

# Defining Reactions and Mass Transfer in Part of the Floridan Aquifer

L. N. PLUMMER

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# Defining Reactions and Mass Transfer in Part of the Floridan Aquifer

L. N. PLUMMER

U.S. Geological Survey, Reston, Virginia 22092

This paper examines the observed changes in water chemistry down a hydraulic gradient in part of the Floridan aquifer. Through the use of mass balance relationships and mass transfer calculations several reactions are derived that simulate the observed water chemistry. The calculation of  $\delta^{13}\text{C}$  and  $^{14}\text{C}$  activity implied by these reactions limits the number of possible reactions and leads to the following conclusions. The waters of the recharge area near Polk City have an average age of 3200 yr and have formed by congruent solution of dolomite and calcite. Although the calculated isotopic composition of  $\text{CO}_2$  entering the groundwater,  $\delta^{13}\text{C} = -22.5$ , is near that measured for soil gas  $\text{CO}_2$  in the vicinity of the recharge area (Rightmire and Hanshaw, 1973), the mechanism(s) by which soil  $\text{CO}_2$  enters the saturated zone is not well defined. Down the hydraulic gradient from the vicinity of Polk City, isotopically light dolomites ( $\delta^{13}\text{C} = -3.9$  to  $-1.5\text{‰}$ ) and gypsum dissolve. All reactions south of Polk City are incongruent to a low-magnesium calcite. The reaction path between Polk City and Fort Meade is partially open to  $\text{CO}_2$ , presumably soil zone  $\text{CO}_2$ . Further south between Fort Meade and Wauchula the Floridan aquifer becomes essentially closed to  $\text{CO}_2$ . Beyond Wauchula to Arcadia, oxidation of lignite via sulfate reduction adds additional carbon to the water composition.  $^{14}\text{C}$  ages, corrected for the derived mass transfer reactions, are slightly younger than was previously recognized owing to consideration of incongruent dissolution. The age of Arcadia water (at the farthest point down the gradient) is estimated to be 36,000 yr B.P. Flow velocities derived from  $^{14}\text{C}$  ages are in reasonable agreement with flow velocities estimated from hydrologic considerations. The corrected  $^{14}\text{C}$  ages and derived mass transfer reaction coefficients allow estimation of apparent rates of reaction in central Florida from field data. The results of this study point to a complex diagenetic history in central Florida in which the position of the freshwater-saltwater interface appears to determine whether dolomite is a reactant or product mineral.

## INTRODUCTION

Identification of reactions and accompanying mass transfer is an important step in understanding the chemical evolution of natural water systems. If sufficient hydrologic, mineralogic, and water chemistry data are available for the system, mineral-water equilibria calculations and mass balance relationships often allow identification of reactions. A check on the compatibility of mass balance reaction models derived from field data is possible through the use of mass transfer calculations.

Mass transfer calculations involve simulation of proposed reaction models by using rigorous mass transfer calculation schemes, such as those of Helgeson and co-workers [Helgeson, 1968; Helgeson *et al.*, 1969, 1970] and Plummer *et al.* [1975]. Mass transfer simulation of the derived reaction provides a check on the consistency of the reaction model with field data by predicting chemical properties of the system that depend on reaction, such as pH and mineral saturation. Comparison of these predicted parameters with the observed field values enables refinement of reaction models.

When sufficient field data are lacking to define a complete mass-balanced reaction, mass transfer calculations are useful in testing proposed reactions, predicting missing data, and eliminating reactions that do not predict known chemical parameters for the system. If the choice of reactants and/or products along a reaction path is multiple, neither mass balance relationships nor mass transfer calculations can identify the true reactions. What is derived is a set of reactions, each simulating the observed water chemistry, each having different reactant and product mineralogy, and each predicting different masses of these reactant and product minerals dissolved and precipitated along the path. Only one of these reactions may predict the correct mass transfer for the system. In most cases the correct mass transfer for the evolution of a natural water system is not known a priori, so that additional criteria

must be used to further eliminate reaction models that are inconsistent with the observations.

Additional criteria particularly suited for this problem are isotope balances, because they link mass transfer with solution composition. Incorporation of isotopic calculations into rigorous reaction path calculation procedures will be sufficient in some cases for near-unique identification of reactions in natural water systems.

This paper examines the observed water chemistry from four wells aligned down a hydraulic gradient in a portion of the Floridan aquifer. Mass balance and mass transfer calculations are used to identify several reactions that simulate the observed water chemistry. The mass transfer calculation scheme of Plummer *et al.* [1975] has been modified to calculate  $\delta^{13}\text{C}$  and  $^{14}\text{C}$  activity in solution along the reaction path, a procedure that significantly limits the number of possible reactions and allows estimation of water age. The derived stoichiometric coefficients for the identified reactions are examined and shown to be, in part, functions of the apparent rates of reaction down the hydraulic gradient.

## DESCRIPTION OF FLOW REACTION PATH

The four wells in the principal artesian aquifer of central Florida selected for study extend from a large central groundwater mound near Polk City, where the potentiometric surface is 40 m above sea level, southward approximately 105 km to Arcadia, where the potentiometric surface is near 15 m above sea level (Figure 1). Hanshaw *et al.* [1965] and Back and Hanshaw [1970] estimate average flow velocities from 2 to 12 m/yr. Water ages, obtained by using the closed system congruent dissolution  $^{14}\text{C}$  correction of Ingerson and Pearson [1964], increase from 3470 yr B.P. at Polk City to 20,600 yr B.P. at Arcadia [Back and Hanshaw, 1970]. Wigley [1975] uses a model that accounts for both open and closed system congruent evolution and estimates the age of water at Arcadia to be 24,100 yr B.P.

The vicinity of Polk City (and to the north) has been recog-

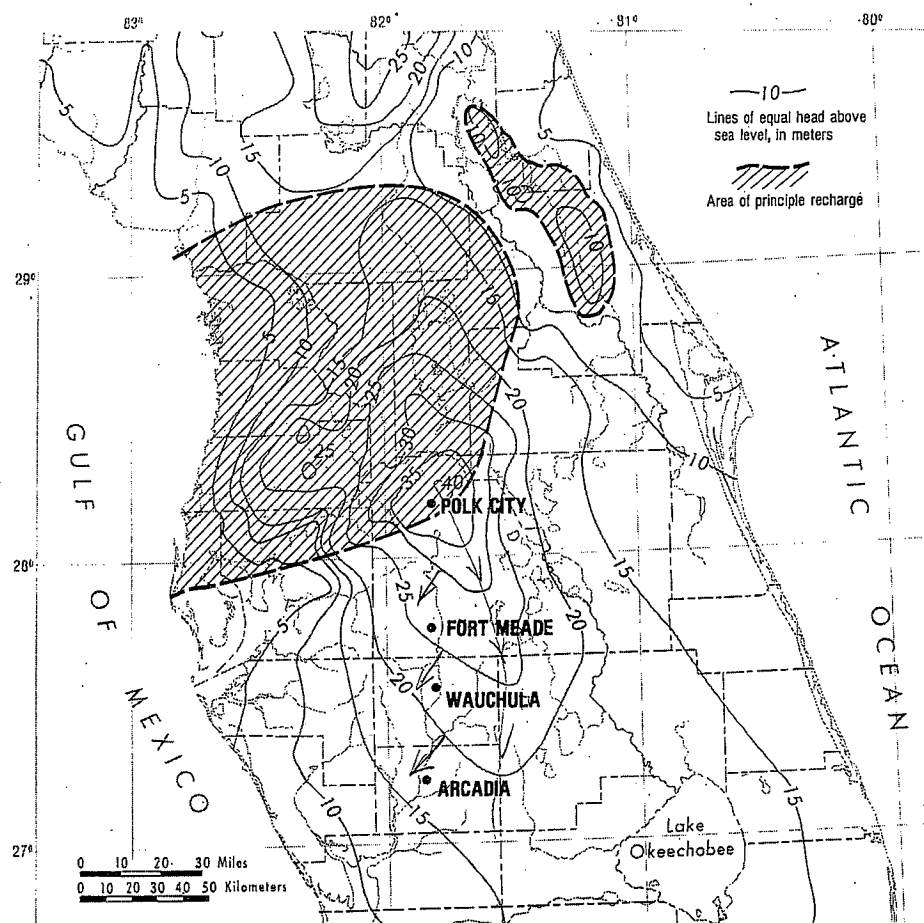


Fig. 1. Potentiometric map of the principal artesian aquifer in central Florida showing the location of the wells [after Stringfield, 1936].

nized as an area of dominant recharge [Back and Hanshaw, 1970], and to the south, recharge is thought to be diminished owing to cover by the relatively less permeable Hawthorn formation of Miocene age [Pride *et al.*, 1961; LeGrand and Stringfield, 1966]. The four wells selected for study range in depth from 150 to 300 m and penetrate limestone formations of Oligocene to middle Eocene age (Figure 2). These units are among the most productive of the Floridan aquifer and are dominantly limestones and dolostones with minor amounts of gypsum, chert, magnesian calcites, and lignite [Back and Hanshaw, 1970; Hanshaw *et al.*, 1971]. Data of Hanshaw *et al.* [1971] and R. G. Deike (unpublished data, 1972) show that the limestones contain 0–2 mol % magnesium and the dolostones range in composition from stoichiometric dolomite to  $\text{Ca}_{1.05}\text{Mg}_{0.92}(\text{CO}_3)_2$ . Scattered occurrences of magnesian calcites range in composition from 3 to 10 mol %  $\text{MgCO}_3$  with a mean value near  $\text{Ca}_{0.95}\text{Mg}_{0.05}\text{CO}_3$  (R. G. Deike, unpublished data, 1972). Magnesian calcites probably account for less than 0.1% of the limestones by weight.

