ESTIMATION OF DURATION OF SUBAERIAL EXPOSURE IN SHALLOW-MARINE LIMESTONES—AN ISOTOPIC APPROACH

WAN YANG
Department of Geology, Wichita State University, Wichita, Kansas 67260, U.S.A.
e-mail: wan.yang@wichita.edu

ABSTRACT: **Subaerial exposure surfaces in shallow-marine limestones may represent a significant period of nondeposition and/or erosion. The minimum duration of subaerial exposure is estimated through modeling the maximum whole-rock ^{13}C depletion toward exposure surfaces in vadose meteorically altered limestones. The model simulates the water–rock interaction that caused the depletion, and calculates the volume of meteoric water needed to achieve the observed $\delta^{13}C$ value. Then, the duration of vadose meteoric diagenesis, which approximates exposure duration, is the volume of water divided by the infiltration rate of vadose water. Sensitivity tests indicate that estimated duration is moderately sensitive to many input parameters, particularly the isotope composition and concentration of total dissolved carbon in vadose water, sediment porosity, and infiltration rate of vadose water. The method is mostly effective in estimating exposure durations of less than 400 ky. The estimated durations of nine subaerial exposures in Pleistocene reef tracts of Barbados, West Indies agree well with available radiometric dates. Application of the method to subaerial exposures in Mississippian, Pennsylvanian, and Cretaceous shallow-marine limestones confines their durations to 21–54 ky and distinguishes exposures of different durations. The proposed method offers a potential tool and direction in estimating minimum duration of stratal hiatuses in meter-scale stratigraphic studies.**

INTRODUCTION

Many subaerial exposure surfaces in meter-scale depositional cycles of shallow-marine limestones indicate punctuated carbonate deposition resulting from episodic emergence of carbonate platforms (e.g., Fischer 1964; Goodwin and Anderson 1985). Cyclic carbonate sedimentation will be better understood with more knowledge of the duration of nondeposition and erosion. For example, recognition of cycle bundling and estimation of average cycle period require knowledge of the number and duration of ''missing beats'' (Fischer 1964; Salder 1984; Read and Goldhammer 1988), and spectral evaluation of cycle periodicity requires information on the completeness of cyclic successions (e.g., Yang and Kominz 1999).

Systematic variations in $\delta^{13}C$ values of carbonate rocks in vadose zones have been documented in many Recent and ancient limestones (e.g., Allan and Matthews 1977, 1982; Brown 1982; Wagner 1983; Budd and Land 1990; Algeo et al. 1992; Cisneros and Vera 1993). Subaerial exposure places newly deposited marine carbonates in the vadose zone, where they react with meteoric water, causing dissolution of unstable aragonite and high-Mg calcite and reprecipitation of low-Mg calcite. Carbon isotope exchange between ^{13}C-enriched sediments and ^{13}C-depleted vadose water during this process results in ^{13}C depletion in the sediments (Allan and Matthews 1977, 1982; Lohmann 1988), the magnitude of which depends on the duration of meteoric diagenesis and the parameters of the water–rock system (James and Choquette 1984).

In this study, the magnitude of ^{13}C depletion in whole-rock analysis is used as a proxy to estimate the minimum duration of subaerial exposure through modeling carbon isotope exchange during water–rock interaction in the vadose zone. Sensitivity tests of model output to input variations assess the feasibility of the method. Model performance is tested using data from Pleistocene limestones of Barbados, where exposure durations are estimated by radiometric dating. Last, the method is applied to four ancient limestones to demonstrate its potentials and limitations.

THE ITERATIVE MODEL METHOD

Carbon Isotope Exchange during Water–Rock Interaction in the Vadose Zone

The model developed by Banner and Hanson (1990) is used to simulate carbon isotope exchange between newly deposited carbonate sediments and vadose meteoric water. The exchange is assumed to occur in an open system, in which continually replenished vadose water flows incrementally through the sediments. It is also assumed that the sediments reach carbon isotope equilibrium with exposure to each increment of vadose water. After equilibrating with the first increment of water, the $\delta^{13}C$ value of the sediments is (Banner and Hanson 1990):

$$\delta_s^{13}C = \frac{\delta_o^{13}C \cdot C_o \cdot (\alpha_{HCO3\text{-}Cal} - 1000) \cdot C_f \cdot F \cdot (1 - \alpha_{HCO3\text{-}Cal})}{C_s \cdot (1 - F) \cdot \alpha_{HCO3\text{-}Cal} + C_f \cdot F} \quad (1)$$

where $\delta_s^{13}C$ = carbon isotope composition of the altered sediments or limestones

$\delta_o^{13}C$ = carbon isotope composition of the vadose meteoric water–rock system, which is

$$\delta_o^{13}C = [(\delta_{f,o}^{13}C)(C_{f,o})F + (\delta_{s,o}^{13}C)(C_{s,o})(1 - F)]/C_o \quad (2)$$

$\delta_{f,o}^{13}C$ = carbon isotope composition of the vadose meteoric water before interaction

$\delta_{s,o}^{13}C$ = carbon isotope composition of the sediments before interaction

$C_{f,o}$ = concentration of total dissolved carbon in vadose water before interaction

$C_{s,o}$ = carbon concentration in the sediments before interaction (it is 120,000 ppm for calcite)

$\alpha_{HCO3\text{-}cal}$ = carbon isotope equilibrium fractionation factor (1.002) between sediments and water (see Friedman and O'Neil 1977, Lesniak and Sakai 1989, and Romanek et al. 1992)

C_f = concentration of total dissolved carbon in the vadose meteoric water

C_s = carbon concentration in the sediments

C_o = carbon concentration in the water–rock system, which is

$$C_o = F \cdot C_{f,o} + (1 - F) \cdot (C_{s,o}) \quad (3)$$

where F = weight fraction of the vadose meteoric water in the system, which is

$$F = \frac{P \cdot \rho_f}{P \cdot \rho_f + (1 - P) \cdot \rho_s} \quad (4)$$

where P = porosity of the sediments in volume fraction of a volumetric unit

ρ_s and ρ_f = densities of the sediments and water; ρ_s is 2.71 g/cm^3 for calcite, and ρ_f is 1 g/cm^3 for meteoric water.

At the beginning of the interaction between the second increment of vadose water and the sediments, the $\delta^{13}C$ value of the water–rock system is recalculated by replacing the original $\delta^{13}C$ value of the sediments

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($\delta_{s,o}{}^{13}C$ in Eq. 2) with the value of the sediments after first reaction ($\delta_s{}^{13}C$ in Eq. 1). The concentration and $\delta^{13}C$ value of total dissolved carbon in the vadose water ($C_{f,o}$ and $\delta_{f,o}{}^{13}C$ in Eq. 2) are not changed in the recalculation because the water represents a new aliquot of recharge in an open system. The recalculated $\delta^{13}C$ value of the system ($\delta_o{}^{13}C$ in Eq. 2) is then used in Eq. 1 to calculate the $\delta^{13}C$ value of the sediments at equilibrium with the second increment of water. This procedure is repeated until the output $\delta_s{}^{13}C$ value matches the measured value of an altered limestone ($\delta_{s,msr}{}^{13}C$). The number of iterations (*n*) and the cumulative water/rock ratio in weight (N) describe the extent of this iterative process (Banner and Hanson 1990):

$$N = n \cdot \frac{F}{1 - F} = n \cdot \left(\frac{P}{1 - P}\right) \cdot \frac{\rho_f}{\rho_s} \tag{5}$$

Duration of Vadose Meteoric Diagenesis

The duration of vadose meteoric diagenesis of an altered limestone is the time required for the $\delta^{13}C$ value of newly deposited sediments to evolve to the measured whole-rock, $\delta^{13}C$-depleted value of that limestone ($\delta_{s,msr}{}^{13}C$). The number of iterations, *n*, (i.e., freshwater flushes through the sediments) required to reach the $\delta_{s,msr}{}^{13}C$ value of the altered limestone is used to calculate the cumulative volume of vadose water (V) that flowed through a unit area:

$$V = n \cdot P = N \cdot (1 - P) \cdot \frac{\rho_s}{\rho_f} \tag{6}$$

Assuming the infiltration rate of vadose water to be *r* in volume/time, which is equal to distance/time assuming a unit cross-sectional area, the time for the vadose water of volume V to flow through the rock is

$$t = \frac{V}{r} = \frac{N \cdot (1 - P)}{r} \cdot \frac{\rho_s}{\rho_f} \tag{7}$$

where *t* is the duration of exposure to vadose meteoric water and approximates the duration of subaerial exposure. It is a minimum estimate because exposure may have continued even after complete equilibration of $\delta_s{}^{13}C$ to the water-buffered system.

Two major assumptions are applied in this method. First, carbon isotopic equilibrium between the sediments and vadose meteoric water is reached after each iteration, that is, a 100% efficiency of water–rock interaction is assumed in Banner and Hanson's (1990) bulk water–rock interaction model (see also Harris and Matthews 1968; Cander 1995). In accordance with this assumption, the $\delta^{13}C$ values of whole-rock samples of an altered limestone are used to match with model output. Second, sediment porosity is held constant during model runs because dissolution of aragonite and high-Mg calcite and precipitation of low-Mg calcite in the vadose zone, especially upper vadose zone, cause only minor net loss of carbonate and just a change in the style of porosity from intergranular to moldic (James and Choquette 1984). Many studies of porosity evolution during vadose meteoric diagenesis, for example, the Pleistocene Barbados limestones (Pittman 1974; Steinen 1974; Harrison 1975) and Holocene ooid sand in Schooner Cays, Bahamas (Budd 1988a), support this assumption (see also Halley and Harris 1979; Enos and Sawatsky 1981; Moore 1989; Matsuda et al. 1995). The model computer program can easily be modified to take into account porosity changes during vadose diagenesis if documented.

