REACTION-PATH FORMULATION OF A SIMPLE DISSOLUTION MODEL FOR RADIOCARBON DATING GROUNDWATER

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ABSTRACT. Since the pioneer publication of K. O. Münnich (1957), ^{14}C systematics have been used in many hydro-geological studies. Because of the complexity of carbon geochemistry, numerous models have been proposed to correct the dilution effect of "dead" carbon in groundwater. All the ^{14}C correction models for dating groundwater are based on either open- or closed-system conditions. I present here a simple model that accounts for the effects of both open- and closed-system dissolution of carbonate and aluminosilicate minerals. For systems involving precipitation of carbonate minerals and redox reactions of organic matter, reaction-path simulations are essential for reliable ^{14}C dating of groundwater.

INTRODUCTION

As a result of root respiration and decay of organic matter, the partial pressure of CO_2 in soil horizons is generally much higher than in the atmosphere. The typical pCO_2 value in the vadose zone is 0.01 atmosphere. As recharge water percolates through the CO_2-rich vadose zone, any consumption of dissolved CO_2 during water-rock interaction is constantly replenished by the CO_2 reservoir in the vadose zone. The chemical and carbon-isotopic composition of the water is modulated by the CO_2 reservoir. This environment is an open system. As the recharge water moves deeper into the groundwater system and away from the influence of a CO_2 reservoir, any carbonic acid (H_2CO_3) consumed during water-rock interactions is no longer replenished. The chemical and carbon-isotopic composition of water can change as a result of hydrogeochemical reactions without the modulation of a CO_2 reservoir. The water would then be under closed-system conditions.

The ^{14}C content of groundwater may change as a result of water-rock interactions even without any radioactive decay. The main challenge in ^{14}C dating of groundwater is correcting for the contribution of "dead" carbon caused by water-rock interactions under both open- and closed-system conditions. Because of the complexity of carbon geochemistry, many researchers proposed simplified models to estimate this adjustment factor, called the "Q" factor. The age of groundwater is then calculated by

$$\text{time} = 8266.6 \times \ln(QA_o/A) \,,$$

where A_o and A are the ^{14}C activity at time, zero, and the measured activity, respectively.

Most of the ^{14}C groundwater dating models are based on the closed-system dissolution of calcite. They include carbon isotope models (Brinkmann, Münnich, & Vogel 1959; Ingerson & Pearson 1964; Pearson 1965), a chemical model (Tamers 1967, 1975) and a chemical-isotopic model (Reardon & Fritz 1978). Deines, Langmuir and Harmon (1974) proposed separate open- and closed-system models. Mook (1976, 1980) derived a chemical-isotopic model based on open-system dissolution of calcite. In reality, carbonate minerals are likely to dissolve under both open- and closed-system conditions. Based on chemical and carbon-isotopic mass balances, Fontes and Garnier (1979) derived an equation that accounts for the dissolution of carbonate minerals and partial isotopic exchange between CO_2 gas and solid carbonate. Their model implicitly includes both open- and closed-system dissolutions of carbonate minerals, but it fails to include the isotopic fractionation between CO_2 gas and dissolved inorganic carbon (DIC). Models based on stable carbon-isotopic compositions inherit the uncertainty in the carbon-isotopic value of soil CO_2 gas at the time of recharge. Closed-system models are more likely to overcorrect the "dead" carbon

effect than open-system models, and consequently, may underestimate the ^{14}C age of the groundwater. Most of the ^{14}C dating models fail to consider both open- and closed-reaction conditions, which result in erroneous estimates of groundwater ages.