Analyses of water from the four wells selected are given by Back and Hanshaw [1970], and information on the water pertinent to this study is summarized in Table 1. All four wells are largely uncased in the Floridan aquifer (Figure 2), and the extent to which mixing within the well influences their chemical composition is not known. However, the well-documented spatial distribution in water chemistry which parallels the hy-

drologic system [Back and Hanshaw, 1970] is based on much more data than are examined here with depths of 100–500 m. These wells produce from one or more of the limestone units of the Floridan aquifer. This observation suggests that vertical variation in water chemistry is insignificant when it is compared to the spatial variation on a regional scale.

The water chemistry is summarized in Figures 3 and 4. Figure 3 shows systematic increases in calcium, magnesium, bicarbonate, and sulfate with increasing distance down the hydraulic gradient from Polk City to Arcadia. In contrast to the clear dissolution pattern shown in Figure 3, Figure 4 shows systematic increases in the  $\text{Mg}/\text{Ca}$  ratio,  $\log P_{\text{CO}_2}$ , and the saturation index of dolomite; an approximately constant level of supersaturation for calcite; and a decrease in  $\text{pH}$  with increasing distance and reaction progress down the gradient.

In addition, Table 1 shows a progressive increase in  $\delta^{13}\text{C}_{(\text{PDB})}$  from  $-11.4\%$  at Polk City to  $-8.3\%$  at Arcadia. Hanshaw and Back [1972] report  $\delta^{13}\text{C}$  of calcites and dolomites from the principal artesian aquifer in Florida. Two dolomites are recognized: heavy dolomites, which range from  $+0.1$  to  $+1.0\%$  in  $\delta^{13}\text{C}$ , and lighter dolomites, which range from  $-3.1$  to  $-7.5\%$  in  $\delta^{13}\text{C}$ . The heavy dolomites are interpreted by Hanshaw and Back as being older and probably marine in origin, while the lighter dolomites suggest freshwater diagenetic origins. The  $\delta^{13}\text{C}$  of calcites reported by Hanshaw and Back range from  $-0.4$  to  $+0.6\%$ . In modeling  $\delta^{13}\text{C}$  in the four waters selected

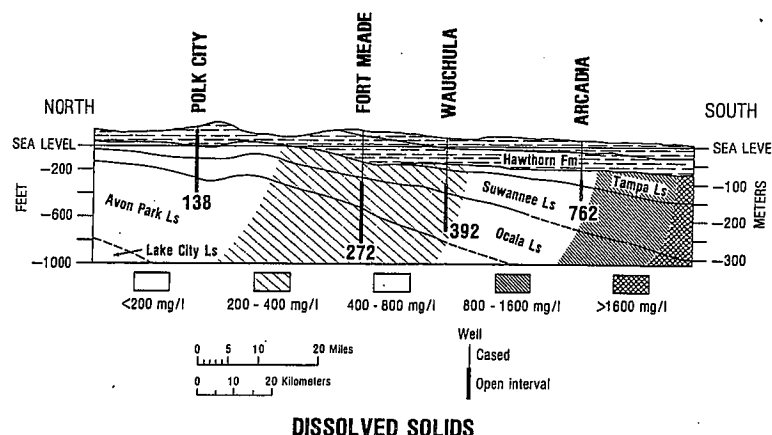


Fig. 2. Cross section of the Floridan aquifer between Polk City and Arcadia showing the trend in total dissolved solids and the location of the open interval of the four selected wells (modified from Back *et al.* [1966]).

for study the  $\delta^{13}\text{C}$  of calcite sources is taken to be  $+0.1\%$ , and two values of  $\delta^{13}\text{C}$  for dolomite sources are considered:  $-4.5$  and  $+0.5\%$ .

#### METHODS OF IDENTIFYING REACTIONS

The approach used to identify reactions in the Floridan aquifer is threefold.

1. On the basis of observed changes in water chemistry along the defined flow path and by using known mineralogy for the system, mass balance reactions are derived from the data that account for the observed total concentrations of the major cations and anions in solution.

2. The derived stoichiometric coefficients of the mass balance reactions are refined within the limits of uncertainty in pH and other chemical parameters for the waters by simulation of the reactions in a rigorous mass transfer calculation scheme.

3. Calculation of the inorganic carbon isotopic composition of the aqueous phase identifies mass transfer reactions that can account for the observed water chemistry and its isotopic composition.

#### Mass Balance

The number of mass balance reactions to be derived is relatively large. Because many reactions are possible depending on additional choice of stoichiometry of the magnesium source mineral, it is convenient to derive the mass balance reactions in general notation.

Mass balance on the change in total molality of the  $c$ th constituent along a reaction path is given by

$$\sum_{j=1}^{\phi} \alpha_j \beta_{c,j} = \Delta m_c \quad (1)$$

and summing for all constituents, the complete mass balance reaction is given by the relationship

$$\sum_{j=1}^{\phi} \alpha_j \sum_{c=1}^n \beta_{c,j} = \sum_{c=1}^n \Delta m_c \quad (2)$$

where  $\phi$  is the number of phases (reactants and products) in the mass balance reaction,  $n$  is the number of constituents,  $\alpha_j$  is the number of moles of the  $j$ th phase in the reaction (positive for reactants and negative for products),  $\beta_{c,j}$  is the stoichiometric

coefficient of the  $c$ th constituent in the  $j$ th phase, and  $\Delta m_c$  is the change in moles (per kilogram of  $\text{H}_2\text{O}$ ) of the  $c$ th constituent in the aqueous phase along the path. If values of  $\Delta m_c$  are known and  $n = \phi$ , a mass balance reaction for the chosen phases can be obtained.

For reactions of interest in the Floridan aquifer, four major constituents in the water chemistry ( $m_{\text{Ca}}^T$ ,  $m_{\text{Mg}}^T$ ,  $m_{\text{CO}_2}^T$ , and  $m_{\text{SO}_4}^T$ , where the prefix  $m$  denotes molality and superscript  $T$  denotes a total quantity, that is, individual ion plus related ion pairs) must be considered. Therefore the maximum number of phases that can be considered in obtaining a mass balance is four. Because the stoichiometry of dolomite and calcite shows considerable variation in central Florida, there is little doubt that more than four phases are involved in reactions. In order to obtain mass balance reactions it is necessary to consider only a few idealized mineral compositions that span the known range of mineral stoichiometry for the system. Conclusions regarding the significance of mass balance and mass transfer coefficients derived for idealized limiting mineral compositions must be tempered by the fact that many other minerals (of slightly different compositions) may be involved as well.

The four phases considered in deriving mass balance reactions in central Florida are calcite ( $\text{Ca}_x\text{Mg}_{(1-x)}\text{CO}_3$ ), dolomite ( $\text{Ca}_y\text{Mg}_{(2-y)}(\text{CO}_3)_2$ ), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), and carbon dioxide (soil zone  $\text{CO}_2$ ,  $\text{CO}_2$  derived from the oxidation of lignite, etc.), with stoichiometric coefficients in derived mass balance reactions denoted  $\alpha_{\text{Cal}}$ ,  $\alpha_{\text{Dol}}$ ,  $\alpha_{\text{Gyp}}$ , and  $\alpha_{\text{CO}_2}$ , respectively. Explicit solutions for values of  $\alpha_j$  are obtained by simultaneous solution of four mass balance equations of the form of (1) (one equation for each constituent), which gives

$$\alpha_{\text{Cal}} = \frac{(2-y)(\Delta m_{\text{Ca}}^T - \Delta m_{\text{SO}_4}^T) - y \Delta m_{\text{Mg}}^T}{2x-y} \quad (3)$$

$$\alpha_{\text{Dol}} = \frac{x \Delta m_{\text{Mg}}^T - (1-x)(\Delta m_{\text{Ca}}^T - \Delta m_{\text{SO}_4}^T)}{2x-y} \quad (4)$$

$$\alpha_{\text{CO}_2} = \Delta m_{\text{CO}_2}^T - \Delta m_{\text{Mg}}^T - (\Delta m_{\text{Ca}}^T - \Delta m_{\text{SO}_4}^T) \quad (5)$$

$$\alpha_{\text{Gyp}} = \Delta m_{\text{SO}_4}^T \quad (6)$$

where  $x = \beta_{\text{Ca,Cal}}$ ,  $(1-x) = \beta_{\text{Mg,Cal}}$ ,  $y = \beta_{\text{Ca,Dol}}$ , and  $(2-y) =$

TABLE 1. Chemical and Carbon Isotope Composition of Selected Waters From the Floridan Aquifer

| Well       | pH   | Ca,<br>mmol/l | Mg,<br>mmol/l | CO <sub>2</sub> ,<br>mmol/l | SO <sub>4</sub> ,<br>mmol/l | log <i>P</i> <sub>CO<sub>2</sub></sub> ,<br>atm | Saturation Index |                 |                 | δ <sup>13</sup> C, ‰ | δ <sup>14</sup> C, ‰ | Age, † yr |
|------------|------|---------------|---------------|-----------------------------|-----------------------------|-------------------------------------------------|------------------|-----------------|-----------------|----------------------|----------------------|-----------|
|            |      |               |               |                             |                             |                                                 | SI <sub>C</sub>  | SI <sub>D</sub> | SI <sub>G</sub> |                      |                      |           |
| Polk City  | 8.00 | 0.84          | 0.23          | 2.14                        | 0.025                       | -2.89                                           | 0.17             | -0.07           | -3.10           | -11.4‡               | -657§                | 3,200     |
| Fort Meade | 7.75 | 1.45          | 0.70          | 2.77                        | 0.739                       | -2.55                                           | 0.23             | 0.31            | -1.53           | -10.8                | -827§                | 8,100     |
| Wauchula   | 7.69 | 1.65          | 1.19          | 2.87                        | 1.614                       | -2.48                                           | 0.17             | 0.37            | -1.21           | -8.5                 | -956§                | 16,300    |
| Arcadia    | 7.44 | 2.65          | 2.47          | 3.63                        | 3.584                       | -2.15                                           | 0.14             | 0.43            | -0.81           | -8.3¶                | -988                 | 36,000    |

Data are from *Back and Hanshaw* [1970] unless otherwise noted.