SENSITIVITY TESTS

The estimated minimum duration of subaerial exposure is related to several variables in Eqs. 1 to 7. Some of them, such as sediment porosity, the $\delta^{13}C$ value and concentration of total dissolved carbon in the vadose water, the initial $\delta^{13}C$ value of newly deposited sediments, and infiltration rate of vadose water, cannot be accurately defined for ancient water–rock systems. Thus, the relative sensitivity of model output to variations of input parameters is tested to assess the accuracy of model output. The sensitivity of the minimum estimated duration to a specific parameter is commonly interdependent with some other parameters, as dictated by the complex nonlinear relationships among the model input parameters. Major findings are presented below and in Table 1.

Equation 7 indicates an inverse linear relationship between sediment porosity and duration of vadose meteoric diagenesis. The change in duration with porosity is also related to infiltration rate and cumulative water/rock ratio as in Eqs. 6 and 7. A 1% change in porosity could cause a change of 1–4 ky in the estimated exposure duration (Fig. 1).

The sensitivity of the minimum estimated duration to the $\delta^{13}C$ value of the vadose water ($\delta_{f,o}{}^{13}C$) varies, depending on the $\delta^{13}C$ value of the altered limestone ($\delta_{s,msr}{}^{13}C$) and the concentration of total dissolved carbon in the water ($C_{f,o}$; Fig. 2). First, the duration change per 1‰ change of $\delta_{f,o}{}^{13}C$ is $\sim$ 1 ky when the difference between $\delta_{f,o}{}^{13}C$ and $\delta_{s,msr}{}^{13}C$ is more than 7‰; the change is $\sim$ 9 ky when the difference is 3 to 7‰; but increases dramatically to $\sim$ 73 ky when the difference is less than 3‰ (Fig. 2; Table 1). In other words, the estimated duration is very sensitive to ^{13}C-enriched vadose waters that are ineffective in modifying the isotope composition of newly deposited, commonly ^{13}C-enriched, sediments. The estimated duration is relatively insensitive to the $\delta^{13}C$ value of the vadose water, however, when the concentration of total dissolved carbon in the water ($C_{f,o}$) is high. If $C_{f,o}$ is larger than 100 ppm, the duration change is small regardless of the difference between the $\delta^{13}C$ values of the water and the altered limestone (Fig. 2). Thus, $\delta_{f,o}{}^{13}C$ and $C_{f,o}$ can be regarded as independent because $C_{f,o}$ is commonly greater than 100 ppm in modern carbonate terranes (e.g., Harris and Matthews 1968; Plummer et al. 1976; Budd 1988b; Anthony et al. 1989; Matsuda et al. 1995). This is supported by another test, which shows that the estimated duration is relatively insensitive to the concentration ($C_{f,o}$) when it is larger than 75 ppm, regardless of the $\delta^{13}C$ value of the water (Fig. 3; Table 1).

In addition, the sensitivity is also affected by the difference between the $\delta^{13}C$ value of a newly deposited sediment ($\delta_{s,o}{}^{13}C$) and the altered limestone ($\delta_{s,msr}{}^{13}C$), i.e., $\delta_{s,o}{}^{13}C - \delta_{s,msr}{}^{13}C$. The difference can be viewed as representing the extent of water–rock interaction in the evolution of sediment to the altered limestone. The larger the difference, the more extensive meteoric diagenesis has been. The difference can also be viewed as several newly deposited sediments with different $\delta_{s,o}{}^{13}C$ values, all evolving to altered limestones with the same $\delta_{s,msr}{}^{13}C$ value. Test results indicate that the estimated minimum duration is only slightly sensitive to the $\delta^{13}C$ value of the water when $\delta_{s,o}{}^{13}C - \delta_{s,msr}{}^{13}C$ is small, that is, when meteoric diagenesis is not extensive (Fig. 4).

The sensitivity of the estimated duration to the $\delta^{13}C$ value of newly deposited sediments ($\delta_{s,o}{}^{13}C$) was tested, because the estimated or measured $\delta_{s,o}{}^{13}C$ values for ancient limestones commonly scatter over a range (e.g., Allan and Matthews 1977, 1982; Magaritz and Holser 1990; Algeo et al. 1992). The minimum duration change per 1‰ change of $\delta_{s,o}{}^{13}C$ is nearly constant for a $\delta_{s,o}{}^{13}C$ range of 2 to -7‰, depending inversely on the infiltration rate (*r*) of vadose water (Fig. 5). It is $\sim$ 7 ky when *r* is 10 cm/y (Table 1).

Finally, the estimated minimum duration is very sensitive to small infiltration rates of vadose water and is not sensitive to large rates as suggested by their hyperbolic relationship in Eq. 7 (Fig. 6). The value of *r* is the most variable among all the input parameters because the rate and amount of diffusive meteoric recharge into the vadose zone is controlled by a variety of factors, such as rainfall, vegetation, surface runoff, topography, and soil type and thickness (e.g., Plummer et al. 1976; Bedinger 1987; Falkland and Woodroffe 1997). It is commonly smaller than 10 cm/y in many modern arid coastal areas (Bedinger 1987) but can be up to 200 cm/y in humid

TABLE 1.—*Input and results of sensitivity tests.*

Input parameters	Test 1	Test 2	Test 3	Test 4	Test 5	Change in duration
$\delta_{s,o}{}^{13}C$ (PDB)	1	-1.4	-2	$\boxed{2 \text{ to } -6}$		7 ky/‰ (r = 10 cm/yr)
$\delta_{f,o}{}^{13}C$ (PDB)	-11	$\boxed{-10 \text{ to } -25}$	-9 to -15	-11		73 ky/‰ from -10 to -11‰ 9 ky/‰ from -11 to -15‰ 1 ky/‰ from -15 to -25‰ ($C_{f,o}$ = 250 ppm)
$C_{f,o}$ (ppm)	100	50 to 300	$\boxed{10 \text{ to } 300}$	100		6 ky/ppm from 10 -100 ppm 0.2 ky/ppm from 100 - 300 ppm ($\delta_{f,o}{}^{13}C$ = -11‰)
P (%)	$\boxed{3 \text{ to } 50}$	50	50	50		0.8 to 4 ky/% (N = 2000 - 10000) (r = 7 cm/yr)
r (cm/yr)	5 to 50	7	7	5 to 100	$\boxed{10 \text{ to } 200}$	45 ky/cm from 1 - 10 cm 1 ky/cm from 10 - 50 cm 0.05 ky/cm from 50 - 200 cm (V = 5000 m^3)
$\delta_{s,msr}{}^{13}C$ (PDB)	-6	-8	-6	-6		See Figures 2 and 4 and text for discussion
Referred figures	Fig. 1	Fig. 2	Fig. 3	Fig. 5	Fig. 6	

Boxed number in a test is the parameter being tested.

carbonate terranes (e.g., Plummer et al. 1976; Vacher and Ayers 1980; Vacher and Quinn 1997; Table 2). The duration change per 1 cm/y change in r is ~ 45 ky when r ranges from 1 to 10 cm/y, and is only ~ 1 ky when r ranges from 10 to 50 cm/y, assuming the cumulative volume of water to be 5000 m^3 (Table 1).

In summary, the sensitivity of the estimated minimum duration to model inputs decreases with decreasing cumulative water/rock ratio, increasing sediment porosity and infiltration rate, and increasing ^{13}C-depletion and concentration of total dissolved carbon in vadose meteoric water, all of which speed up carbonate meteoric diagenesis. The sensitivity goes up when vadose meteoric diagenesis reaches the late stage and is generally 0.2–9 ky per unit change in the input parameters (Table 1; Figs. 1–6). The relationships established in the tests are useful in assessing the accuracy of model results for ancient limestones.

EVALUATION OF MODEL PERFORMANCE

The proposed method was evaluated using data from nine wells penetrating Pleistocene reef limestones in the Christ Church Ridge area of Barbados, West Indies (Fig. 7). The $\delta^{13}C$ trends in these limestones are well documented, and ancillary hydrogeologic, geochemical, and petrographic data are also available (e.g., Harris and Matthews 1968; Steinen 1974; Allan and Matthews 1977; Wagner 1983). Furthermore, the radiometrically-dated growth ages of corals at the reef crests, which have undergone vadose meteoric diagenesis since they were subaerially exposed by continuous tectonic uplift, approximate the true duration of subaerial exposure (e.g., Mesolella et al. 1969; Bender et al. 1979). The corals in the nine wells on six terraces have growth ages ranging from 66 to 261 ky (Fig. 7; Table 3).

Input Parameters

Some parameters, namely the $\delta^{13}C$ value and concentration of total dissolved carbon in the vadose water, the $\delta^{13}C$ value of the newly deposited sediments, the most depleted $\delta^{13}C$ value of altered limestones, sediment porosity, and infiltration rate of vadose water, are variably constrained for the Barbados water–rock system. They are critical to the accuracy of model results and are discussed below in length.

First, $\delta^{13}C$ values of vadose water ($\delta_{f,o}{}^{13}C$) in this area are scarce. Kimbell and Humphrey (1994) reported a range from −11.5 to −6.5‰, encompassing that of −11 to −12‰ for Barbados groundwater (Banner, personal communication 1994). The more negative values are probably the best estimate of initial vadose waters because isotope exchange between newly deposited ^{13}C-enriched sediments and the ^{13}C-depleted vadose water will enrich ^{13}C in the water.