Wigley (1975) discussed the open-system effects on carbon-isotopic composition and the ^{14}C adjustment factor by constructing a hybrid open-to-closed-system dissolution path. Deines, Langmuir and Harmon (1974) used a set of dual chemical-isotopic equilibrium equations to calculate the carbon isotopic composition for open-system conditions. Wigley, Plummer and Pearson (1978) formulated a general mass-balance-transfer equation for modeling the carbon-isotopic composition of water under closed-system conditions. Cheng and Long (1984) implemented these two sets of equations as a subroutine, CSOTOP, to the hydrogeochemical program, PHREEQE (Parkhurst, Thorstenson & Pearson 1980). The PHREEQE-CSOTOP combination is also capable of simulating the hybrid-reaction path. Detailed computer simulation has the advantage of being rigorous, but it may be time-consuming.

The increments in DIC and alkalinity during calcite dissolution are different under open- and closed-system conditions. These important reaction signatures can be used to estimate the "Q" factor. I present below a simple equation that accounts for both open- and closed-system effects on the adjustment factor, "Q," based on these reaction signatures.

FORMULATION OF THE SIMPLE DISSOLUTION MODEL

Open System

In the recharge areas of most groundwater systems, the water is typically in contact with a CO_2 reservoir in the unsaturated zone. The water-rock interactions under this condition are modulated by the partial pressure of CO_2 gas. The concentration of H_2CO_3 is solely controlled by $p(CO_2)$ and Henry's law constant (Eq. 1). Any reactions that consume H^+ will induce the dissociation of H_2CO_3 and HCO_3 (Eqs. 2 & 3)

$$CO_2(gas) + H_2O \rightarrow H_2CO_3 \tag{1}$$

$$H_2CO_3 \rightarrow HCO_3^+ + H^+ \tag{2}$$

$$HCO_3^- \rightarrow CO_3^- + H^+ . \tag{3}$$

Under open-system conditions, any dissociated H_2CO_3 will be replenished by dissolving more CO_2 from the CO_2 reservoir. The DIC increases as a result of H^+ consumption.

Calcite dissolution under open-system conditions is better described by Equation 4

$$x\, CaCO_3 + (x+h)\, H_2CO_3 \rightarrow x\, Ca^{++} + 2x\, HCO_3^- + h\, H_2CO_3 . \tag{4}$$
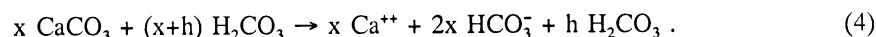
The amount of DIC resulting from calcite dissolution under open-system conditions is $(2x + h)$ moles, where "h" is a fixed quantity controlled by temperature and pCO_2 (Eq. 1), and is called initial carbonic acid, $(H_2CO_3)°$. Under this condition, x moles of H_2CO_3 are consumed by calcite dissolution and subsequently replenished by dissolving x moles of CO_2 gas to maintain a constant H_2CO_3 activity. The alkalinity increases by 2x (Eq. 4).

Individual DIC species have different carbon isotope fractionation factors. Their relative concentrations are controlled by solution pH. Mook, Bommerson and Staverman (1974) and Deines, Langmuir and Harmon (1974) have studied these isotope fractionation factors. By integrating DIC

speciation and their fractionation factors, the carbon-isotopic composition of the DIC under open-system conditions can be calculated by