\*Calculated from the reported analysis and the aqueous model (see text and Table 2). For consistency, all calculations are at 25°C, since all four waters are within 1.6° of 25°C. Saturation indices of calcite (CaCO<sub>3</sub>), dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>), and gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), SI<sub>C</sub>, SI<sub>D</sub>, and SI<sub>G</sub>, respectively, are calculated in relation to the equilibrium constants given in Table 2.

†Mean estimates calculated by the method discussed in the text.

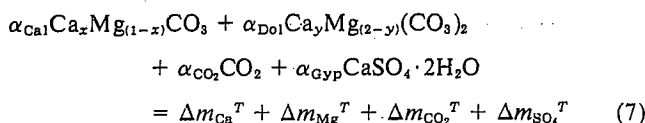
‡*Rightmire and Hanshaw* [1973].

§*Hanshaw et al.* [1965].

||*W. Back and B. B. Hanshaw* (unpublished data, 1967).

¶*Pearson and Hanshaw* [1970].

$\beta_{\text{Mg,Dol}}$ . The mass balance reactions are then of the form of (2):



where the water released from gypsum solution is neglected and values of  $\alpha_j$  are positive for reactants and negative for product minerals, as derived from (3)–(6).

#### Mass Transfer

Simulation of reaction paths has been facilitated by the Fortran IV computer program MIX2 [Plummer *et al.*, 1975]. The program utilizes an aqueous model and the constraints of mass balance and electrical balance to compute the pH and equilibrium distribution of inorganic species in solution as a function of net reaction progress in the closed system CaO-MgO-K<sub>2</sub>O-Na<sub>2</sub>O-CO<sub>2</sub>-H<sub>2</sub>SO<sub>4</sub>-HCl-H<sub>2</sub>O. In addition, MIX2 allows for mineral precipitation along the reaction path in maintaining a fixed ion activity product in solution for a given mineral. The aqueous model of MIX2 is similar to that of WATEQ [Truesdell and Jones, 1974; Plummer *et al.*, 1976] except that fewer species are considered. Table 2 lists the aqueous species considered in the calculations and the thermochemical data used. Individual ion activity coefficients of charged species have been calculated from the extended Debye-Hückel equations of Truesdell and Jones [1974]. Activity coefficients of neutral species have been calculated from the relation  $\log \gamma_i^0 = 0.1I$ , where  $I$  is ionic strength, except for  $\gamma_{\text{H}_2\text{CO}_3}$ , which has been computed from the Henry's law constants of Harned and Davis [1943] by the expression of Wigley and Plummer [1976].

Details of the numerical calculation scheme of MIX2 are given by Plummer *et al.* [1975]. In general, the program employs an iterative procedure to solve the aqueous model maintaining equilibrium among all dissolved species and conservation of mass and charge in the aqueous phase. Conservation of mass in the aqueous phase is defined by relations similar to the relation given below for the total molality of magnesium in solution,

$$m_{\text{Mg}}^T = m\text{Mg}^{2+} + m\text{MgHCO}_3^+ \\ + m\text{MgCO}_3^0 + m\text{MgSO}_4^0 + m\text{MgOH}^+ \quad (8)$$

Conservation of charge in the aqueous phase is defined by

$$\sum_i m_i z_i = 0 \quad (9)$$

where  $z_i$  is the charge of the  $i$ th ion.

Before reaction simulation begins, the starting solution is balanced in charge through the aqueous model by small changes in the total molality of either K<sup>+</sup> or Cl<sup>-</sup>, depending on the sign of the charge imbalance. This initial adjustment allows the charge balance criteria to be used later in the calculation to solve for pH following a change in solution composition due to simulated mineral dissolution and/or precipitation by using an iterative procedure [Plummer *et al.*, 1975].

The total molality of the  $c$ th constituent in solution following reaction is given by

$$m_c^T = m_c^T(\text{initial}) + \Delta m_c \quad (10)$$

where  $m_c^T(\text{initial})$  is the total molality of the  $c$ th constituent in the initial solution and  $\Delta m_c$  is the net change in moles of the  $c$ th constituent in solution due to dissolution and/or precipitation of minerals containing the  $c$ th constituent. Parameter  $\Delta m_c$  is defined by (1). In mass balance calculations,  $\Delta m_c$  is an independent variable used to derive  $\alpha_j$ , while in mass transfer calculations,  $\Delta m_c$  becomes the dependent variable. For example, in MIX2 mass transfer calculations, values of  $\beta_{c,j}$  and  $\alpha_j$  (equation (1)) for reactants are defined (independent variables), as well as  $\beta_{c,j}$  for possible product minerals that are assumed to precipitate if their particular saturation level in solution exceeds a specified value. After the initial solution has been adjusted to give charge balance, the proposed reaction is initiated by adding to the initial solution the quantity  $\sum_j \sum_c \alpha_j \beta_{c,j}$  for the proposed reactants. The  $\Delta m_c$  and thus  $m_c^T$  (equation (10)) values are computed, and solution pH is found through iterative use of the mass balance and charge balance constraints for the aqueous phase. If this solution has a saturation level greater than the specified level, the value(s) of  $\alpha_j$  for the desired product mineral(s), necessary to maintain the desired saturation level in solution, is computed in an iterative procedure that defines the mass transfer and final composition of the aqueous phase (see Plummer *et al.* [1975] for details).

Selected reactions that do not predict the observed water chemistry within the uncertainties of the observations may be eliminated from consideration. This procedure allows identi-

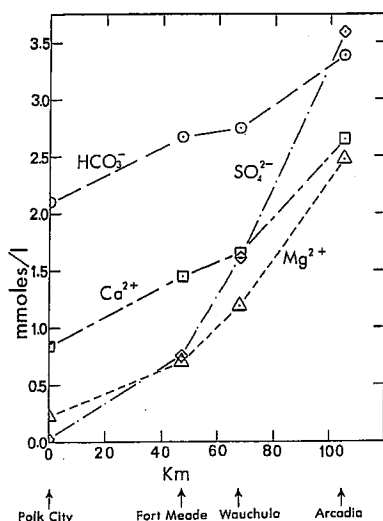


Fig. 3. Variation in concentration of total dissolved calcium, magnesium, sulfate, and bicarbonate down the gradient. Polk City is at 0.0 km, Fort Meade is 47 km down the hydraulic gradient from Polk City, Wauchula is at 68 km, and Arcadia is 105 km from Polk City.

fication of the stoichiometric coefficients of reactants and products for, in many cases, a large number of reactions that predict the observed water chemistry. The number of these possible reactions can be narrowed on the basis of mineralogic data for the system and limited further by theoretical evaluation of the isotopic composition of solution along the path.

#### Calculation of Carbon Isotopic Composition

Implicit in the above calculation of mass transfer is the assumption that the relative rates of simultaneous dissolution of reactant minerals remain constant as a function of reaction progress (and that incongruent product minerals precipitate in maintaining a constant saturation (i.e., supersaturation) level in solution). Although this assumption allows accurate simulation of solution composition at the end of reaction paths, calculation of solution composition at intermediate points along the path depends on the kinetics of mineral dissolution (and precipitation) as a function of reaction progress. In systems where the kinetics of reactions vary significantly, the average relative rates of reactions obtained from mass balance considerations by using initial and final solution composition will no longer simulate solution composition as a function of (intermediate) reaction progress. Significant deviation of reaction paths from those estimated by using average relative rates of reaction will affect the predicted isotopic composition of all solutions (intermediate and final). Preliminary calculations indicate, however, that kinetic effects on computed isotopic compositions of solutions can be ignored in the Floridan aquifer.

If a reaction is congruent,  $\delta^{13}\text{C}$  of the solution at the end of reaction  $\delta^{13}\text{C}_{(\text{final})}$  is determined from a mass balance relationship:

$$\delta^{13}\text{C}_{(\text{final})} = \frac{m_{\text{CO}_2(\text{initial})}^T \delta^{13}\text{C}_{(\text{initial})} + \sum_j \alpha_j \beta_{\text{CO}_2, j} \delta^{13}\text{C}_j}{m_{\text{CO}_2(\text{final})}^T} \quad (11)$$

where  $m_{\text{CO}_2(\text{initial})}^T$  and  $\delta^{13}\text{C}_{(\text{initial})}$  are the total molality of inorganic carbon and its value of  $\delta^{13}\text{C}$  in the starting water, respectively,  $\delta^{13}\text{C}_j$  is  $\delta^{13}\text{C}$  for the  $j$ th (reactant) phase, and  $m_{\text{CO}_2(\text{final})}^T$  is, by mass balance,

$$m_{\text{CO}_2(\text{final})}^T = m_{\text{CO}_2(\text{initial})}^T + \sum_j \alpha_j \beta_{\text{CO}_2, j} \quad (12)$$

If a reaction is incongruent to a carbon-bearing phase, calculation of  $\delta^{13}\text{C}$  at the completion of the reaction (and at any intermediate point along the path) is a complex problem [Downing et al., 1977; Wigley, 1976; Wigley et al., 1977].

In the present study the mass transfer program MIX2 (described above) was modified to calculate in an iterative procedure the value of  $\delta^{13}\text{C}$  in solution along incongruent (and congruent) reaction paths. It was necessary to divide the desired amount of reaction progress  $\xi$  into  $k$  steps. Thus instead of adding  $\xi$  mol of a net reaction to solution and then precipitating the incongruent product from the computed metastable solution, the modified version of MIX2 performs  $k$  solution-precipitation steps in which each step accumulates  $\xi/k$  mol of reaction progress. The isotopic composition of each carbonate species in solution is calculated after each solution and each precipitation step.