In general, three sources contribute to the concentration of dissolved carbon in freshwater of modern carbonate terranes: soil CO_2 from organic respiration, atmospheric CO_2, and amount of dissolved aragonite (Budd and Land 1990). Their contributions are calculated for the vadose freshwater in the ooid sands of Schooner Cays (see Appendix): 51–70% ^{12}C-enriched

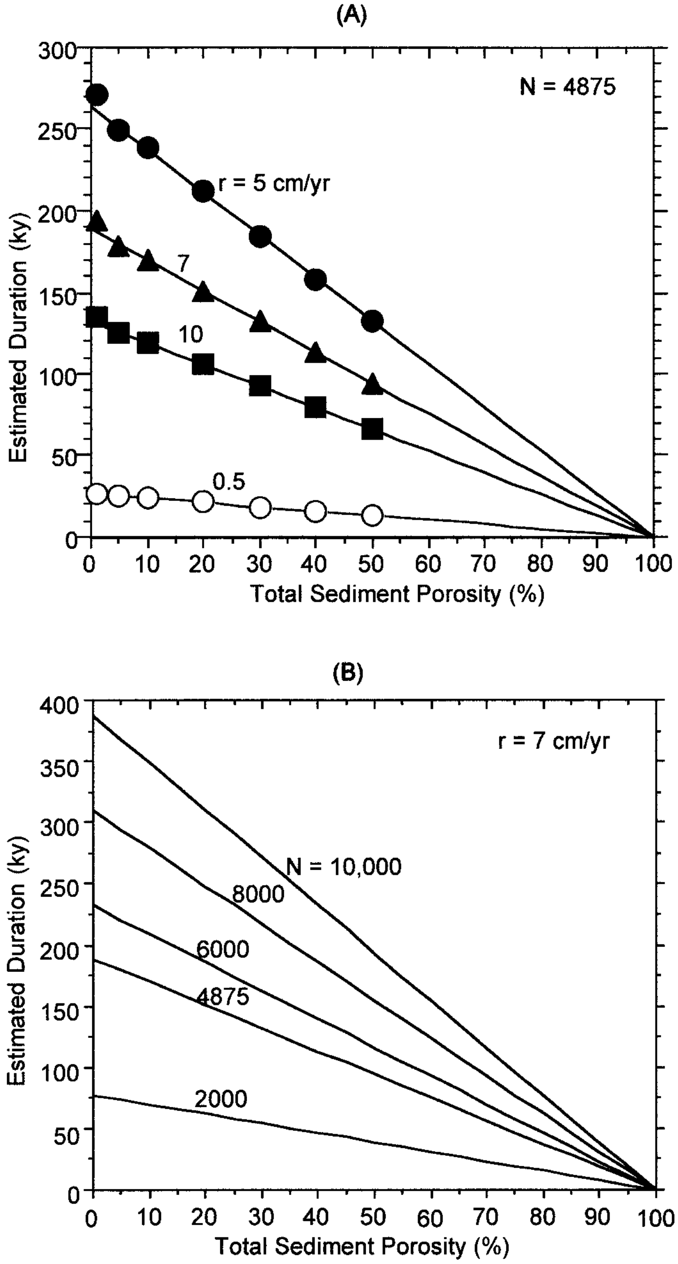

FIG. 1.—Inverse linear relationship between the estimated duration of subaerial exposure and total sediment porosity (P). The test results (points) conform to the relationship (solid lines) in Eq. 7. The relationship is also affected by the cumulative water/rock ratio (N) and infiltration rate of vadose water (r). The change in duration per 1% change of P increases with decreasing r (A) and with increasing N (B). See Table 1 for test parameters.

carbon from soil CO_2 and 49–30% ^{13}C-enriched carbon from dissolved aragonite. Contribution from atmospheric CO_2 is negligible, suggesting soil CO_2 as the only significant source for ^{13}C-depleted waters. These proportions are used to calculate the $\delta^{13}C$ value of the Barbados vadose water. An average $\delta^{13}C$ value of −11‰ (all values in this paper are relative to PDB) for the Barbados water is then calculated, assuming that the $\delta^{13}C$ value of soil CO_2 is −22‰ and that of newly deposited sediments is 0.4‰ (Allan 1979; see also Kimbell and Humphrey 1994). This average value is similar to the more negative values reported by Kimbell and Humphrey (1994). In the model runs, a range from −10 to −12‰ was used to reflect the geological uncertainties (Table 3).

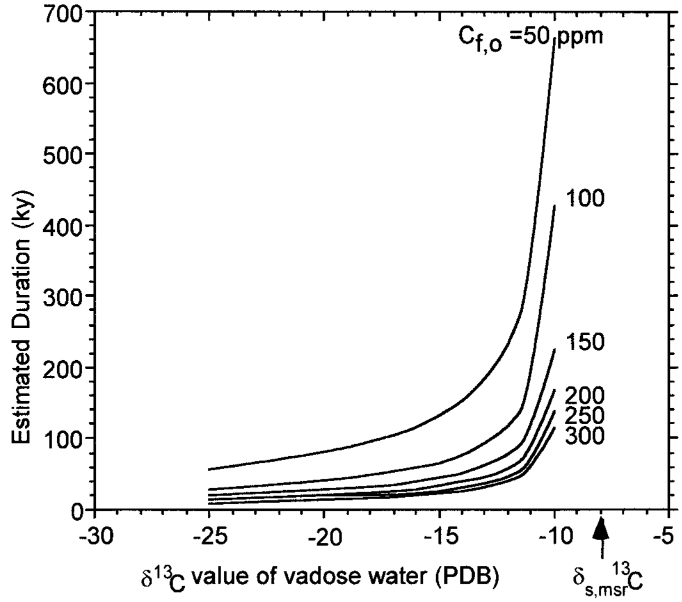

FIG. 2.—Nonlinear relationship between the estimated duration of subaerial exposure and the $\delta^{13}C$ value of vadose water ($\delta_{f,o}{}^{13}C$). The relationship is also affected by the concentration of TDC in vadose water. The change in duration per 1‰ change of $\delta_{f,o}{}^{13}C$ is small when the difference between $\delta_{f,o}{}^{13}C$ and $\delta_{s,msr}{}^{13}C$ (the composition of the diagenetic limestone) is less than 3‰. See Table 1 for input parameters and text for discussion.

Second, the $\delta^{13}C$ value of newly deposited sediments ($\delta_{s,o}{}^{13}C$) is given a range from 0.2 to 1‰, encompassing the values of modern subtidal sediments of Barbados (Table 3; Allan 1979). Third, a model is run until its output equals the most negative whole-rock $\delta^{13}C$ values observed in the upper vadose zone. In five of nine wells, the $\delta^{13}C$ value of an altered limestone ($\delta_{s,msr}{}^{13}C$) sampled more than 1 m beneath soil zones probably does not represent that of the most altered limestone. Thus, a $\delta_{s,msr}{}^{13}C$ value is estimated by linear extrapolation into the uppermost zone (e.g., Fig. 7C; Table 3).

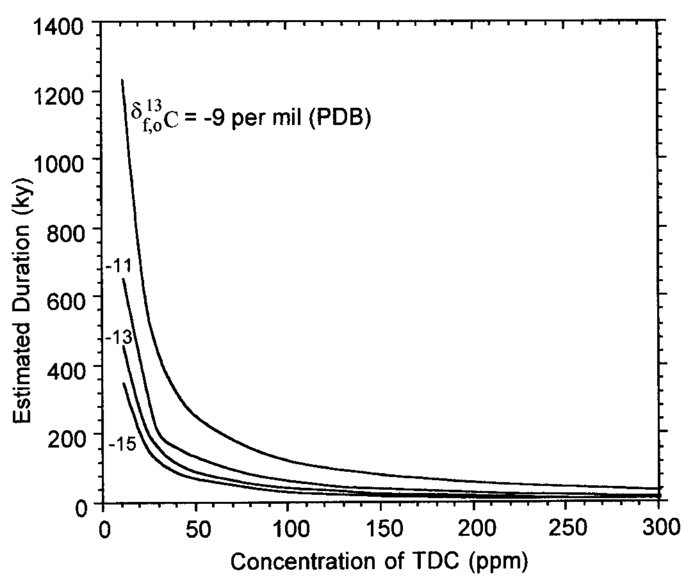

FIG. 3.—Nonlinear relationship between the estimated duration of subaerial exposure and the concentration of TDC in vadose water ($C_{f,o}$). It is also affected by the $\delta^{13}C$ value of vadose water ($\delta_{f,o}{}^{13}C$). The change in duration is small when $C_{f,o}$ is larger than 75 ppm. See Table 1 for input parameters.