$$\alpha_{DIC/CO2} = \Sigma\{mC_i \times \alpha_{i/CO2}\}/DIC \qquad (5)$$

where α is a carbon-isotope fractionation factor relative to CO_2 gas, and mC_i is the molal concentration of aqueous carbon species, i. The equations proposed by Deines, Langmuir and Harmon (1974) are used to construct Figure 1. It should be noted that the carbon-isotopic composition of dissolving carbonate has no effect on the DIC ^{13}C and ^{14}C. The carbon-isotopic composition of DIC changes as a result of H^+ consumption and respeciation of DIC (Eqs. 1–3).
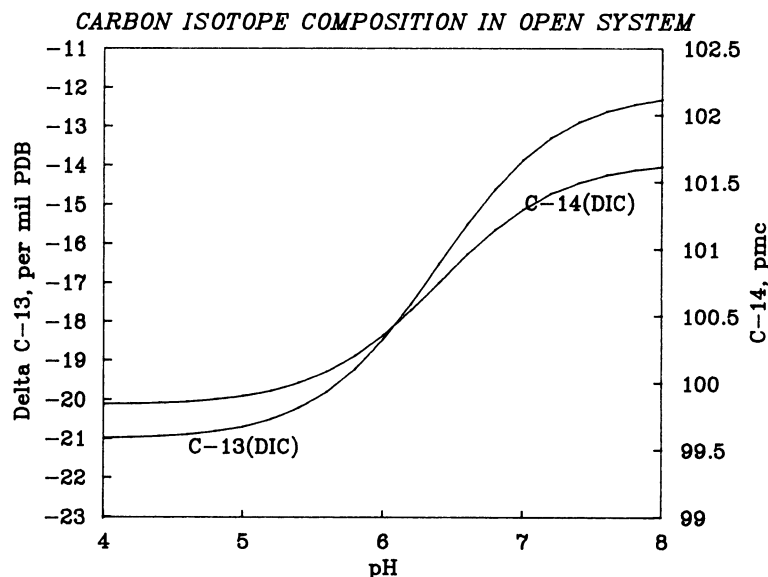

Fig. 1. Carbon isotope composition of water as a function of pH in an open system. Isotope fractionation factors of Deines, Langmuir and Harmon (1974) are used. The following parameters are used for this figure: temperature = 20°C; pCO$_2$ = 0.01 atm; $\delta^{13}C_{CO2\ gas}$ = −20.2‰; $^{14}C_{CO2\ gas}$ = 100 pMC.

Closed System

As the recharge water moves deeper into the aquifer system, it may be isolated from the influence of a CO_2 reservoir. As a result, any H_2CO_3 dissociation will not be replenished as it would be under open-system conditions. Carbonate dissolution increases pH and DIC according to

$$yCaCO_3 + yH^+ \rightarrow yCa^{++} + yHCO_3^- . \qquad (6)$$

For every mole of calcite dissolution under closed-system conditions, the solution increases alkalinity by two moles (one for H^+ consumption and one for the increment of HCO_3^-) and DIC by only one mole.

From Open-to-Closed System

From the recharge area to the deeper aquifer, groundwater experiences both open- and closed-system conditions. From Equations 4 and 6, total DIC and total alkalinity can be calculated by

$$Total\ DIC = 2x + y + (H_2CO_3)^\circ \tag{7}$$

$$Total\ Alk. = 2x + 2y . \tag{8}$$

It should be noted that $(H_2CO_3)^\circ$ is the concentration of initial carbonic acid at the end of the open system, not that of the water sample.

For a simple dissolution system, the "Q" factor is simply the ratio of DIC (open) to DIC (total), and can be calculated as

$$Q = \frac{2x + (H_2CO_3)^\circ}{2x + y + (H_2CO_3)^\circ} . \tag{9}$$

By rearranging Equations 7, 8 and 9 to eliminate x and y, Q can be expressed as

$$Q = \frac{2DIC - ALK. - (H_2CO_3)^\circ}{DIC} \tag{10}$$

or

$$Q = \frac{2DIC - ALK. - pCO_2 x K_H}{DIC} \tag{11}$$

where, K_H is the Henry's Law constant for CO_2 gas. Once $(H_2CO_3)^\circ$ under open-system conditions can be reasonably estimated, the simple equation above can be used to calculate the adjustment factors for groundwater that have evolved from open-to-closed-system conditions.

Equation 10 can be rearranged to

$$Q = \frac{(DIC - 0.5\ ALK.) + (DIC - 0.5\ ALK.) - pCO_2 x K_H}{DIC}$$
$$= \frac{DIC\ 0.5\ ALK.}{DIC} + \frac{x}{DIC} . \tag{12}$$

The first half of Equation 12 is identical to the "q" or "F" value of the closed-system dissolution equation (Tamers 1975). The second half of Equation 12 is the ratio of calcite dissolved in open-system conditions to the total DIC. It is clear from this equation that existing closed-system models neglect the open-system effect of carbonate dissolution.

