1.01 \times 10^{-4}T^2$, (Wigley, 1973), where T is temperature in degrees K.

The calculations indicate that approx 0.28 mmoles of calcium carbonate have dissolved and approx 0.38 mmoles of CO_2 have outgassed per liter of solution at one sampling point in the south arm (fig. 2) while approx 0.40 mmoles of CO_2 have evolved per liter of solution in the north arm with little or no dissolution or precipitation of $CaCO_3$. Predicted $\delta^{13}C$ values are in close agreement with values observed in the lagoon and support the derived mass transfer.

The thermodynamic potential for $CaCO_3$ dissolution in mixtures of calcium bicarbonate groundwater and seawater is well documented in theory (see for example, Wigley and Plummer, 1976). Actual field verification of this process is more difficult to obtain. At Xel Ha, groundwater discharged along bedrock fractures into the lagoon is derived from the regional zone of dispersion that exists at shallow depths along the Yucatan coast. Prior to discharge into the lagoon, considerable mixing with seawater occurs in the groundwater zone. Based on chloride content, samples of upper water in the north arm, for example, have already mixed to about 27 percent seawater prior to their discharge into the lagoon. Although we understand these processes, it is difficult to determine the amount of calcium carbonate that has dissolved as a result of underground mixing. However, preliminary calculations using assumed end-member waters selected from the data of Back and Hanshaw (1976)

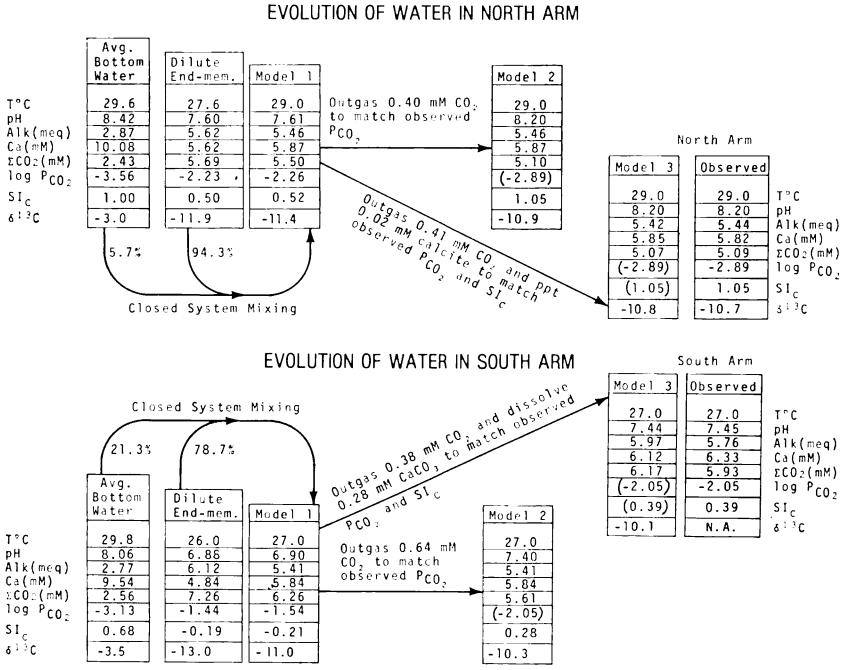

Fig. 2. Summary diagram of mass balance calculations in lagoon, Yucatan. Numbers in parentheses denote thermodynamic constraints imposed during detailed reaction simulation.

give evidence of calcium carbonate dissolution in seawater mixtures in the regional zone of dispersion (Back and others, 1979). Clearly, other processes such as CO_2 outgassing with precipitation and recharge of additional CO_2 with accompanying dissolution precede discharge of regional groundwater at station 9, but without identification of the intermediate waters we cannot quantify these processes. However, by choosing end-member water that occurs naturally in the lagoon, we can identify processes that occur after discharge into the lagoon.

Our study shows that although water discharging into the lagoon at station 9 is undersaturated with calcite, the process of CO_2 gas evolution (or possibly photosynthesis) from the upper layer of water is too rapid to allow significant solution of additional calcium carbonate in the lagoon. The calculations show that only at one sampling point in the south arm (fig. 2) is there evidence of solution of calcium carbonate. Here, the close agreement between the amount of calcium carbonate dissolved and the theoretical solubility of calcite in that solution (0.28 mmoles/kg H_2O) suggests that the water evolved by mixing under closed-system conditions with $CaCO_3$ dissolution followed by loss of carbon dioxide from the topwater.

REACTIONS IN CARBONATE-ROCK AQUIFERS

As further examples of the use of the mass balance approach in hydrochemical systems, we demonstrate the chemical and carbon isotopic evolution of groundwater down hydraulic gradients in parts of the Floridan aquifer and the Madison Limestone aquifer. Two wells were chosen from each system. In each case, the upgradient well is coincident with the area of dominant recharge, and the second well is as far downgradient as it is possible to sample. Chemical isotopic details of these end-member waters are summarized in table 2. The reactions necessary to explain the observed chemical and carbon isotopic composition of the upgradient and downgradient waters are summarized in figure 3.