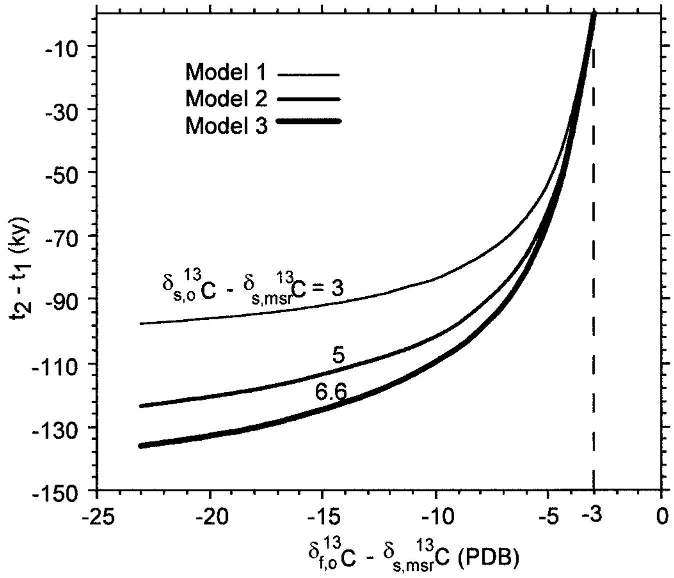

FIG. 4.—Sensitivity of estimated duration of meteoric diagenesis (t) to $\delta_{f,o}{}^{13}C$ (composition of vadose water) is dependent on the difference between $\delta_{s,o}{}^{13}C$ (composition of pristine sediments) and $\delta_{s,msr}{}^{13}C$ (composition of diagenetic limestone). For the abscissa, t_1 is the time for a pristine sediment to evolve to the most negative $\delta^{13}C$ values possible in a vadose water when $(\delta_{f,o}{}^{13}C - \delta_{s,msr}{}^{13}C) = -3‰$. t_2 is the elapsed time when $(\delta_{f,o}{}^{13}C - \delta_{s,msr}{}^{13}C) < -3‰$; The difference $(t_2 - t_1)$ is negative because t_2 is smaller than t_1, and signifies how much less time is needed for a pristine sediment to evolve to the most negative $\delta^{13}C$ values possible in the water with a more negative $\delta^{13}C$ value. The slope of model curves indicates that t is less sensitive to $\delta_{f,o}{}^{13}C$ when $(\delta_{s,o}{}^{13}C - \delta_{s,msr}{}^{13}C)$ is small, although it takes a longer time (i.e., $(t_2 - t_1)$ is relatively small) for the $\delta_{s,o}{}^{13}C$ to approach $\delta_{s,msr}{}^{13}C$. The diagram also reinforces the results in Figure 2, i.e., t is less sensitive to $\delta_{f,o}{}^{13}C$ when $\delta_{f,o}{}^{13}C$ is more negative than $\delta_{s,msr}{}^{13}C$. Model parameters are: $C_{f,o} = 100$ ppm, $P = 50\%$, $\alpha = 1.002$; for Model 1, $\delta_{s,o}{}^{13}C = 1‰$, $\delta_{s,msr}{}^{13}C = -2‰$, $\delta_{f,o}{}^{13}C = -5$ to $-25‰$; for Model 2, $\delta_{s,o}{}^{13}C = 1‰$, $\delta_{s,msr}{}^{13}C = -4‰$, $\delta_{f,o}{}^{13}C = -7$ to $-27‰$; for Model 3, $\delta_{s,o}{}^{13}C = -1.4‰$, $\delta_{s,msr}{}^{13}C = -8‰$, $\delta_{f,o}{}^{13}C = -10$ to $-31‰$.

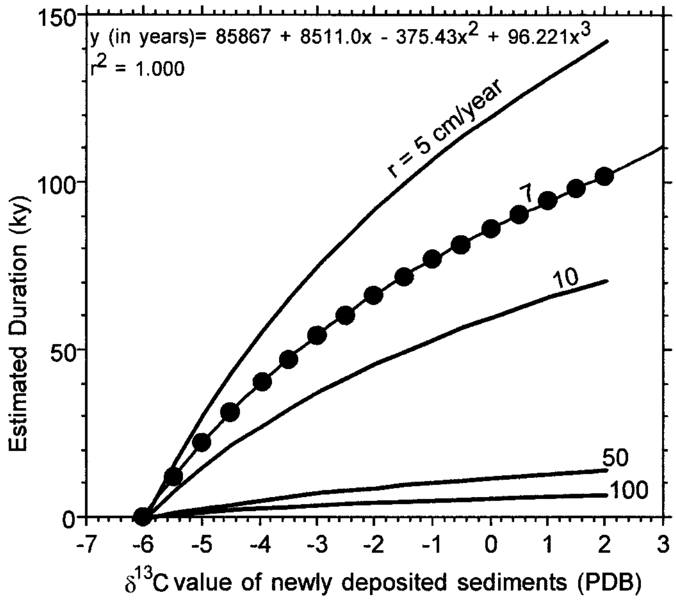

FIG. 5.—The polynomial relationship between the estimated duration of subaerial exposure and the $\delta^{13}C$ value of newly deposited sediments ($\delta_{s,o}{}^{13}C$), which is also affected by the infiltration rate of vadose water (r). The change in duration per 1‰ change of $\delta_{s,o}{}^{13}C$ is nearly constant. Thin line represents a polynomial fit to the test results (solid dots) for $r = 7$ cm/y. See Table 1 for input parameters.

Fourth, the concentration of total dissolved carbon (TDC) in vadose water ($C_{f,o}$) has not been reported in Barbados. Harris (1971) reported values of fresh phreatic waters that range from 175 to 308 ppm in the lower elevation area and from 126 to 227 ppm in the higher-elevation area of southern Barbados. Waters in the upper vadose zone likely have lower concentrations than phreatic waters because of lesser dissolution in vadose zone (Wagner 1983; James and Choquette 1984; Budd and Land 1990). Thus, a range of 176–218 ppm for the lower-elevation wells was calculated from the average and standard deviation of 10 arbitrarily selected lowest values measured by Harris (1971). The same procedure was used to calculate a range of 139–161 ppm for the higher-elevation wells (Table 3).

Fifth, the total porosity, including primary and secondary porosities, of the Pleistocene reef sediments is ~ 20 to 40% (Steinen 1974; Harrison 1975; Steinen et al. 1977). Harrison (1975) demonstrated that the total porosity of vadose-zone grainstones is balanced through dissolution and reprecipitation (see Budd 1984 for similar observations in the ooid sands of Schooner Cays; cf. Pittman 1974; Matsuda et al. 1995). Porosity values of 20% and 40% are used as the model input except where measurements are available (Table 3).

Sixth, Harris (1971) estimated the infiltration rates of vadose water in southern Barbados from the relationship between rainfall, evapotranspiration, and moisture content (see also Steinen et al. 1977; cf. Humphrey 1997). An average rate of 4.5 cm/y between 7 and 2 cm/y in the lower-elevation and higher-elevation areas (Harris 1971) was selected as the lower limit for all wells. Rates of 10 and 7 cm/y were assigned as the upper limit for the lower-elevation and higher-elevation areas, respectively, to take into account the geologic uncertainties (Table 3). In reality, the infiltration rate for a reef terrace must have changed over time when the terrace was uplifted and moved away from the coast, where precipitation is lower (Banner et al. 1994; Humphrey 1997). The model computer codes can be modified to take into account changes of infiltration rate during vadose meteoric diagenesis if documented.

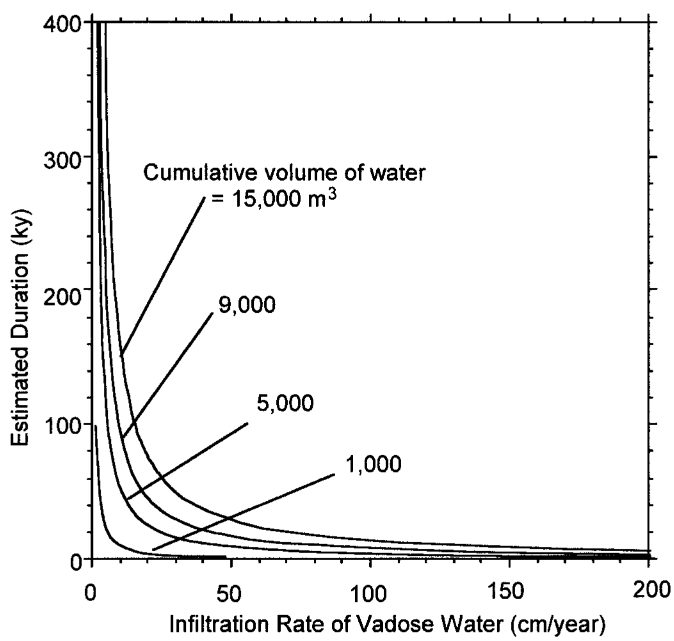

FIG. 6.—The hyperbolic relationship between the estimated duration of subaerial exposure and infiltration rate of vadose water (r). It is also affected by the cumulative volume of vadose water (N). The change in duration is small when r is larger than 50 cm/y but is large when r is smaller than 10 cm/y.