The Effect of Aluminosilicate Minerals

Incongruent dissolution of aluminosilicate minerals, such as for K-feldspar and the precipitation of kaolinite, changes the pH of the aqueous solution. Under open-system conditions, dissolution of silicate minerals consumes dissolved H_2CO_3, which is replenished by dissolving more CO_2 gas from the CO_2 reservoir. Under closed-system conditions, the same reaction will convert H_2CO_3 to HCO_3^- by consuming H^+ without affecting DIC. Equations 13 and 14 represent this reaction under open- and closed-system conditions, respectively,

$$a\ KAlSi_3O_8 + a\ CO_2(gas) + 1.5a\ H_2O \rightarrow$$
K-feldspar

$$0.5a\ Al_2Si_2O_5(OH)_4 + a\ K^+ + a\ HCO_3^- + 2a\ SiO_{2(aq)} \tag{13}$$
Kaolinite

$$b\ KAlSi_3O_8 + b\ H^+ + 0.5b\ H_2O \rightarrow$$
K-feldspar
$$0.5b\ Al_2Si_2O_5(OH)_4 + b\ K^+ + 2b\ SiO_{2(aq)} \tag{14}$$
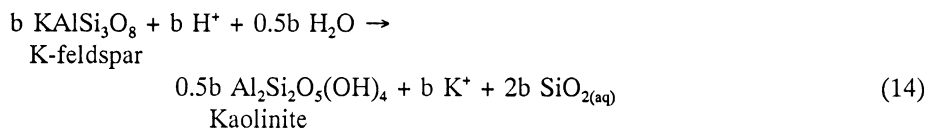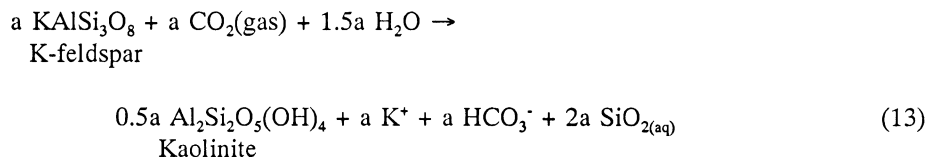Kaolinite

Table 1 summarizes the increments of DIC and alkalinity as a result of calcite and aluminosilicate dissolution under both open- and closed-system conditions. Through the similar manipulations for Equation 10, Equation 15 is derived for the system including both calcite and incongruent dissolution of K-feldspar

$$Q = \frac{2DIC - ALK. + b - (H_2CO_3)^o}{DIC} \ . \tag{15}$$

It should be noted that the incongruent dissolution of aluminosilicate under open-system conditions does not affect the estimation of the Q factor. The quantity, "b," is the increment of alkalinity due to H^+ consumption caused by K-feldspar-to-kaolinite alteration under closed-system conditions. It is difficult to estimate this quantity accurately without proper hydrogeochemical understanding of the groundwater system. Fortunately, the "b" value is likely to be small in most groundwater systems. For example, if the reaction of Equation 12 generated 0.25 meq liter^{-1} (15 ppm) of SiO_2, the correspondent "b" would be 0.125 meq liter^{-1} (7.6 ppm) as bicarbonate. The above discussion is for K-feldspar-to-kaolinite alteration only. Incongruent dissolution of different mineral pairs may have different SiO_2-to-alkalinity ratios.