This iterative numerical procedure is necessary because (1) the speciation of aqueous carbon changes along the reaction path, (2) changes in moles of carbon dissolved relative to moles precipitated are not constant along the path, and (3) the isotopic composition of the incongruent product depends on the instantaneous isotopic composition of individual carbonate species in solution, which in turn depends on both the masses and the instantaneous fractionations of individual carbonate species in solution. The carbon isotope fractionation factors used in the calculations were taken from Deines et al. [1974]. For the reactions considered, it was found that the predicted value of  $\delta^{13}\text{C}$  at  $k = 20$  is within 0.03‰ of the extrapolated value for large  $k$ .

When reactions are found that predict both the composition of the aqueous phase and the observed value of  $\delta^{13}\text{C}$ , calculation of  $\delta^{14}\text{C}$  down the hydraulic gradient (by a method similar to that described above for  $\delta^{13}\text{C}$ ) gives a further check on predicted reactions and has application to the estimation of time required for flow between the initial water and the final solution. Calculated values of  $\delta^{14}\text{C}$ , when its radioactive decay along the flow path was ignored, were also found to be linear with  $k^{-1}$ . The extrapolated values of  $\delta^{14}\text{C}$  at large  $k$  represent theoretical values of  $\delta^{14}\text{C}$  that account for dilution due to dissolution of 'dead' carbon sources and for incorporation of radiogenic carbon in incongruent products. These theoretical values of  $\delta^{14}\text{C}$ , denoted ' $^{14}\text{C}$  corrected,' have been calculated by ignoring loss of  $^{14}\text{C}$  activity due to radioactive decay. The elapsed time  $\Delta t$  required for flow between the starting water (A) and a point down the hydraulic gradient (B) is then computed from the corrected  $^{14}\text{C}$  activity at B and the measured  $^{14}\text{C}$  activity at B from the relation

$$\Delta t_{A \rightarrow B} \text{ (yr)} = \frac{5730}{\ln 2} \ln \left[ \frac{^{14}\text{C corrected (B)}}{^{14}\text{C measured (B)}} \right] \quad (13)$$

By using the distance between A and B and the derived mass transfer reaction coefficients,  $\Delta t_{A \rightarrow B}$  can be used to calculate average flow velocities and apparent rates of reaction between A and B.

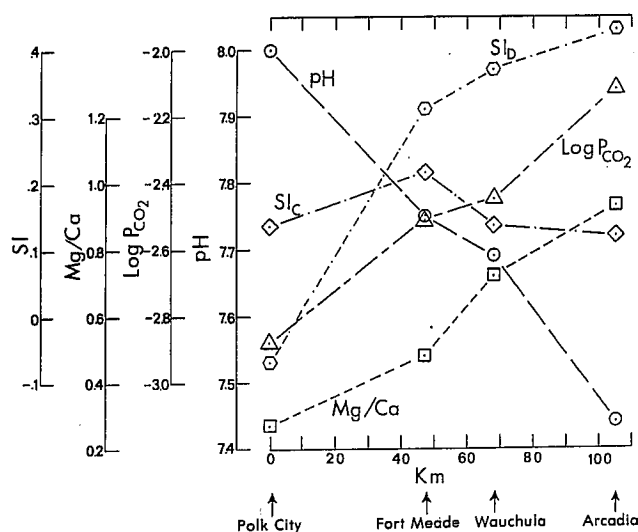


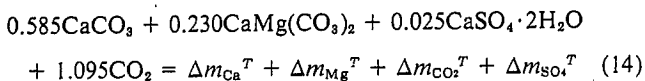
Fig. 4. Trends in pH,  $\log P_{\text{CO}_2}$ , saturation index of calcite ( $\text{SI}_c$ ) and dolomite ( $\text{SI}_b$ ), and Mg/Ca ratio with distance down the gradient from Polk City. Trends in pH,  $\log P_{\text{CO}_2}$ , and  $\text{SI}_c$  are contrary to those expected for congruent dissolution of carbonate minerals but can be explained by solution of dolomite and gypsum with precipitation of low-magnesian calcite.

#### MODELING REACTION PATHS

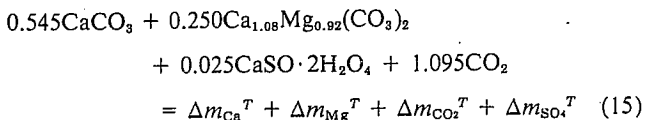
In analysis of the data, two hydrochemical processes can be recognized: (1) net reaction (including interaction of meteoric water with the soil zone, the unsaturated zone, and the saturated zone) that accounts for the water chemistry of the recharge area, taken to be the Polk City water, and (2) net reaction that accounts for the observed changes in water chemistry down the hydraulic gradient between Polk City and Arcadia.

#### Evolution of Polk City Water

In describing the evolution of Polk City water chemistry a number of examples could be considered depending on the choice of magnesium source mineral. However, on the basis of the abundance of dolomite in the Floridan aquifer relative to magnesian calcites and the observation that Polk City water is undersaturated with dolomite (Table 1), there is little doubt that the dominant source of magnesium for Polk City water is dolomite. As was mentioned earlier, the composition of dolomite in the Floridan aquifer varies from  $\text{CaMg}(\text{CO}_3)_2$  to  $\text{Ca}_{1.08}\text{Mg}_{0.92}(\text{CO}_3)_2$ . When we use these two limiting compositions as sources of magnesium and take gypsum as the source of sulfate, calcite as an additional source of calcium, and  $\text{CO}_2$  (soil zone) as a source of carbon, (3)–(7) give two mass balance relations which limit the range of reactions in the evolution of Polk City water. These are



and



Values of  $\Delta m_{\text{Ca}}^T$ ,  $\Delta m_{\text{Mg}}^T$ ,  $\Delta m_{\text{CO}_2}^T$ , and  $\Delta m_{\text{SO}_4}^T$  at Polk City are 0.840, 0.230, 2.140, and 0.025 mmol/l, respectively (Table 1), rain being taken to be essentially pure water.

Reactions (14) and (15) show that with dolomite as the source of magnesium, there must be an additional source of calcium (taken to be calcite) and that the path to Polk City is essentially congruent. As was discussed earlier, these mass balance reactions only show net effects and do not indicate the sequence or simultaneity of reactions.

The derivation of mass balance reactions (14) and (15) (as well as any other mass balance relation resulting from choosing another stoichiometry for dolomite) depends in part on the accuracy of the analyzed total molalities of calcium, magnesium, carbon, and sulfate in the Polk City water. Any uncertainty in the analytical measurements must be reflected, by the mass balance calculation procedure, in the derived coefficients of the relation. In deriving the mass balance relations, minor constituents in solution, such as  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Cl}^-$ , were ignored, and we have no way of determining through the defined mass balance equations (above) and within the uncertainty of the analytical data if all important reactions have been accounted for.

The validity of the derived mass balance relations can be checked by a detailed mass transfer simulation. If any important reactions have been missed in the mass balance or if there is error in the analyzed values used to obtain the mass balance relations, the value of pH predicted by mass transfer simulation will differ from the measured value.

When a  $\pm 0.05$  pH error in the measured pH at Polk City (Table 1) is allowed for, mass transfer simulation using MIX2 and  $\Delta m_{\text{Ca}}^T$ ,  $\Delta m_{\text{Mg}}^T$ , and  $\Delta m_{\text{SO}_4}^T$  of reactions (14) and (15) refines the coefficient of  $\text{CO}_2$  in reactions (14) and (15) to  $1.066 \pm 0.007$  mmol/l. In other words, the combined errors in calcium, magnesium, carbon, and sulfate in the Polk City analysis are equivalent to a maximum error of 1.7% in the reported alkalinity (or total dissolved carbon). This error is clearly within the analytical uncertainties and offers no justification for consideration of the occurrence of other reactions in the evolution of Polk City water. That is, even though other reactions, in addition to those identified, may be occurring in the evolution of Polk City water, they do not contribute significantly to the mass transfer. For example, it is likely that the sulfate in Polk City water results from evaporative concentration of rainwater [Rightmire et al., 1974] rather than gypsum dissolution, but whatever the source, its contribution to the overall reaction at Polk City is not significant.

Variation in the stoichiometry of dolomite does not alter the carbon balance ((14) and (15)), and therefore both mass transfer reactions require 1.066 mmol/l of (soil zone)  $\text{CO}_2$  to balance. Thus for Polk City water to evolve as a closed system to  $\text{CO}_2$  after passing through the soil zone, the amounts of  $\text{CO}_2$  required to balance reactions (14) and (15) would require an initial soil zone  $P_{\text{CO}_2}$  of nearly  $10^{-1.5}$  atm. This amount of  $\text{CO}_2$  is approximately 10 times the amount of  $\text{CO}_2$  dissolved in the soil pore water in the vicinity of Polk City. Of the six soil  $P_{\text{CO}_2}$  measurements reported by Rightmire and Hanshaw [1973] in the recharge area of central Florida, the range of values is  $10^{-2.46}$ – $10^{-2.77}$  atm. This discrepancy between the implied soil zone  $P_{\text{CO}_2}$  when closed system evolution is assumed after the recharge passes through the soil zone,  $10^{-1.5}$  atm, and the measured soil  $P_{\text{CO}_2}$ ,  $10^{-2.46}$ – $10^{-2.77}$  atm, indicates that either the soil zone  $P_{\text{CO}_2}$  measurements of Rightmire and Hanshaw [1973] are not representative of the average soil  $P_{\text{CO}_2}$  recharged to the aquifer or Polk City water evolves in a system of at least partial ingassing of  $\text{CO}_2$ , across the unsaturated zone into the groundwater. Although the  $P_{\text{CO}_2}$  in Polk City water,  $10^{-2.89}$  atm, is less than all soil zone  $P_{\text{CO}_2}$  measurements of Rightmire