TABLE 2.—*Recharge or infiltration rates of selected carbonate and coastal terranes, from data in Bedinger (1987) and Vacher and Quinn (1997)*

Location	Climate	Annual Rainfall (mm/y)	Mean Annual Recharge (mm/y)	Geologic Setting	References
Bermuda, West Atlantic	Humid subtropical	1460	180[a]	Carbonate platform	Vacher and Rowe (1997)
Bahamian Archipelago, West Atlantic	Humid tropical	690 (SE)–1550 (NW)	172–390[a]	Carb. platform & island	Whitaker and Smart (1997)
Cayman Islands, Caribbean	Humid tropical—subtr.	900 − 1600	180–320[a]	Carbonate islands	Jones et al. (1997)
St. Croix, Virgin Islands, Caribbean	Humid tropical—subtr.	1270 (wet)	38–152[a]	Carbonate islands	Gill et al. (1997)
	Dry tropical—subtr.	<890 (dry)	27–107[b]	Carbonate islands	Gill et al. (1997)
Niue, West Pacific	Humid tropical	1065–3185 (2041)	624	Carbonate islands	Wheeler and Aharon (1997)
Tonga, West Pacific	Humid tropical—subtr.	1707–2236	478–917	Reef terraces	Furness (1997)
Tarawa, Kiribati, West Pacific	Humid tropical	2024	735–1020	Carbonate atoll	Falkland and Woodroffe (1997)
Christmas Island, Kiribati, West Pacific	Humid tropical	869	95–250	Carbonate atoll	Falkland and Woodroffe (1997)
Kwajalein Island, Marshall Is., West Pacific	Humid tropical	2600	1300	Carbonate atoll	Peterson (1997)
Roi-Namur, Marshall Is., West Pacific	Humid tropical	2600	580	Carbonate atoll	Peterson (1997)
Majuro Atoll, Marshall Is., West Pacific	Humid tropical	3560	1780	Carbonate atoll	Peterson (1997)
Bikini, Marshall Is., West Pacific	Humid tropical	1500 (?)	500	Carbonate atoll	Peterson (1997)
Enewetak Atoll, Marshall Is., West Pacific	Humid tropical	605–2422 (1470)	250–515	Carbonate atoll	Buddemeier and Oberdorfer (1997)
Micronesia, West Pacific	Humid tropical	2800–4000	1400–2000	Carbonate atoll	Anthony (1997)
Nauru Island, West Pacific	Humid tropical	280–4590 (2085)	834	Carbonate atoll	Jacobson et al. (1997)
Northern Guam, Mariana Is., West Pacific	Humid tropical—subtr.	2200–2500	770–1500	Carbonate atoll	Mink and Vacher (1997)
Rottnest Island, Western Australia	Mediterranean	720	144[b]	Carbonate island	Playford (1997)
Cocos Islands, West Pacific	Humid tropical	850–3300 (1950)	560–950	Carbonate atoll	Woodroffe and Falkland (1997)
Diego Garcia Atoll, North Indian	Humid tropical	2700	1020	Carbonate atoll	Hunt (1997)
Coastal plain, Western Australia	Dry mediterranean	800	4.6–194[b]	Soils and sand dunes of eolian origin	Sharma et al. (1983)
Gambier Plain, South Australia	Dry mediterranean	700–750	130–155[b]	Terra rosa or sandy loam over limestone	Allison and Hughes (1978)
Akrotiri Peninsula, southern Cyprus, Mediterranean	Dry mediterranean	420	50[b]	Unconsolidated Holocene dune sands	Kitching et al. (1980)
Coastal plain of Israel	Dry mediterranean		10–75[b]	Sandy sequence with thin clayey strata	Eriksson and Khunakasem (1969)
Dana sand dunes, 100 km east of Riyadh, Saudi Arabia	Arid	81.9	20[b]	Sand dunes overlie Paleocene limestone	Dincer et al. (1974)
Central zone of Saudi Arabia	Arid	80–130	3–15[b]	Sand and sandstone	Caro and Eagleson (1981)

[a] Data used to calculate average infiltration rates (143–261 mm/y) in humid and subhumid terrane. Rates of carbonate atolls in the ocean basins are not used because the Pennsylvanian Strawn limestones (see ''Applications to Ancient Limestones'') were deposited in the epi-cratonic Midland Basin, Texas.
[b] Data used to calculate average infiltration rates (49–65 mm/y) in arid and semi-arid terrane.

Finally, the radiometric dates of coral growth during sea-level highstands are greater than the true durations of subaerial exposures, because the corals were exposed some time later during ensuing sea-level lowstands (Table 3). This difference is increased by subaerial erosion of coral reefs, especially the old reefs, because erosion has removed the most ^{13}C-depleted rocks in the uppermost vadose zone and has exposed older corals for age dating. The difference may be $\sim$ 10 ky (time between interglacial highstand and glacial lowstand of precession-scale sea-level cycles) or greater (e.g., Mesolella et al. 1969).

Results

The proposed method produced reasonable estimates of exposure durations for the Pleistocene Barbados reef limestones. For each well, two sets of average duration and standard deviation were calculated from 16 model outputs for each set (Fig. 8; Table 3). The average durations of eight subaerial exposures are within the range of radiometric dates and increase progressively from younger to older reef tracts. A ninth, Well 33, is located on the slope of the Worthing reef tract at an elevation of 5.5 m (Bender et al. 1979, their fig. 2; Radtke et al. 1988), where the coral growth ages likely are much younger than 66 to 92 ky, which is the age of corals at the Worthing crest at $\sim$ 12 m (Fig. 7B). Thus, the estimated average duration of 16–21 ky for this well is reasonable.

The standard deviations of the estimates vary from 12 to 102 ky and increase from younger to older reef tracts. The uncertainty in infiltration rate contributes significantly to the deviations (Tables 1, 3).

APPLICATION OF THE PROPOSED METHOD TO ANCIENT LIMESTONES

Trends of ^{13}C-depletion associated with subaerial exposure surfaces in the Cretaceous Glen Rose Formation and James Limestone, the Pennsylvanian Strawn Formation, and the Mississippian Newman Limestone were described by Allan and Matthews (1982), and these data were used to estimate minimum exposure durations in theses units (Fig. 9). Well-developed calcrete or regolith in these units indicates subaerial exposure. Rocks in the paleo-vadose zone include skeletal and oolitic grainstones in the Glen Rose, James, and Strawn limestones and lime mudstone in the Newman Limestone (Fig. 9; Allan and Matthews 1982). The Glen Rose and Strawn grainstones have high moldic porosity caused by meteoric leaching, whereas the James grainstones show no petrographic evidence of meteoric leaching.

Parameters of vadose meteoric diagenesis for these (and any other ancient) limestones can be estimated only on the basis of modern analogs. For the δ^{13}C value of newly deposited sediments ($\delta_{s,o}{}^{13}$C), the most positive δ^{13}C value of whole-rock samples in a section was identified. It is probably the least altered by vadose diagenesis. These values are from the lower part of the vadose interval and are within the range of pristine limestones in the literature. Choosing less positive values cannot be justified. In the model runs, however, a 20% uncertainty range was assigned to the most positive value of each limestone to reflect the geologic uncertainties (Table 4). These values were also used to estimate the δ^{13}C values of vadose water ($\delta_{f,o}{}^{13}$C). The $\delta_{f,o}{}^{13}$C values were estimated using the proportions of three carbon sources derived from the oolitic sands in the Schooners Cays, Bahamas (Appendix). The δ^{13}C value of soil CO_2 was taken as -27‰ because ^{13}C-rich C_4 plants did not appear until Miocene time (Deines 1981; Cerling 1991), and a 20% uncertainty range was assigned to this value to reflect possible geologic variations. The maximum range of $\delta_{f,o}{}^{13}$C values calculated for each limestone was used as the model input (Table 4). Lastly, the most negative δ^{13}C values of whole-rock samples in the uppermost vadose zones or soil zones are used as the final values of the altered limestones ($\delta_{s,msr}{}^{13}$C) (Table 4). The selected $\delta_{s,msr}{}^{13}$C values tend to maximize the estimated durations.

The concentration of total dissolved carbon in vadose water ($C_{f,o}$) is assigned as 100 and 200 ppm, encompassing the range of modern Barbados vadose waters under both dry and wet conditions (Harris 1971). The original total sediment porosity is taken as 40–50% in the paleo-vadose zone, according to the porosity range of Holocene carbonate sediments compiled by Enos and Sawatsky (1981) and the pre-burial, zero-depth porosity value of Halley and Schmoker (1983) (Fig. 9; Table 4). Allan and Matthews