TABLE 1. Summary of DIC and alkalinity increments from calcite dissolution and incongruent dissolution of K-feldspar to kaolinite

	K-feldspar/kaolinite		Calcite	
	Open	Closed	Open	Closed
DIC	1a	0	$2x + (H_2CO_3)^o$	y
Alkalinity	1a	1b	2x	2y

APPLICATION OF THE EQUATION TO THE SAN JUAN BASIN, NEW MEXICO

The dominant hydrogeochemical reaction at the San Juan Basin, New Mexico, is calcite dissolution driven by Na/Ca ion exchange reaction (Phillips *et al.* 1989). The equation presented here is based on simple dissolution of calcite and, therefore, is applicable to the San Juan Basin. Phillips *et al.* (1989) presented adjustment factors, "Q," estimated from many ^{14}C dating models and reaction-path simulations. The application of the proposed equation to the San Juan Basin has the benefit of having adjustment factors from various models for comparison. Table 2 lists the input data for the proposed equation. The DIC concentrations are calculated from the chemical compositions of water presented in Phillips *et al.* (1989) with the computer program, PHREEQE (Parkhurst, Thorstenson & Plummer 1980). Table 3 lists the adjustment factors, "Q," estimated from various ^{14}C models.

TABLE 2. Input Data for the Proposed Model

Sample	Temp. °C	pH	$\log(K_H)$*	(H_2CO_3)** mmoles liter^{-1}	Alkalinity mmoles liter^{-1}	DIC mmoles liter^{-1}
SJB-01-OA	24.8	9.48	−1.464	0.344	5.82	4.896
SJB-02-OA	15.8	9.62	−1.356	0.441	5.79	4.879
SJB-04-OA	16.0	8.96	−1.359	0.441	5.34	5.090
SJB-05-OA	13.5	8.51	−1.328	0.470	4.30	4.243
SJB-11-OA	17.5	8.47	−1.377	0.420	4.44	4.392
SJB-16-OA	15.5	9.27	−1.353	0.444	6.65	6.072

*Henry's law constant for CO_2 gas
**$(H_2CO_3)°$ (mmoles liter^{-1}) = K_H x pCO_2 x 1000, where pCO_2 is 0.01 atm

TABLE 3. The adjustment factor, Q, of water samples from the San Juan Basin estimated from various ^{14}C-age correction models

Sample	Proposed model	Tamers	Mook	Pearson	Fontes-Garnier	Reaction simulation
SJB-01-OA	0.741	0.435	0.801	0.846	0.685	0.730
SJB-02-OA	0.723	0.414	0.927	0.819	0.695	0.749
SJB-04-OA	0.864	0.480	0.798	0.812	0.654	0.868
SJB-05-OA	0.876	0.496	0.917	0.846	0.702	0.927
SJB-11-OA	0.893	0.497	0.909	0.914	0.739	0.907
SJB-16-OA	0.832	0.458	1.10	0.887	0.778	0.805

The Tamers model is based on closed-system dissolution of calcite and overestimates the effect of dead carbon on the ^{14}C activity of DIC; Mook's model is based on open-system dissolution of calcite and results in under-correction of dead carbon contribution. The Pearson model is based on stable carbon-isotopic composition of carbonate minerals and soil CO_2 gas, which is not well defined and might have fluctuated in the past. The Fontes and Garnier model is similar to the Pearson model, with the addition of isotopic exchange between CO_2 gas and solid carbonate. The reaction-path simulations account for both open- and closed-system dissolutions of carbonate minerals. The agreement in the estimated "Q" factors between the proposed equation and the reaction-path simulation is very good. The source of discrepancy between these two approaches is the initial pCO_2 used in each method. The initial pCO_2 used in reaction-path simulations ranges from $10^{-1.85}$ to $10^{-2.15}$ atm; a pCO_2 of 10^{-2} atm is used for the proposed equation. Better agreement can be achieved if the same pCO_2 is used for both methods.

LIMITATIONS AND APPLICATIONS

Because the equations presented here are based on mass transfer during the dissolution of carbonate, the uncertainty in stable carbon-isotopic composition in aquifer systems does not affect the applicability of this equation. The equations presented here are simple to use. However, many limitations exist.