TABLE 2. Equilibrium Constants at 25°C

| Reaction                                                                                                              | log K   |
|-----------------------------------------------------------------------------------------------------------------------|---------|
| $\text{CaCO}_3^0 = \text{Ca}^{2+} + \text{CO}_3^{2-}$                                                                 | -3.15*  |
| $\text{CaOH}^+ = \text{Ca}^{2+} + \text{OH}^-$                                                                        | -1.40   |
| $\text{CaSO}_4^0 = \text{Ca}^{2+} + \text{SO}_4^{2-}$                                                                 | -2.31   |
| $\text{MgHCO}_3^+ = \text{Mg}^{2+} + \text{HCO}_3^-$                                                                  | -1.07†  |
| $\text{MgCO}_3^0 = \text{Mg}^{2+} + \text{CO}_3^{2-}$                                                                 | -2.98†  |
| $\text{MgOH}^+ = \text{Mg}^{2+} + \text{OH}^-$                                                                        | -2.60   |
| $\text{MgSO}_4^0 = \text{Mg}^{2+} + \text{SO}_4^{2-}$                                                                 | -2.24   |
| $\text{NaHCO}_3^0 = \text{Na}^+ + \text{HCO}_3^-$                                                                     | 0.25    |
| $\text{NaCO}_3^- = \text{Na}^+ + \text{CO}_3^{2-}$                                                                    | -1.27   |
| $\text{NaSO}_4^- = \text{Na}^+ + \text{SO}_4^{2-}$                                                                    | -0.23   |
| $\text{NaCl}^0 = \text{Na}^+ + \text{Cl}^-$                                                                           | 1.60    |
| $\text{KSO}_4^- = \text{K}^+ + \text{SO}_4^{2-}$                                                                      | -0.85   |
| $\text{KCl}^0 = \text{K}^+ + \text{Cl}^-$                                                                             | 1.59    |
| $\text{H}_2\text{SO}_4^0 = 2\text{H}^+ + \text{SO}_4^{2-}$                                                            | 1.00    |
| $\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{2-}$                                                                      | -1.99   |
| $\text{HCl}^0 = \text{H}^+ + \text{Cl}^-$                                                                             | 6.10    |
| $\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$                                                                       | -14.00  |
| $\text{CO}_{2(\text{g})} + \text{H}_2\text{O} = \text{H}_2\text{CO}_3^*$                                              | -1.47‡  |
| $\text{H}_2\text{CO}_3^* = \text{H}^+ + \text{HCO}_3^-$                                                               | -6.35‡  |
| $\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$                                                                      | -10.33§ |
| $\text{CaCO}_3^{\text{calcite}} = \text{Ca}^{2+} + \text{CO}_3^{2-}$                                                  | -8.42   |
| $\text{CaMg}(\text{CO}_3)_2^{\text{dolomite}} = \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$                  | -17.00  |
| $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}^{\text{(gypsum)}} = \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$ | -4.76   |

Equilibrium constants and species used in the aqueous model, except where it is noted, have been taken from *Truesdell and Jones* [1974]. The temperature dependence of log K is not given because all calculations are at 25°C (see the second footnote to Table 1). Because of uncertainties in the aqueous model [*Jacobson and Langmuir*, 1974; *Plummer and Mackenzie*, 1974] the  $\text{CaHCO}_3^+$  ion pair has been ignored in all equilibria and mass transfer calculations.

\**Reardon and Langmuir* [1974].

†*Siebert* [1974].

‡*Harned and Davis* [1943],  $\text{H}_2\text{CO}_3^* = \text{H}_2\text{CO}_3^0 + \text{CO}_{2(\text{aq})}$ .

§*Harned and Scholes* [1941].

||*Jacobson and Langmuir* [1974].

and Hanshaw and would allow a flux of  $\text{CO}_2$  across the unsaturated zone into the saturated zone, the mechanism by which  $\text{CO}_2$  enters the saturated zone is not well defined. However, one can determine the net stable carbon isotopic composition of the  $\text{CO}_2$  entering the saturated zone and compare this value with the observed isotopic composition of soil zone  $\text{CO}_2$ .

Because the reaction path to Polk City water appears to be congruent, we can use the derived mass balance reactions, the value of  $\delta^{13}\text{C}$  in Polk City water, the estimates of  $\delta^{13}\text{C}$  in calcite and dolomite given earlier, and (11) to calculate the average  $\delta^{13}\text{C}$  of  $\text{CO}_2$  recharged to the aquifer. When the range -4.5 to +0.5‰ is used for  $\delta^{13}\text{C}$  of dolomite and the value +0.1 for  $\delta^{13}\text{C}$  for calcite, values of  $\alpha_f$  from reactions (14) and (15), and  $m_{\text{CO}_2(\text{final})}^T$  and  $\delta^{13}\text{C}_{(\text{final})}$  for Polk City (Table 1) are used, (11) indicates that  $\delta^{13}\text{C}$  of  $\text{CO}_2$  recharged to the aquifer is near -21.9 to -23.0‰. These estimates are in excellent agreement with the measurement of  $\delta^{13}\text{C}$  of soil gas at Polk City reported by *Rightmire and Hanshaw* [1973] of -21.3‰ and support the derived mass balance reactions. The close agreement between calculated  $\delta^{13}\text{C}$  of  $\text{CO}_2$  recharged to the aquifer and the  $\delta^{13}\text{C}$  soil gas measurements of *Rightmire and Hanshaw* [1973] indicates that if the  $\delta^{13}\text{C}$  soil gas measurements of *Rightmire and Hanshaw* are representative of the average isotopic composition of  $\text{CO}_2$  recharged to the aquifer, the mechanism (undefined) of  $\text{CO}_2$  input to the saturated zone involves little fractionation.

#### Reaction Path From Polk City to Arcadia

In this section, changes in the total molalities of calcium, magnesium, carbon, and sulfate are examined between Polk

City and Fort Meade, Fort Meade and Wauchula, and Wauchula and Arcadia in order to define subsurface reactions down the hydraulic gradient. Although one can argue from a thermodynamic basis that in the evolution of Polk City water, dolomites are the most likely sources of magnesium, the choice of the magnesium source mineral along the path from Polk City to Arcadia is not so obvious. Figure 4 shows that south of Polk City the groundwater becomes supersaturated with respect to dolomite and that the level of supersaturation continues to increase with reaction progress through Arcadia. Thus either the dolomite of the Floridan aquifer is less stable than is indicated by a  $pK$  of 17.0, or there are other sources of magnesium along the path. The most likely alternative to dolomite sources is magnesian calcites. The stability data on magnesian calcites of *Plummer and Mackenzie* [1974] show that the waters from Polk City to Arcadia are near saturation (stoichiometric saturation of *Thorstenson and Plummer* [1977]) with magnesian calcites of approximately 6-7 mol % Mg. Thus one could suggest that the more soluble magnesian calcites are the source of magnesium down the gradient and that because crystal growth of dolomite is kinetically slow (or inhibited), dolomite does not precipitate. Instead, the ion activity product of dolomite continues to increase to higher levels of supersaturation in response to magnesian calcite dissolution. According to this hypothesis, dolomite is essentially inert in the Floridan aquifer beyond the recharge area.

Because no other sources of magnesium seem possible for the Floridan aquifer, examples of mass balance reactions are derived below by using the observed range of possible magnesium source minerals:  $\text{CaMg}(\text{CO}_3)_2$ ,  $\text{Ca}_{1.08}\text{Mg}_{0.92}(\text{CO}_3)_2$ , and  $\text{Ca}_{0.98}\text{Mg}_{0.02}\text{CO}_3$ . The mass balance reactions consider  $\text{CO}_2$  and gypsum as sources of carbon and sulfate, respectively, and allow for reactions incongruent to the phase  $\text{Ca}_{0.98}\text{Mg}_{0.02}\text{CO}_3$ , which, according to the data of *Plummer and Mackenzie* [1974], is more stable than pure calcite.

Because the path from Polk City to Arcadia is being considered in three steps (between the four selected wells) and because there is one reaction for each choice of magnesium source mineral along a particular path, a total of nine (i.e., three reaction segments, each with three possible magnesium source minerals) mass balance relations are derived. By using values of  $\Delta m_{\text{Ca}}^T$ ,  $\Delta m_{\text{Mg}}^T$ ,  $\Delta m_{\text{CO}_2}^T$ , and  $\Delta m_{\text{SO}_4}^T$  computed from Table 1 between each successive water analysis, values of  $\alpha_f$  have been computed from (3)-(6) for each mass balance reaction of interest and are summarized in Table 3.

All nine reactions (Table 3) indicate that the path from Polk City to Arcadia is incongruent to a calcium rich phase ( $\text{Ca}_{0.98}\text{Mg}_{0.02}\text{CO}_3$ ). An incongruent path with gypsum as the driving force qualitatively explains the observed trends, that is, a decrease in  $pH$  and an increase in  $P_{\text{CO}_2}$  with reaction progress; opposite trends in  $pH$  and  $P_{\text{CO}_2}$  would be observed if the path (in closed system) were congruent.

Simulation of mass balance reactions in a mass transfer calculation scheme is, again, a useful tool in identifying possible errors in  $\Delta m_c$ , refining values of  $\alpha_f$  that minimize differences in computed and observed parameters, such as  $pH$ , and testing whether other reactions need be considered. Although the coefficients of Table 3 give perfect mass balance, mass transfer simulation using the mass balance reaction coefficients results, in some cases, in significant departure of predicted mineral saturation and  $pH$  from the observed. Mass transfer calculations were made with MIX2 in order to minimize these departures within their uncertainties and thus better define values of  $\alpha_f$ .