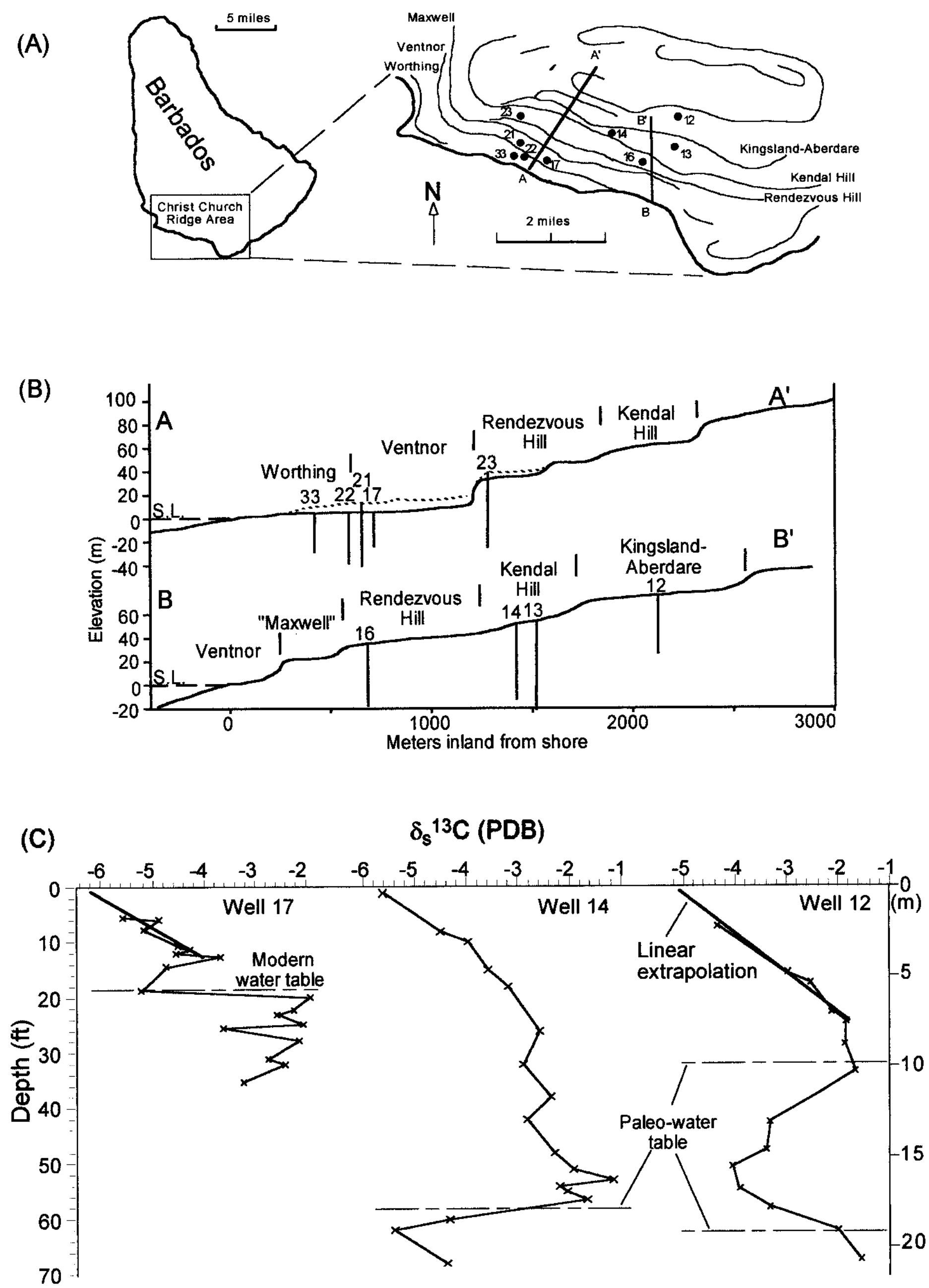

FIG. 7.—**A)** Location of nine wells and cross sections A–A′ and B–B′ in Christ Church Ridge area, Barbados, West Indies. Thin lines are trends of prominent reef tracts. **B)** Topographic profiles along A–A′ and B–B′ showing projected well location and prominent reef terraces. **C)** Examples of ^{13}C-depletion trends and position of water tables in three wells. The $\delta^{13}C$ trends of wells 17 and 12 are linearly extrapolated 30 cm below ground surface. Data and interpretation are from Wagner (1983).

(1982) postulated that evaporation was intense, climate was arid, and exposure time was short for the James Limestone. From petrographic, isotopic, and minor-element evidence, Allan and Matthews (1982) and Wagner (1983) suggested that the Glen Rose and Newman limestones were altered in arid environments whereas the Strawn limestone was altered in a humid environment. Thus, the ranges of infiltration rates, 4.9–9.5 cm/y and 14.3–26.1 cm/y, are used for the arid and humid environments, respectively, on the basis of the compiled infiltration rates of similar climate and/or carbonate terrane (Tables 2, 4; Bedinger 1987; Vacher and Quinn 1997).

Two sets of average duration and standard deviation were produced for each subaerial exposure corresponding to the variations in the input parameters (Table 4). The average minimum durations of the four subaerial exposures range from 21 to 54 ky (Fig. 10; Table 4). The largest estimates correspond to small values of $C_{f,o}$ (concentration of TDC), P (porosity), and *r* (infiltration rate), and large $\delta^{13}C$ values of vadose water and newly deposited sediments, and vice versa. The average minimum estimates for each exposure differs by 5 ky for the humid examples and up to 20 ky for the arid examples (Table 4). Better constraints on the input parameters in future studies may reduce the uncertainty of the estimated durations.

Knowledge of the minimum duration of stratal hiatuses at a resolution of tens of thousands of years would improve our understanding of sedimentary processes in ancient environments. The estimated minimum duration might be used to partition time between deposition, represented by rocks, and stratal hiatuses, represented by subaerial exposure surfaces. For example, eight shallowing-upward cycles and associated exposure surfaces have been recognized in the Desmoinesian Strawn Group in Horseshoe Atoll of the Midland basin, Texas (Reid and Reid 1991), and a total duration of 4 my for the Strawn Group is estimated using the time scale of Harland et al. (1989). Assuming that the eight exposures in the Strawn

TABLE 3.—*Input parameters and estimated durations of subaerial exposures, Christ Church Ridge area, Barbados, West Indies.*

Wells	Well position[a] on terraces	$\delta_{f,o}{}^{13}C$ (PDB)	$\delta_{s,o}{}^{13}C$[b] (PDB)	$\delta_{s,msr}{}^{13}C$[c] (PDB)	$C_{f,o}$[d] (ppm)	P (%)[e]	r (cm/y)[f]	Radiometric[g] dates (ky)	Estimated[h] duration (ky)
33	Lower Worthing	−10 to −12	0.2 to 1	(−2)	176–218	20/40	10–4.5	82,[B] 87.7,[E] 92 ± 15[R] 75.5–85.2,[K] 66–88[M]	21 ± 15 / 16 ± 12
22	Middle Worthing	−10 to −12	0.2 to 1	(−6)	176–218	20/40	10–4.5	82,[B] 87.7,[E] 92 ± 15[R] 75.5–85.2,[K] 66–88[M]	85 ± 39 / 61 ± 30
17	Lowermost Ventnor, possibly Worthing based on its elevation	−10 to −12	0.2 to 1	(−6.2)	176–218	20/30	10–4.5	105,[B] 112.0,[E] 110 ± 15[R] 101.5–129.2,[K] 110–112[M]	109 ± 45 / 95 ± 40
21	Lower Ventnor	−10 to −12	0.2 to 1	−6.65	176–218	20/40	10–4.5	105,[B] 112.0,[E] 110 ± 15[R] 101.5–129.2,[K] 110–112[M]	109 ± 45 / 81 ± 35
23	Lowermost Rendezvous, possibly Maxwell[i]	−10 to −12	0.2 to 1	−7.59	176–218	20/40	10–4.5	125,[B] 125 ± 6,[E] 136 ± 15[R] 99.4–133.7,[K] 99–129[M]	146 ± 61 / 112 ± 46
16	Lowermost Rendezvous, possibly Maxwell	−10 to −12	0.2 to 1	−7.23	176–218	20/40	10–4.5	125,[B] 125 ± 6,[E] 136 ± 15[R] 99.4–133.7,[K] 99–129[M]	131 ± 54 / 99 ± 41
14	Lower to middle Kendal Hill	−10 to −12	0.2 to 1	−5.6	139–161	20/40	7–4.5	180,[B] 219–236[R]	252 ± 102 / 188 ± 77
13	Middle Kendal Hill	−10 to −12	0.2 to 1	(−5)	139–161	20/40	7–4.5	180,[B] 219–236[R]	211 ± 86 / 157 ± 65
12	Middle Kingsland-Aberdare	−10 to −12	0.2 to 1	(−5)	139–161	20/40	7–45	200–220,[B] 205–261[R]	211 ± 86 / 157 ± 65

[a] Well positions on the coral terranes are from Allan (1979), Wagner (1983), and Radtke et al. (1988).
[b] The range encompasses the values of modern subtidal sediments of Barbados in Allan (1979).
[c] Values of wells 12, 13, 14, 19, 21, 22, 23, and 33 from Wagner (1983) and wells 16 and 17 from Allan (1979). Values in brackets are those projected to the base of soil zone. No uncertainty ranges were assigned because these are the values to be modeled.
[d] The mean of the 10 lowest values in the Christ Church area (Harris 1971) is 197 ppm with a standard deviation 21 ppm, giving a range of 176–218 ppm. The same in the higher Exchange area is 150 ppm with a standard deviation of 11 ppm, giving a range of 139–161 ppm.
[e] Primary porosity before vadose diagenesis is 20–30% for Well 17 (Steinen 1974), and is assigned as 20–40% for the other wells (Harrison 1975).
[f] Infiltration rates compiled from rainfall and evapotranspiration data for Christ Church Ridge and Exchange and Sweet Vale areas are 7 and 2 cm/y in the low and high elevation, respectively (Harris 1971); the rate of 45 cm/y is the average. See text for discussion.
[g] Dates from: B—Bender et al. (1979); E—Edwards et al. (1987); R—Radtke et al. (1988); K—Ku et al. (1990); M—Muhs (1992).
[h] For each well, the estimate above the bar was calculated using a 20% porosity and that below the bar using a 40% porosity, with other parameters in the same range; each mean and standard deviation were calculated from 16 model output.
[i] The radiometric date of Maxwell reef tract is 114 to 128 ky based on data from Mesollela et al. (1969), Ku et al. (1990), and Muhs (1992).