Initial pCO_2

Based on the previous discussions, the initial pCO_2 in the open system is needed for the proposed open-to-closed system equation. Figure 2 illustrates the effect of pCO_2 on the adjustment factor for

a water sample with 4 meq liter^{-1} of total alkalinity. Parada, Long and Davis (1983) found significant areal and temporal variations of pCO_2 in the Tucson Basin. An investigation of pCO_2 characteristics in the recharge area should help determine the most appropriate pCO_2 value. Climatic effects on pCO_2 variation should also be studied further.
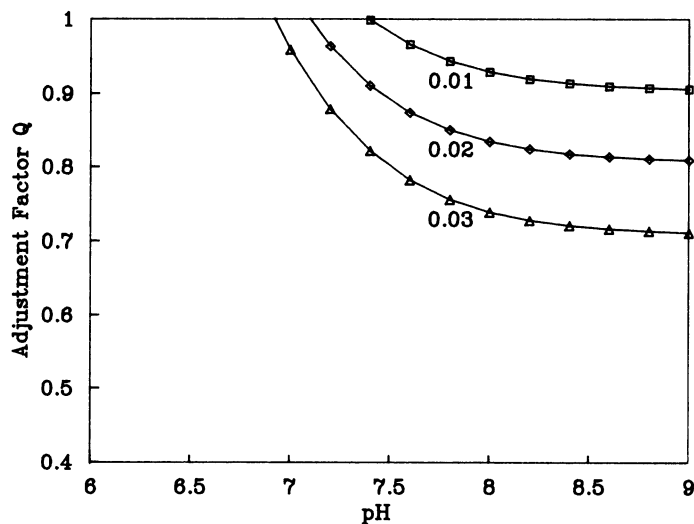

Fig. 2. The effect of CO_2 partial pressure in the vadose zone on the adjustment factor, "Q." The total alkalinity of the water is 4 meq liter^{-1}. The labels are partial pressure of CO_2 in atmosphere. Equation 11 is used for constructing this figure.

Other Reactions

The proposed equations are valid for the simple dissolution of carbonate minerals and incongruent dissolution of aluminosilicate minerals. The equations are not applicable to groundwater systems where such reactions as oxidation of organic matter under closed-system conditions, methane fermentation or oxidation, and precipitation of calcite occur. Wigley (1976: 221) studied the effect of mineral precipitation and concluded, "Ignoring mineral precipitation, or neglecting isotopic fractionation during precipitation, may lead to estimates of ^{14}C ages that are many thousands of years too old." Under these conditions, reaction-path simulation with computer programs, such as PHREEQE-CSOTOP (Cheng & Long 1984) or NETPATH (Plummer & Prestemon 1991), will be helpful.

Isotope Fractionation

Isotopic fractionation is not included in the proposed equations. Figure 1 shows that ^{14}C of DIC under open-system conditions is *ca.* 1 ± 0.5% higher than the CO_2 gas. This correction can be included in Equations 10, 11 and 15 by multiplying Q by 1.01 ± 0.005. For most groundwater systems, this correction is probably not significant.

CONCLUSIONS

This paper presents a simple dissolution model for adjusting ^{14}C groundwater ages, that can be used for both open- and closed-system dissolutions of carbonate and aluminosilicate minerals. This model is simple to use, but its applicability is limited to the reaction pathway upon which the model is based. Reaction-path modeling, either as a forward simulation, such as PHREEQE-CSOTOP (Cheng & Long 1984), or inverse modeling, such as NETPATH (Plummer & Prestemon

1991), should be considered for aquifer systems involving precipitation of calcite, methane fermentation or oxidation, and oxidation of organic matter.

The main uncertainty in ^{14}C groundwater dating is the initial pCO_2 in the recharge area at the time of recharge. An understanding of hydrogeochemical, hydrogeological and paleoclimatic factors in an aquifer system will help estimate these crucial values.

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