TABLE 3. Summary of Mass Balance Reaction Coefficients

| Reaction | Path† | Values of $\alpha_j$ ,* mmol/l      |                                                                       |                                                       |                                      |                                                       |
|----------|-------|-------------------------------------|-----------------------------------------------------------------------|-------------------------------------------------------|--------------------------------------|-------------------------------------------------------|
|          |       | CaMg(CO <sub>3</sub> ) <sub>2</sub> | Ca <sub>1.08</sub> Mg <sub>0.92</sub> (CO <sub>3</sub> ) <sub>2</sub> | Ca <sub>0.95</sub> Mg <sub>0.05</sub> CO <sub>3</sub> | CaSO <sub>4</sub> ·2H <sub>2</sub> O | Ca <sub>0.98</sub> Mg <sub>0.02</sub> CO <sub>3</sub> |
| 1        | PC-FM | 0.482                               |                                                                       |                                                       | 0.714                                | -0.598                                                |
| 2        | PC-FM |                                     | 0.526                                                                 |                                                       | 0.714                                | -0.686                                                |
| 3        | PC-FM |                                     |                                                                       | 15.423                                                | 0.714                                | -15.057                                               |
| 4        | FM-W  | 0.514                               |                                                                       |                                                       | 0.875                                | -1.214                                                |
| 5        | FM-W  |                                     | 0.561                                                                 |                                                       | 0.875                                | -1.307                                                |
| 6        | FM-W  |                                     |                                                                       | 16.457                                                | 0.875                                | -16.642                                               |
| 7        | W-A   | 1.327                               |                                                                       |                                                       | 1.970                                | -2.344                                                |
| 8        | W-A   |                                     | 1.448                                                                 |                                                       | 1.970                                | -2.585                                                |
| 9        | W-A   |                                     |                                                                       | 42.460                                                | 1.970                                | -42.150                                               |

\*Reactants are positive, and products are negative.

†PC stands for Polk City, FM for Fort Meade, W for Wauchula, and A for Arcadia.

In making the mass transfer calculations a constant level of supersaturation for Ca<sub>0.98</sub>Mg<sub>0.02</sub>CO<sub>3</sub> was maintained at 1.5 times saturation ( $pK_{Ca_{0.98}Mg_{0.02}CO_3} = 8.47$  [Thorstenson and Plummer, 1977]), which coincides with the approximately constant level of supersaturation observed in the four waters (Table 1). (This level of supersaturation may be that necessary for crystal growth of calcite in the Floridan aquifer.)

The method used in refining the coefficients in the mass transfer reactions was to obtain accurate mass balance on sulfate and magnesium and vary the CO<sub>2</sub> source term until departures in computed and observed total calcium, carbon, and pH were minimized. Table 4 summarizes the refined mass transfer coefficients for the nine reactions considered, which may be compared with the corresponding mass balance coefficients in Table 3. The reactions in Table 4 have maximum departures in mass balance on calcium and carbon of  $\pm 0.18$  and  $\pm 0.14$  mmol/l, respectively, and  $\pm 0.03$  pH. The differences between predicted and observed water chemistry at Fort Meade, Wauchula, and Arcadia determined by the reactions of Table 4 are less than 7% of the observed values, and many are within 3% of the observed. The refined coefficients of the mass transfer reactions show slightly different amounts of minerals dissolved and precipitated along the path and, interestingly, indicate that (1) there is a net input of CO<sub>2</sub> to the aquifer between Polk City and Fort Meade, (2) the path from Fort Meade to Wauchula is a closed system, and (3) an additional source for CO<sub>2</sub> within the aquifer must be proposed between Wauchula and Arcadia if the groundwater system remains closed down the gradient. The subject of CO<sub>2</sub> sources is returned to below following discussion of the observed changes in  $\delta^{13}C$  and  $^{14}C$  activity along the reaction path.

Nine reactions have been derived (Table 4) that represent the range of possible mass transfer reactions for the Floridan aquifer on the basis of known mineralogy. Because the correct mass transfer reaction must predict both the observed water chemistry and the observed isotopic composition, the number of possible reactions can be narrowed. Table 4 shows that all reactions considered between Polk City and Arcadia are incongruent to a low Mg calcite, and thus in order to calculate values of  $\delta^{13}C$  and  $^{14}C$  activity along the reaction paths it is necessary to use the numerical procedure described earlier.

In calculations of  $\delta^{13}C$  for the proposed nine reactions,  $\delta^{13}C$  of incoming CO<sub>2</sub> was first assumed to be -22.5‰. Although it is consistent with the value found for CO<sub>2</sub> recharge at Polk City, its choice is not meant to imply similar mechanisms and/or processes by which CO<sub>2</sub> enters the system between Polk City and Fort Meade and Wauchula and Arcadia. As is shown in a later section of this paper, the value of  $\delta^{13}C$  of

incoming CO<sub>2</sub> is not independent of  $\delta^{13}C$  for the reactant magnesium source mineral. Calculations were made for two values of  $\delta^{13}C$  of dolomite, -4.5 and +0.5‰, and  $\delta^{13}C$  of reactant magnesian calcite was assumed to be +0.1‰. The choice of these values of  $\delta^{13}C$  for reactant carbonate minerals is consistent with the measurements of *Hanshaw and Back* [1972] for samples of calcite and dolomite from central Florida, as was discussed earlier. By using these isotopic values for carbon sources and their mass transfer coefficients (Table 4) the  $\delta^{13}C$  of source carbon entering the reaction was calculated:

$$\delta^{13}C_{\text{net reactant}} = \frac{\sum_j \alpha_j \beta_{CO_2,j} \delta^{13}C_j}{\sum_j \alpha_j \beta_{CO_2,j}} \quad (16)$$

where the subscript  $j$  refers to the  $j$ th reactant phase. It was assumed that the value of  $\delta^{13}C_{\text{net reactant}}$  is constant along the reaction path, that is, that the relative rates of individual reactants entering solution are constant and enter solution in proportion to their derived mass transfer reaction coefficients.

Table 5 summarizes the results of the  $\delta^{13}C$  and  $^{14}C$  calculations for the nine reactions of Table 4. All reaction paths can be explained if dolomite is the source of magnesium. The implied  $\delta^{13}C$  compositions of reactant dolomite from Polk City to Fort Meade, Fort Meade to Wauchula, and Wauchula to Arcadia are -3.9‰, -1.5‰, and -3.8‰, respectively. These implied values of  $\delta^{13}C$  for dolomite are in the range of observed values in central Florida [Hanshaw and Back, 1972]. The calculations also show that marine magnesian calcites ( $\delta^{13}C$  taken to be +0.1) cannot be the major source of magnesium because as reactants they predict far too heavy values of  $\delta^{13}C$  in solution. Only if  $\delta^{13}C$  of magnesian calcites in Florida range from -6 to -7‰ can the reaction paths studied be explained by Mg calcite sources of magnesium. While it is not impossible, isotopically light Mg calcites as sources of magnesium would require previous diagenetic events in central Florida in which magnesian calcites averaging 5 mol % MgCO<sub>3</sub> precipitated from freshwater (isotopically light). Although isotopically light calcites commonly form during freshwater diagenesis of carbonate sediments, they usually contain less than 5 mol % MgCO<sub>3</sub> [Land, 1970, 1973a, b; Benson and Matthews, 1971].

A more convincing argument against Mg calcites as reactants in central Florida is the calculation of  $^{14}C$  activity for the nine reactions (Table 5). In calculating the corrected  $^{14}C$  activities, two limiting cases were considered in which the  $^{14}C$  activity of the additional CO<sub>2</sub> source was taken to be (1) 100% modern, indicative of soil zone derived CO<sub>2</sub>, and (2) 0.0% modern, suggestive of an older source of carbon within the

TABLE 4. Summary of Mass Transfer Coefficients

| Reaction | Path‡ | Values of $\alpha_j$ ,* mmol/l      |                                                                       |                                                       |                                      |                 |                                                       |
|----------|-------|-------------------------------------|-----------------------------------------------------------------------|-------------------------------------------------------|--------------------------------------|-----------------|-------------------------------------------------------|
|          |       | CaMg(CO <sub>3</sub> ) <sub>2</sub> | Ca <sub>1.08</sub> Mg <sub>0.92</sub> (CO <sub>3</sub> ) <sub>2</sub> | Ca <sub>0.95</sub> Mg <sub>0.05</sub> CO <sub>3</sub> | CaSO <sub>4</sub> ·2H <sub>2</sub> O | CO <sub>2</sub> | Ca <sub>0.98</sub> Mg <sub>0.02</sub> CO <sub>3</sub> |
| 1        | PC-FM | 0.479                               |                                                                       |                                                       | 0.714                                | 0.37            | -0.649                                                |
| 2        | PC-FM |                                     | 0.521                                                                 |                                                       | 0.714                                | 0.37            | -0.733                                                |
| 3        | PC-FM |                                     |                                                                       | 15.667                                                | 0.714                                | 0.37            | -15.357                                               |
| 4        | FM-W  | 0.500                               |                                                                       |                                                       | 0.875                                | 0.00            | -1.015                                                |
| 5        | FM-W  |                                     | 0.544                                                                 |                                                       | 0.875                                | 0.00            | -1.103                                                |
| 6        | FM-W  |                                     |                                                                       | 16.333                                                | 0.875                                | 0.00            | -16.347                                               |
| 7        | W-A   | 1.306                               |                                                                       |                                                       | 1.970                                | 0.51            | -2.226                                                |
| 8        | W-A   |                                     | 1.419                                                                 |                                                       | 1.970                                | 0.51            | -2.453                                                |
| 9        | W-A   |                                     |                                                                       | 42.667                                                | 1.970                                | 0.51            | -42.279                                               |

\*Reactants are positive, and products are negative.

‡PC stands for Polk City, FM for Fort Meade, W for Wauchula, and A for Arcadia.

aquifer, such as lignite. Both cases clearly eliminate magnesian calcites as sources of magnesium by predicting <sup>14</sup>C activities in solution less than the observed values (Table 5). Because radioactive decay of <sup>14</sup>C is not considered in computing corrected values of <sup>14</sup>C along reaction paths (Table 5), the calculated <sup>14</sup>C activity must, for the correct mass transfer reaction, be higher than the observed value in order to account for the passage of time. In the limiting case of very fast flow the corrected <sup>14</sup>C activity could only equal the observed value. Reactions with magnesian calcites as sources predict an impossible situation, that is, corrected <sup>14</sup>C activity less than the observed.