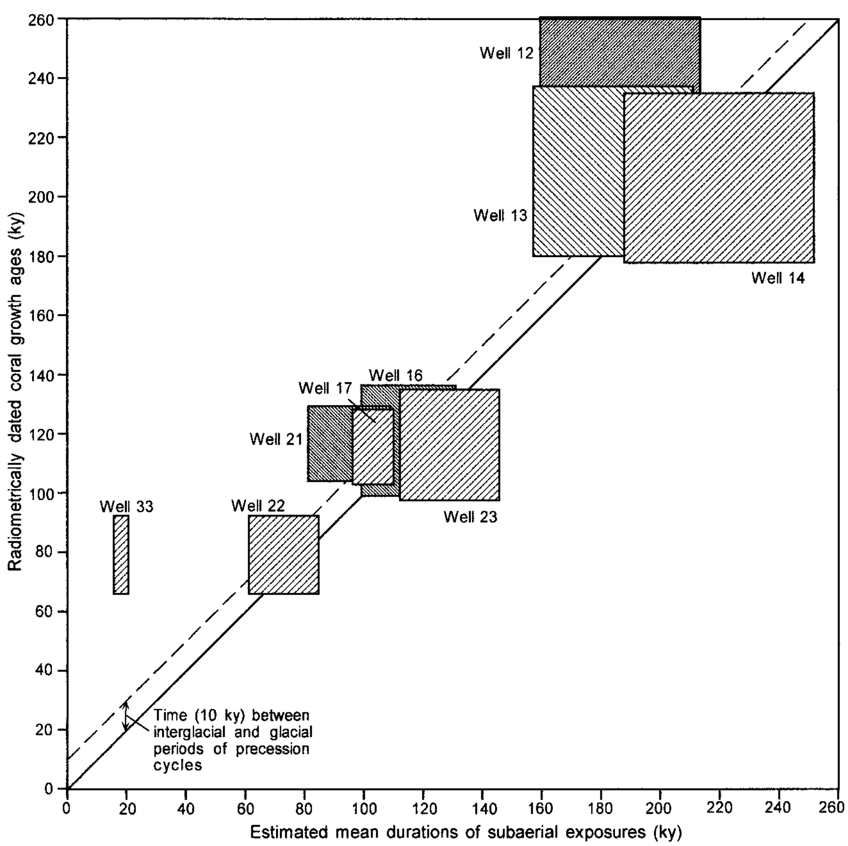

FIG. 8.—Estimated mean durations of nine subaerial exposures against the coral growth ages in the Pleistocene Barbados limestones. The diagonal 1:1 line (solid) is elevated by 10 ky to the dashed line to account for the time between interglacial highstand and glacial lowstand. The height of hachured rectangles corresponds to the range of radiometric dates for a reef terrace, and the width indicates the range of estimated mean durations. See Table 3 for input values and standard deviations associated with the estimated mean durations.

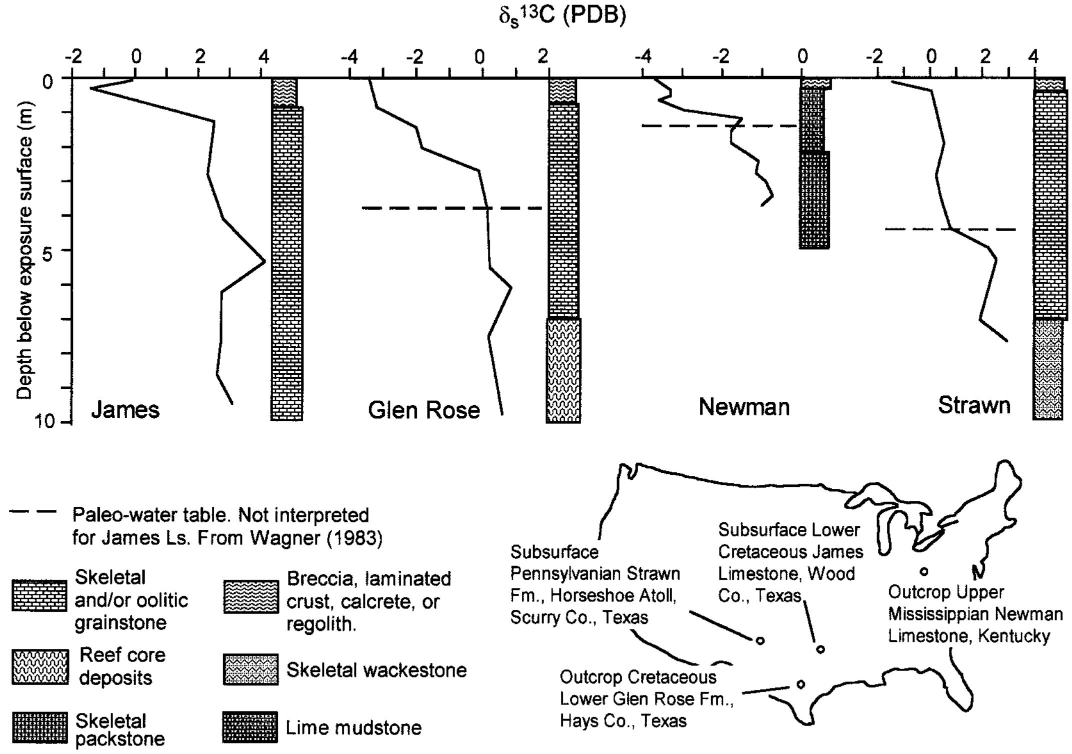

FIG. 9.—Lithologies and ^{13}C-depletion trends of four ancient shallow-marine limestones. Allan and Matthews (1982) interpreted these trends as products of vadose meteoric diagenesis. Modified from Allan and Matthews (1982).

Group have the same duration of 21–26 ky as estimated in this study, 4–5% of the Strawn time is represented by the eight exposures. This percentage for the amount of time represented by exposure is significantly smaller than that estimated for limestones in general (Wilkinson et al. 1992; see also Yang et al. 1995; Yang and Kominz 1999).

The proposed method might also be able to differentiate subaerial exposures of different durations. For example, the minimum duration of the Strawn exposure is about two times shorter than the minimum durations of the exposures in the Glen Rose and James limestones (Fig. 10). The short duration of the Strawn exposure is mainly due to the large infiltration rate of a humid to subhumid climate, which is about three times larger than that of the arid to semiarid climate. The time difference may also shed light into the geologic processes controlling cyclic carbonate sedimentation, such as the frequency of sea-level changes, and aid in studies of meteoric diagenesis that is dependent on exposure time. The full potential and limitation of the proposed method await further exploration.

DISCUSSION

Application of the proposed method depends largely on how well the input parameters are constrained and on the mechanisms and assumptions of the geochemical models used. The following discussion on input variability and the geochemical model, although not exhaustive, provides some insights on the potentials and limitations of this method.

Controls on Carbon Isotope Exchange in Vadose Meteoric Environments

Three major factors control the magnitude of ^{13}C-depletion during meteoric vadose-zone alteration of limestones: (1) duration of subaerial exposure, (2) diagenetic potential of original marine carbonates and (3) conditions at the land surface and in soil zones, such as rainfall, vegetation density and type, soil development, and topography (Plummer et al. 1976; Allan and Matthews 1977, 1982; James and Choquette 1984; Lohmann 1988). Subaerial exposure of newly deposited carbonate sediments is a prerequisite for vadose meteoric diagenesis. Holding other factors constant, the exposure duration affects the amount of meteoric water recharge and, essentially, the extent of carbon isotope exchange in water–rock interaction.

Carbon isotope exchange in newly deposited carbonate sediments in a vadose meteoric environment is dominantly driven by the diagenetic stabilization of aragonite and/or high-Mg calcite to low-Mg calcite (e.g., Budd 1988b; McClain et al. 1992). As a result, the proposed method is mostly applicable to limestones that are originally composed mainly of aragonite and high-Mg calcite. A stabilized limestone may undergo renewed diagenesis, but the ensuing dissolution and reprecipitation of calcite and associated carbon isotope exchange in a low-Mg calcite-meteoric water system are water-controlled and require a large amount of water and, thus, a long period of time (e.g., James and Choquette 1984; Budd 1988b; Budd et al. 1993; Lohmann 1988; Matsuda et al. 1995). Nevertheless, this method is still applicable to simulate the water–rock interaction in this system as long as the system is open. However, the final whole-rock carbon isotope profile is an overprinted record. Its impact on estimating the duration of subaerial exposures is discussed in the next section.

The method can estimate only exposure durations within the time window when dissolution of aragonite and high-Mg calcite and reprecipitation of calcite occurs, and, thus carbon isotope exchange is active in vadose meteoric environments. The results of sensitivity tests indicate that the low-sensitivity window spans from 0 to ~ 400 ky, within which the estimated duration is not very sensitive to input variations (Figs. 1–6).

The proposed method is an innovative application of Banner and Hanson's (1990) model, which was designed for examining simultaneous isotopic and trace-element variations during diagenesis. They cautioned against the use of absolute cumulative water/rock ratio (N) because of the assumptions in its determination. In this study, the sensitivity test results and, especially, the reasonable match between the estimated durations and

TABLE 4.—*Input parameters and estimated minimum durations of four ancient subaerial exposures.*

Formations	$\delta_{f,o}{}^{13}C$[a] (PDB)	$\delta_{s,o}{}^{13}C$[b] (PDB)	$\delta_{s,msr}{}^{13}C$[c] (PDB)	$C_{f,o}$ (ppm)	P (%)	r (cm/y)	Estimated duration (ky)[d]
Cretaceous Glen Rose Fm.	−10.1 to −15.6	0.9 to 1.3	−3.4	100 / 200	40–50	4.9–9.5	48 ± 18 / 32 ± 15
Cretaceous James Ls.	−8.7 to −14.7	3.2 to 4.8	−1.6	100 / 200	40–50	4.9–9.5	54 ± 21 / 34 ± 18
Pennsylvanian Stran Fm.	−9.1 to −14.9	2.7 to 4.0	−1.4	100 / 200	40–50	14.3–26.1	26 ± 16 / 21 ± 16
Mississippian Newman Ls. (Loc. R-7)	−10.2 to −15.7	0.8 to 1.1	−3.7	100 / 200	40–50	4.9–9.5	38 ± 17 / 27 ± 15

[a] The range was calculated using the percentages of contributions from soil CO_2 (51–70%) and newly deposited sediments (49–30%) in Appendix. An uncertainty range of 20% was assigned to the carbon isotope compositions of soil CO_2 and sediments, as an attempt to acknowledge possible uncertainty in these values. Four values of carbon isotope composition of vadose water were calculated for each scheme of contribution percentages. The two values of the same combination from each scheme were averaged. The resulting four averaged values show a range, and the minimum and maximum values were used as the input range.
[b] The range was derived by assigning a 20% uncertainty range to the most positive carbon isotope composition of a rock in the section.
[c] No uncertainty ranges were assigned because these are the values to be modeled.
[d] For each exposure, the estimate above the bar was calculated using a TDC concentration of 100 ppm and that below the bar using a concentration of 200 ppm, with other parameters in the same range; each mean and standard deviation were calculated from 16 results.

coral growth ages for subaerial exposures in the Barbados limestones suggest that the N values can be used in estimating the minimum durations of subaerial exposures within the low-sensitivity time window.