Figure 3 shows that in both systems, the chemical evolution of the upgradient water is explained by dissolution of calcite and dolomite along with trace amounts of gypsum and anhydrite in CO_2-charged water. If the recharge area waters at Polk City (Floridan aquifer) and Rhoads Fork (Madison Limestone aquifer) evolve as closed systems after passing through the soil zone, the amount of CO_2 required for the reactions (fig. 3) indicates partial pressures for CO_2 of $10^{-1.5}$ and $10^{-1.3}$ respectively in the soil zone. These soil P_{CO_2} estimates are more than an order of magnitude larger than soil zone P_{CO_2} measurements in Florida (Rightmire and Hanshaw, 1973) and in the Black Hills (Rightmire, unpub. data). If these measured soil zone P_{CO_2} values are representative of the average composition of recharge to the systems, other mechanisms, such as open system evolution during recharge, must be considered in order to account for the observed amounts of dissolved inorganic carbon in the upgradient waters. Detailed study of the mechanisms of CO_2 production and reactions in the evolution of the recharge area groundwater is required in

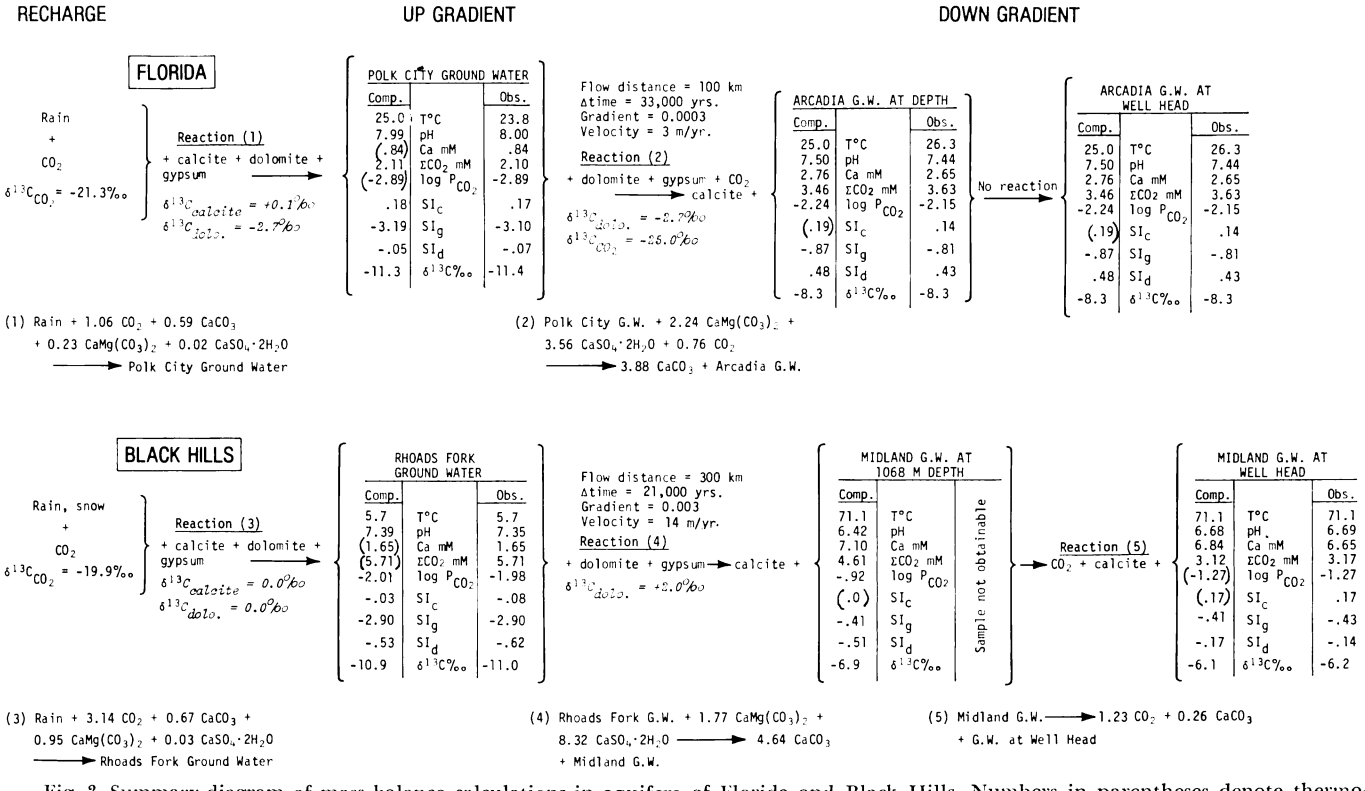

Fig. 3. Summary diagram of mass balance calculations in aquifers of Florida and Black Hills. Numbers in parentheses denote thermodynamic constraints imposed during detailed reaction simulation.

order to resolve this problem. Although the mechanism by which CO_2 is introduced into the recharge area groundwater is unclear, the $\delta^{13}C$ values of the Polk City and Rhoads Fork groundwaters are described accurately by the mass balance reactions and the $\delta^{13}C$ of soil CO_2 measured by Rightmire (fig. 3).