With dolomites as reactants, quite reasonable values of  $\delta^{13}\text{C}$  and <sup>14</sup>C activity in solution are calculated (Table 5). Although the carbon isotopic data show dolomite to be the source of magnesium in central Florida, these data are not known sufficiently well to define the stoichiometry of reactant dolomite. In order to allow dissolution of dolomite in central Florida, thermodynamic considerations require the source dolomite to be somewhat more soluble ( $pK$  near 16.6) than is commonly recognized ( $pK$  near 17.0). Until the kinetic and thermodynamic properties of dolomite are better understood, further discussion of the significance of dolomite dissolution in central Florida is not warranted.

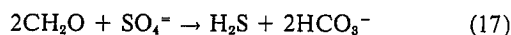
#### DISCUSSION

##### Source of CO<sub>2</sub>

It was shown above that as the water passes from Polk City to Fort Meade, additional CO<sub>2</sub> must enter the saturated zone and that the isotopic composition of this CO<sub>2</sub> (if dolomite is the source of magnesium) is near the observed values of soil CO<sub>2</sub>, as is evidenced by the close agreement in computed and observed  $\delta^{13}\text{C}$  at Fort Meade. The calculations show that farther south from Fort Meade to Wauchula the reaction path is essentially closed to CO<sub>2</sub>. These observations are consistent with the geologic and hydrologic framework of the Floridan aquifer in central Florida. That is, the system is partially open to CO<sub>2</sub> near Polk City, where the Floridan aquifer is shallow, coincident with the area of dominant recharge, and has minimal cover by the Hawthorn formation, and to the south the system becomes closed as the Floridan aquifer increases in depth, flow is farther from the area of major recharge, and the Hawthorn formation increases in thickness. The position on the flow path where the system becomes closed to CO<sub>2</sub> is somewhere north of Fort Meade, since the path from Fort Meade to Wauchula is closed.

This picture becomes more complicated to the south be-

tween Wauchula and Arcadia, where the system appears to become 'open' again to CO<sub>2</sub>. However, there is no geologic or hydrologic reason to suggest that an open system exists farther south along the flow path. A more reasonable interpretation of the additional source of CO<sub>2</sub> south of Wauchula is oxidation of lignite via sulfate reduction within the (closed system) Floridan aquifer. This conclusion is supported by total sulfide levels which reach 1.5 mg/l at Arcadia [Rightmire *et al.*, 1974]. The reported levels of dissolved sulfide are less than the level expected for sulfate reduction alone, as is indicated by the reaction



The reaction coefficient for CO<sub>2</sub> between Wauchula and Arcadia (Table 4) requires, according to (17), an increase of approximately 8 mg/l of total dissolved sulfide between Wauchula and Arcadia. The observed increase in total dissolved sulfide [Rightmire *et al.*, 1974] is 0.3 mg/l, which suggests that other reactions, presumably precipitation of iron sulfide(s), are occurring. Simulation of mass transfer reactions between Wauchula and Arcadia, taking into account sulfate reduction with and without consideration of accompanying iron sulfide precipitation, does not alter the derived mass transfer reaction coefficients for the carbonate minerals considered within the uncertainties of the analytical data. Calculation of  $\delta^{13}\text{C}$  shows that the source of CO<sub>2</sub> between Wauchula and Arcadia ranges from -22.5 to -34.6‰ if  $\delta^{13}\text{C}$  of reactant dolomite varies from -3.8 to -1.5‰.

##### Age of Waters

In view of the above discussion the corrected <sup>14</sup>C activities at Fort Meade, Wauchula, and Arcadia (Table 5) have been calculated by assuming that the additional source of CO<sub>2</sub> between Polk City and Fort Meade is 100% modern (soil zone CO<sub>2</sub>) and that the CO<sub>2</sub> source between Wauchula and Arcadia (lignite) has a <sup>14</sup>C activity of zero. The corrected <sup>14</sup>C activity at Polk City has been calculated from an equation similar to (11) by taking the additional source of CO<sub>2</sub> as 100% modern. The corrected <sup>14</sup>C activity at Polk City varies from 51.2 to 49.8% modern depending on the choice of either the mass balance CO<sub>2</sub> coefficient (1.095) or the mass transfer derived CO<sub>2</sub> coefficient (1.066), respectively. When we use the observed activity of <sup>14</sup>C at Polk City, 34.3% modern (Table 1), (13) gives the average age of Polk City water as 3200 yr. Similar calculations using corrected <sup>14</sup>C activities at Fort Meade, Wauchula, and Arcadia (Table 5) and observed <sup>14</sup>C activity at these locations (Table 1) give the times required for flow between

TABLE 5. Summary of Calculated Values of  $\delta^{13}\text{C}$  and  $^{14}\text{C}$  Activity

| Reaction | Path  | $\delta^{13}\text{C}$<br>Measured† | $\delta^{13}\text{C}$ Calculated*                 |                                                   | Implied<br>$\delta^{13}\text{C}$ of<br>Magnesium<br>Source<br>Mineral‡ | $^{14}\text{C}$ Activity, % modern |            |
|----------|-------|------------------------------------|---------------------------------------------------|---------------------------------------------------|------------------------------------------------------------------------|------------------------------------|------------|
|          |       |                                    | $\delta^{13}\text{C}_{\text{Dol}} = -4.5\text{‰}$ | $\delta^{13}\text{C}_{\text{Dol}} = +0.5\text{‰}$ |                                                                        | Measured§                          | Calculated |
| 1        | PC-FM | -10.8                              | -11.0                                             | -9.6                                              | -3.7                                                                   | 17.3                               | 31.6       |
| 2        | PC-FM | -10.8                              | -10.9                                             | -9.4                                              | -4.1                                                                   | 17.3                               | 30.8       |
| 3        | PC-FM | -10.8                              | -2.3                                              | -2.3                                              | -6.0                                                                   | 17.3                               | 2.2        |
| 4        | FM-W  | -8.5                               | -9.5                                              | -8.0                                              | -1.2                                                                   | 4.4                                | 12.0       |
| 5        | FM-W  | -8.5                               | -9.4                                              | -7.8                                              | -1.7                                                                   | 4.4                                | 11.7       |
| 6        | FM-W  | -8.5                               | -1.9                                              | -1.9                                              | -6.8                                                                   | 4.4                                | 0.0        |
| 7        | W-A   | -8.3                               | -8.8                                              | -6.2                                              | -3.5                                                                   | 1.2                                | 1.7        |
| 8        | W-A   | -8.3                               | -8.6                                              | -6.0                                              | -4.0                                                                   | 1.2                                | 1.6        |
| 9        | W-A   | -8.3                               | -2.0                                              | -2.0                                              | -6.2                                                                   | 1.2                                | 0.0        |

PC stands for Polk City, FM for Fort Meade, W for Wauchula, and A for Arcadia.

\* Calculated by the iterative method described in the text by using  $\delta^{13}\text{C}_{\text{CO}_2} = -22.5\text{‰}$ ,  $\delta^{13}\text{C}_{\text{Cal}} = +0.1\text{‰}$ ,  $\delta^{13}\text{C}_{\text{Dol}} = -4.5$  and  $+0.5\text{‰}$ , and the reaction coefficients of Table 4.

† Measured value of  $\delta^{13}\text{C}$  in solution (Table 1) at the end of the path.

‡ Value of  $\delta^{13}\text{C}$  of the magnesium source mineral for the particular reaction required if the reaction (Table 4) is to predict the observed value of  $\delta^{13}\text{C}$ .

§ Measured  $^{14}\text{C}$  activity of solution at the end of the path (Table 1).

|| Calculated value of  $^{14}\text{C}$  activity corrected for predicted mass transfer in the absence of radioactive decay. The  $^{14}\text{C}$  activity of the  $\text{CO}_2$  source between Polk City and Fort Meade is taken to be 100% modern, and between Wauchula and Arcadia the source is assumed to be 0.0% modern. (See text for discussion.)

each well. These results are summarized in Table 6. The reaction numbers of Table 6 are keyed to reactions of Tables 3–5 in order to show the effect of reactant dolomite stoichiometry on calculated apparent flow time. These values of flow time have been summed with the age of Polk City water (above) to obtain estimates of water ages (Table 1). The derived estimates of water ages are slightly younger than those of *Back and Hanshaw* [1970] because in the present study, effects of congruent and incongruent reactions have been considered in obtaining correct  $^{14}\text{C}$  activities. The method used by *Back and Hanshaw* [1970] to calculate water age [*Ingerson and Pearson*, 1964] accounts only for congruent solution.

Table 6 compares estimates of flow velocity computed from hydrologic considerations by *Hanshaw et al.* [1965] with velocities implied by  $^{14}\text{C}$  ages and compares apparent rates of reaction calculated from the mass transfer reaction coefficients (Table 4) with the computed values of  $\Delta\text{time}$  (Table 6). Because of uncertainties introduced in sampling and handling procedures of waters with low  $^{14}\text{C}$  activities (as well as the possibility of soil water leakage into the well), older waters become increasingly difficult to date by the  $^{14}\text{C}$  method. The values of flow time reported in Table 6 have been computed by assuming no uncertainty in the measured  $^{14}\text{C}$  activity at Fort Meade, Wauchula, and Arcadia. In the Arcadia water (1.2% modern), uncertainties of 1–2% modern in the reported  $^{14}\text{C}$  activity are quite possible (M. Rubin, personal communication, 1976). Uncertainty in the measured  $^{14}\text{C}$  activity at Arcadia seems the most plausible explanation for the calculated short duration of flow time between Wauchula and Arcadia (and the implied higher flow velocities and faster rates of reaction (Table 6)).