Last, surface environmental factors determine the properties of vadose meteoric water and, ultimately, the direction and pattern of meteoric diagenesis (e.g., Plummer et al. 1976; Lohmann 1988). Their values are difficult to estimate for ancient limestones. The optimal case is that they would vary over a narrow range on a carbonate platform over its life span. That is, first, spatial variations of vegetation, rainfall, topography, and soil types would be minimal on a platform during an exposure event of tens to hundreds of thousands of years. However, this need not be the case because climatic, biologic, physiographic, and tectonic conditions can change through the history of a platform. Above all, detailed petrographic studies of altered limestones are imperative before modeling, because they may provide clues on mineralogy of original sediments, degrees of soil development and vadose meteoric diagenesis, original porosity, and climatic conditions.

Uncertainties Related to Geological Processes

Emplacement of late-stage (e.g., burial) cements may cause porosity loss and overprint the $\delta^{13}C$ signatures of vadose meteoric diagenesis. If porosity loss is by local dissolution (e.g., stylolitization), then the trend of ^{13}C depletion may be preserved (e.g., Algeo et al. 1992; Cisneros and Vera 1993). If the loss is by filling of allochthonous cements, then the trend may be destroyed. In either case, the trend is probably shifted. If the trend is preserved and its vadose meteoric origin is confirmed by other evidence, however, then the effect of burial diagenesis is likely minimal. This problem has to be considered on a case-by-case basis.

An altered limestone may reenter the vadose zone because of multiple episodes of platform emergence. The low-Mg calcite in the limestone will have a relatively low diagenetic potential (e.g., Budd et al. 1993; Matsuda et al. 1995). In addition, if the vadose water reacts with newly deposited ^{13}C-rich sediments overlying this altered limestone, then the water will be enriched in ^{13}C and ineffective in altering the $\delta^{13}C$ of this limestone. Alternatively, if there is no overlying newly deposited sediment, water-controlled dissolution and reprecipitation and associated carbon isotope exchange between the vadose water and limestone (James and Choquette 1984; Budd 1988b; cf. Budd et al. 1993) may enhance the magnitude of ^{13}C depletion of the altered limestone if the vadose water is more depleted in ^{13}C than the water during the previous vadose meteoric diagenesis. The enhancement will cause overestimation of exposure duration.

Additionally, the upper part of an altered limestone and associated trend of ^{13}C depletion could be eroded during subsequent marine transgression, as documented in the Barbados limestones (Kimbell and Humphrey 1994) and the Pennsylvanian Holder Formation, New Mexico (Allan and Matthews 1982). This truncation will cause underestimation of exposure duration.

Finally, a note of caution related to the compounding of uncertainty is warranted. As noted previously, the sensitivity analyses presented herein illustrate that the minimum durations of subaerial exposure calculated by the model are sensitive to porosity, infiltration rate, and the $\delta^{13}C$ value and TDC concentration of vadose waters. As has also been emphasized, most of these parameters must be assumed, with those assumptions based on geologically reasonable data sets or arguments. The reasonably good fit between the modeled durations and known ages for the Barbados exposures suggests that reasonable assumptions will indeed give reasonable estimates of minimum durations. Estimating the compounded uncertainty associated with each variable is a much more daunting task. The reasonable estimates of uncertainty for each specific model parameter that were used in generating Tables 3 and 4 give some insight. For example, the mean duration calculated from 16 model runs using a TDC concentration of 100 ppm for the James Limestone is 54 ky with a standard deviation of 21 ky. Similarly, the mean duration calculated from 16 runs using the same TDC concentration for the Strawn Formation is 26 ky with a standard deviation of 16 ky. These data suggest that the model can differentiate between minimum exposure durations with an accuracy of several tens of thousand years, and

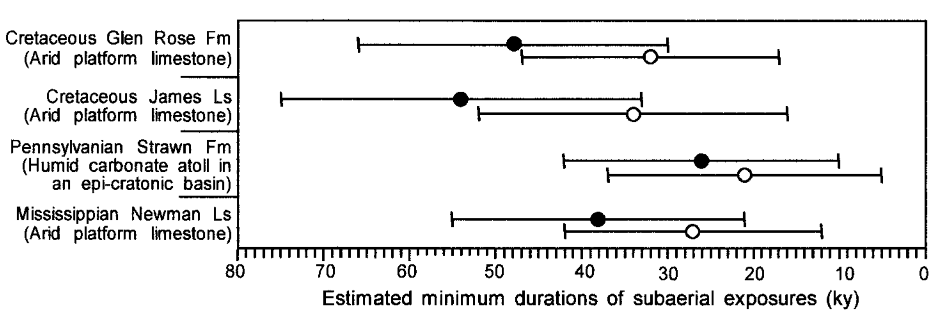

FIG. 10.—Estimated mean durations and standard deviations of four ancient subaerial exposures. Two mean durations (solid and open circles) and associated standard deviations (line through the circles) were calculated for each exposure. See Table 4 for input parameters.

this accuracy could be improved with better constraint on the uncertainties of the model's parameters.

SUMMARY

(1) ^{13}C depletion in vadose diagenetic limestones is largely controlled by the duration of subaerial exposure. The volume of water needed to reach a given $\delta^{13}C$ value of a vadose meteorically altered limestone is calculated using the bulk water–rock interaction model of Banner and Hanson (1990). The minimum exposure duration is equal to the volume of water divided by the infiltration rate of vadose meteoric water. The values are a minimum only, because exposure may have continued even after complete equilibration of $\delta_s{}^{13}C$ to the water-buffered system.

(2) Sensitivity tests establish the relationships between the estimated duration and input parameters. The change in duration per unit change of a given parameter ranges from 0.2 to 9 ky. The model is most sensitive to sediment porosity, infiltration rate of vadose water, the concentration and $\delta^{13}C$ value of total dissolved carbon in the vadose water, and the $\delta^{13}C$ value of fresh sediments.

(3) The estimated durations of subaerial exposures in the Pleistocene Barbados limestones agree well with coral growth ages, which demonstrates that the model can yield reasonable results. The estimated durations for four ancient vadose diagenetic limestones have uncertainties of ~ 20 ky but are confined to a range of 21 to 54 ky, with the largest values reflective of more arid conditions.

(4) The accuracy of estimated durations depends largely on how well the input parameters are constrained. Better constraints may come from a variety of geochemical and cyclostratigraphic data. The method awaits further refinement and exploration.

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APPENDIX: CONTRIBUTIONS OF THREE CARBON SOURCES TO VADOSE METEORIC WATERS

In Schooner Cays, CO_2 from organic respiration has a $\delta^{13}C$ value slightly less than −22‰, atmospheric CO_2 has a value of −6‰, and dissolved aragonite has a value of 4.6‰, all relative to PDB (Budd and Land 1990). The three sources make up the carbon isotope composition of the freshwater, which range from −9 to −14‰. Thus, the following equations can be established:

$$-22‰ \cdot x + 4.6‰ \cdot y - 6‰ \cdot z = -9‰ \quad (\text{or } -14‰) \tag{1}$$

$$x + y + z = 1 \tag{2}$$

where *x, y,* and *z* are contributions from soil CO_2, dissolved aragonite, and atmospheric CO_2, respectively. Furthermore, the carbonate dissolution and reprecipitation reaction:

$$CaCO_3 \text{ (aragonite)} + CO_2 + H_2O = Ca_2^{+} + 2HCO_3^{-} \tag{3}$$

indicates that half of the carbon in the freshwater is from dissolved aragonite, the other half is from soil and atmospheric CO_2 (Salomons and Mook 1986). Thus,

$$y = 0.5 \tag{4}$$

$$x + z = 0.5 \tag{5}$$

Solution for Eqs. 1, 2, 4, and 5 results in negative values for *z*. To keep $z \geq 0$, either the $\delta^{13}C$ value of soil CO_2 must be less than the measured value (−22‰) or the contribution from atmospheric CO_2 must be negligible and that from dissolved aragonite must be less than 0.5. The latter option is more reasonable, thus, assuming $z = 0$, Eqs. 1 and 2 are modified as:

$$-22‰ \cdot x + 4.6‰ \cdot y = -9‰ \quad \text{or} \quad -14‰ \tag{6}$$

$$x + y = 1 \tag{7}$$

Solution of Eqs. 6 and 7 indicates that the contribution from organic CO_2 ranges from 51 to 70%, and that from dissolved aragonite ranges from 49 to 30%. The assumption of $z = 0$ implies that soil CO_2 is the only source of ^{13}C-depleted waters.