Subsurface reactions occurring along the hydraulic gradient in Florida and South Dakota result in increases in dissolved calcium, magnesium, sulfate, and inorganic carbon, with a decrease in pH and an increase in P_{CO_2}. Mass balance and reaction simulation (fig. 3) show that both systems can be described by the incongruent solution of dolomite to calcite, a reaction that is driven irreversibly by the solution of gypsum or anhydrite. The calculations also indicate an additional source of CO_2 for the Florida system which probably results from oxidation of lignite accompanying sulfate reduction within the aquifer. Although the calculated groundwater composition for Arcadia (fig. 3) is within the analytical uncertainties observed at the well head, the calculated ground-water composition at Midland differs significantly from the composition observed at the well head and has a lower pH and higher dissolved carbon and calcium content. Figure 3 shows that the well-head water at Midland is described by CO_2 gas evolution and accompanying precipitation of calcite in the implied down-hole groundwater. CO_2 gas evolution was evident in the sampling procedure, and scale deposits are common at well heads.

The $\delta^{13}C$ content of groundwater at Arcadia and Midland is explained by the mass balance reactions (fig. 3), if in Florida the reactants are isotopically-light, diagenetic dolomite ($\delta^{13}C = -2.7$ per mil) and in the Black Hills they are isotopically-heavier, marine dolomite ($\delta^{13}C = +2.0$ per mil).

The time of flow down the hydraulic gradient between Polk City and Arcadia in Florida, a distance of 100 km, was estimated to be 33,000 yrs (Plummer, 1977). This estimate is based on detailed analysis of rates of reaction at intermediate wells along the flow path from Polk City to Arcadia, for which reliable ^{14}C data are available and on the derived mass transfer to the Arcadia well. The time of flow between Rhoads Fork and Midland in South Dakota (300 km) is estimated to be 21,000 yrs based on ^{14}C measurements in the groundwater and predicted ^{14}C content at Midland corrected for the derived mass transfer. The hydraulic gradient in Florida (0.0003) is one-tenth that of the Black Hills which is a major control on the differences in the average flow velocities of the two systems of 3 m/yr and 14 m/yr, respectively.

The average rates of solution of gypsum and dolomite and precipitation of calcite in Florida and the Black Hills (moles per kg H_2O per yr) are summarized in table 3. These apparent rates are quite similar — the Black Hills reaction rates, which occur at higher temperatures, range from 1.4 to 4.0 times those of the Florida system. These rates are, however, uncorrected for effects of hydrodynamic dispersion, mineral surface area, and true mineral stoichiometry.

SUMMARY

It is seen from the above field examples that by coupling chemical mass balance with isotopic calculations, valuable insight may be gained in the identification of reactions and their rates in natural water systems.

The mass balance approach shows that waters in the lagoon Xel Ha on the east coast of the Yucatan Peninsula evolve primarily by mixing with seawater with accompanying loss of CO_2 gas (probably as outgassing or photosynthesis). Although the water discharged into the lagoon is initially undersaturated with calcite, loss of CO_2 gas is, for the most part, too rapid to allow dissolution of calcium carbonate. Although the water approaches tenfold supersaturation with respect to calcite, calculations show that little or no precipitation occurs. Our calculations have identified one water that has dissolved approx 0.28 mmoles of $CaCO_3$ (per kg H_2O) within the lagoon, a value close to the theoretical solubility of calcite in the mixture.

Application of the mass balance approach to the regional carbonate rock aquifers of Florida and South Dakota shows that similar reactions occur in each hydrochemical system. Groundwater in the Floridan and Madison Limestone aquifers evolves by the incongruent solution of dolomite to calcite (de-dolomitization), a reaction that is driven irreversibly by the solution of gypsum and anhydrite. Introduction of time into the hydrochemical system through ^{14}C measurements corrected for the derived mass transfer allows estimation of average flow velocities and rates of reactions. The calculated average flow velocities correlate well with the known hydrologic gradients in the aquifers, and average rates of reaction, uncorrected for differences in mineral surface area, are quite similar: the higher temperature waters of the Madison Limestone system imply rates of reaction 1.4 to 4.0 times that of the Floridan aquifer.

As studies in these carbonate systems proceed, the results of the mass balance and reaction simulations will be combined with mineralogic and hydrologic data to delineate more clearly the total functioning of the hydrologic systems.

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TABLE 3

Average rates of reaction*

Reaction	Florida	Black Hills	$R_{B.H.}/R_{Fla.}$
Dolomite solution	6.8×10^{-8}	9.3×10^{-8}	1.4
Gypsum solution	1.1×10^{-7}	4.4×10^{-7}	4.0
Calcite precipitation	-1.2×10^{-7}	-2.4×10^{-7}	2.0

* Moles reacted per kg H_2O in the groundwater per year (uncorrected for surface area). Positive sign indicates dissolution and negative sign indicates precipitation.

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