If we rely on the derived mass transfer coefficients between Wauchula and Arcadia (Table 4) and assume that the rates of reaction between Wauchula and Arcadia are less than or equal to those calculated between Fort Meade and Wauchula (Table 6), we can calculate minimum estimates of the time of flow between Wauchula and Arcadia. Depending on the choice of mass transfer coefficient and reaction this procedure indicates that the flow time between Wauchula and Arcadia is greater

than 17,500–21,800 yr. These estimates imply, from (13), that the true  $^{14}\text{C}$  activity in Arcadia water is near 0.1–0.2% modern, which is within the uncertainty of the reported value (1.2%). The revised calculations of flow time between Wauchula and Arcadia are more consistent with the hydrologic and geochemical framework of the Floridan aquifer and indicate that the flow velocity between Wauchula and Arcadia is less than 1.7–2.1 m/yr and that the age of Arcadia water is greater than approximately 36,000 yr (roughly twice that calculated from the corrected and the observed  $^{14}\text{C}$  activities).

Interpretation of the significance of the apparent rates of reaction (Table 6) must take into account other factors which are, no doubt, an integral part of these apparent rates.

1. The isotopic composition and  $P_{\text{CO}_2}$  of soil water recharged to the aquifer may have varied, in response to changes of climate over the past 36,000 yr. As a result, for example, one could argue that the derived values of  $\delta^{13}\text{C}$  of reactant dolomite (–3.9‰ Polk City–Fort Meade, –1.5‰ Fort Meade–Wauchula, and –3.8‰ Wauchula–Arcadia) indicate a period of heavier soil  $\text{CO}_2$  some 16,000 yr ago in central Florida when the groundwater, presently at Wauchula, was recharged to the aquifer.

2. Effects of hydrodynamic dispersion along flow paths cause a ‘dilution’ of dissolved constituents with increasing distance down hydrologic gradients. As a result, actual rates of reaction tend to be faster than rates implied by mass balance considerations along flow lines.

3. The calculated rates are for ‘idealized’ choices of single-mineral compositions. In reality, a host of dolomite compositions (as well as the possibility of traces of Mg calcites) may be dissolving simultaneously. The rates of dissolution of dolomites of differing compositions may not be equal.

4. The derived apparent rates are relative to a liter of groundwater. The amount of mineral surface area in contact with the liter of solution is thus incorporated in the apparent rate. Calculation of rates per unit surface area requires detailed knowledge of the mineral abundances, porosity, permeability, and pore space geometry in order to calculate mineral surface area in contact with a liter of groundwater.

TABLE 6. Summary of Estimated Flow Velocities and Apparent Rates of Reaction

| Reaction | Path  | $\Delta$ Time, † yr | Flow Velocity, m/yr  |                   | Apparent Rates of Reaction,* mol/yr per liter of solution |                                                   |                                           |                      |                                               |
|----------|-------|---------------------|----------------------|-------------------|-----------------------------------------------------------|---------------------------------------------------|-------------------------------------------|----------------------|-----------------------------------------------|
|          |       |                     | Hydrologic Estimate‡ | $^{14}\text{C}$ § | $\text{CaMg}(\text{CO}_3)_2$                              | $\text{Ca}_{1.08}\text{Mg}_{0.92}(\text{CO}_3)_2$ | $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ | $\text{CO}_2$        | $\text{Ca}_{0.98}\text{Mg}_{0.02}\text{CO}_3$ |
| 1        | PC-FM | 5,000               | 10.0                 | 9.4               | $9.6 \times 10^{-8}$                                      |                                                   | $1.4 \times 10^{-7}$                      | $7.4 \times 10^{-8}$ | $-1.3 \times 10^{-7}$                         |
| 2        | PC-FM | 4,800               | 10.0                 | 9.8               |                                                           | $1.1 \times 10^{-7}$                              | $1.5 \times 10^{-7}$                      | $7.7 \times 10^{-8}$ | $-1.5 \times 10^{-7}$                         |
| 4        | FM-W  | 8,300               | 7.0                  | 2.5               | $6.0 \times 10^{-8}$                                      |                                                   | $1.1 \times 10^{-7}$                      | 0                    | $-1.2 \times 10^{-7}$                         |
| 5        | FM-W  | 8,100               | 7.0                  | 2.6               |                                                           | $6.7 \times 10^{-8}$                              | $1.1 \times 10^{-7}$                      | 0                    | $-1.4 \times 10^{-7}$                         |
| 7        | W-A   | 2,900               | 4.8                  | 12.9              | $4.5 \times 10^{-7}$                                      |                                                   | $6.8 \times 10^{-7}$                      | $1.8 \times 10^{-7}$ | $-7.7 \times 10^{-7}$                         |
| 8        | W-A   | 2,400               | 4.8                  | 15.6              |                                                           | $5.9 \times 10^{-7}$                              | $8.2 \times 10^{-7}$                      | $2.1 \times 10^{-7}$ | $-1.0 \times 10^{-6}$                         |
| 7-8      | W-A   | 19,700              | 4.8                  | 1.9               |                                                           |                                                   |                                           |                      |                                               |

PC stands for Polk City, FM for Fort Meade, W for Wauchula, and A for Arcadia.

\*Calculated from the reaction coefficients of Table 4 and the  $^{14}\text{C}$  estimates of  $\Delta$ years.

†Calculated from the data of Table 5 by using (13).

‡Estimated by *Hanshaw et al.* [1965] from hydrologic considerations.

§Calculated from the corrected  $^{14}\text{C}$  estimates of  $\Delta$ years and the distances PC-FM = 47 km, FM-W = 21 km, and W-A = 37 km.

||Mean estimate calculated from the derived rates of reaction between Fort Meade and Wauchula (Table 6) and the derived mass transfer coefficients between Wauchula and Arcadia (Table 4).

The derived rates in Table 6 represent a first step toward obtaining kinetic information on mineral-water reactions from field data. Hopefully, they will serve as future reference for comparison with rate data from other natural water systems and with laboratory kinetic studies.

#### Florida Diagenesis

The results of this study point to a rather complex diagenetic history for central Florida. Presently, isotopically light dolomite appears to be dissolving in the Floridan aquifer. Other reactions must have occurred in the past in order to account for the formation of the isotopically light dolomite. These dolomites may have formed during previous high stands of sea level when the freshwater-seawater interface was at higher stratigraphic levels in the Floridan aquifer. The resulting mixing zones presumably account for the 'boulder zone' (R. O. Vernon, unpublished manuscript, 1969), a cavernous zone of high permeability which occurs at various stratigraphic levels through peninsular Florida. As has been discussed by *Badiazamani* [1973] and *Plummer* [1975], dolomite can form by replacement of calcite in freshwater-seawater mixing zones. It is likely that this dolomite would be isotopically light. Today, with the mixing zone at greater depths below the land surface in central Florida, isotopically light diagenetic dolomites, which were once stable in freshwater-seawater mixing zones, are found in a freshwater aquifer where they are unstable and dissolve irreversibly. This cycle between precipitation and dissolution of dolomite may have a long history of repetition in central Florida in response to changes in the position of the freshwater-seawater interface. These arguments lead to further speculation that dolomite may be forming today in the mixing zone which occurs at greater depths below the Floridan aquifer.

#### SUMMARY AND CONCLUSIONS

Use of mass balance relationships, mass transfer simulation procedures, and prediction of carbon isotopic composition of waters leads to the following conclusions regarding reactions occurring down the gradient in a portion of the Floridan aquifer:

1. The waters of the recharge area near Polk City have an average age of 3200 yr and have formed by congruent solution of dolomite and calcite.  $\text{CO}_2$  entering the saturated zone in the

vicinity of Polk City has a mean  $\delta^{13}\text{C}$  composition of  $-22.5 \pm 0.6\text{‰}$  and is similar to the measured value of  $\delta^{13}\text{C}$  of soil zone  $\text{CO}_2$  at Polk City of *Rightmire and Hanshaw* [1973]. However, either the soil  $P_{\text{CO}_2}$  measurements of *Rightmire and Hanshaw* are not representative of soil water recharged to the aquifer, or other processes are required to account for transport of dissolved  $\text{CO}_2$  into the saturated zone, such as diffusion of soil  $\text{CO}_2$  across the unsaturated zone into the saturated zone.

2. Down the hydraulic gradient from the vicinity of Polk City, isotopically light dolomites ( $\delta^{13}\text{C} = -3.9$  to  $-1.5\text{‰}$ ) and gypsum dissolve. All reactions south of Polk City are incongruent to low-magnesian calcites. The reaction path between Polk City and Fort Meade is partially open to  $\text{CO}_2$ , presumably soil zone  $\text{CO}_2$ . Further south down the gradient, between Fort Meade and Wauchula, the Floridan aquifer becomes essentially closed to  $\text{CO}_2$ . Further south, between Wauchula and Arcadia, oxidation of lignite (possibly via sulfate reduction) adds additional carbon to the water composition. (Computed stoichiometric reaction coefficients are summarized in Table 4.)  $^{14}\text{C}$  ages, corrected for the derived mass transfer reactions, are slightly younger than was previously recognized owing to consideration of incongruent dissolution. At the farthest point down the gradient the age of (Arcadia) water is estimated to be 36,000 yr B.P.

3. Flow velocities derived from  $^{14}\text{C}$  ages are in reasonable agreement with flow velocities estimated from hydrologic considerations and are approximately 2–10 m/yr.

4. Apparent rates of reaction, uncorrected for dispersion effects, multiple simultaneous reactions, and mineral surface area, have been derived from the field data and await comparison with rate data from other natural water systems and laboratory rates.

5. The derived mass transfer reactions point to a complex diagenetic history in central Florida. The position of the freshwater-seawater interface appears to determine whether dolomite will be a product or reactant mineral. Today, isotopically light diagenetic dolomites, which presumably formed when the mixing zone stood at a higher stratigraphic level in central Florida, are reactants in the freshwater of the Floridan aquifer.

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