^{13}C VARIATION IN LIMESTONE ON AN AQUIFER-WIDE SCALE AND ITS EFFECTS ON GROUNDWATER ^{14}C DATING MODELS*

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ABSTRACT. In modeling the initial ^{14}C activity of ground waters, the δ^{13}C of marine limestone is taken conventionally to vary little about 0‰ PDB. This variation was found to be 6.28‰ in samples taken over intervals from 10^{-2} to 10^5m in the Mooney Falls Member of the Redwall Limestone in northern Arizona. Such a variation will cause appreciable variability in the results of all four initial activity models tested. The variability, due primarily to a numerical instability in the models dependent on this parameter, can introduce significant uncertainty into groundwater "age" calculations.

NOTATION

Variables

a — molal concentration of aqueous CO_2 in a water sample, used only in mole fraction a/Σ

A — ^{14}C activity of material indicated by its subscript (pmc)

b — molal concentration of bicarbonate ion in a water sample, used only in mole fraction b/Σ

C_M — molal concentration of carbon in solution from mineral origin

C_T — molal concentration of TDIC

F — fraction of carbon in water sample calculated to be of gaseous origin (dimensionless)

[H^+] — hydrogen ion activity

pK_1 — negative of the log of the first dissociation constant of carbonic acid

pK_2 — negative of the log of the second dissociation constant of carbonic acid

t — temperature (°C)

T — calculated groundwater "age" (years before present)

δ — stable isotope composition "delta value"

ϵ — isotopic enrichment factor for ^{13}C between two reservoirs, $\epsilon_{12} = (\delta_1 - \delta_2)/(1 + \delta_2/10^3)^{-1}$

Σ — total molal concentration of carbon species in solution in a water sample

Subscripts

bg — indicating enrichment between bicarbonate and soil gas CO_2

bm — indicating enrichment between bicarbonate and mineral carbonates

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g — soil gas carbon reservoir
m — mineral carbon reservoir
s — dissolved carbon in water sample

Abbreviations

PDB — "Pee Dee Bellemnite" [13]C standard
pmc — "percent modern carbon" unit for reporting ^{14}C content
TDIC — "total dissolved inorganic carbon"

INTRODUCTION

In order to determine the "age"[1] of a groundwater sample, it is necessary to know not only its ^{14}C activity (A_s) but also its initial activity (A_o). A number of models have been developed to estimate A_o (for a review, *cf* Fontes, 1983). All but the simplest (chemical mixing) and the most complex (mass transfer) of these models use the ^{13}C content of the mineral carbonate (δ_m) and soil gas (δ_g) carbon reservoirs in contact with the ground water in estimating the relative ^{14}C contributions of these sources to the carbonate species in solution.

Each of the models using δ_m and δ_g includes these terms in a denominator. The models become numerically unstable as this denominator approaches zero. The sensitivity of the models to δ_g has often been examined (eg, Muller, 1977; Fontes & Garnier, 1979), showing that no model may be applied under all possible environmental conditions. The sensitivity of the models to variability in δ_m has generally been considered unimportant (eg, Mook, 1980). Generally, values of δ_m for old marine carbonates are either taken to be 0‰[2] (since the PDB standard is itself such a carbonate) or are obtained from ^{13}C measurements on a very limited number of carbonate samples from the surface. A number of studies have shown δ_m to vary several per mil about 0‰ but these studies have been based on occasional samples from a variety of origins or have been on a limited geographic scale.

The objectives of this study are 1) to test in the field the validity of the assumption that δ_m varies little from 0‰ on a variety of scales, and 2) to quantify the sensitivity of the A_o model to δ_m and assess its importance.

FIELD STUDY

Sampling Strategy

The sampling strategy was to select sites that would permit the study of ^{13}C variations in mineral carbonates at a variety of sampling intervals on an aquifer-wide scale. This was achieved by sampling along two approximately east–west trending transects ca 40km long, one ca 125km north of the other. Figure 1 shows the location of the sites in northwestern Arizona.

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[1] For a discussion of the concept of groundwater "age" as used in this paper, see Evans *et al* (1983, Pt 3.5, p 16–21).
[2] All $\delta^{13}C$ and $\delta^{18}O$ values in this paper are reported in ‰ with respect to the PDB standard (Craig, 1957).
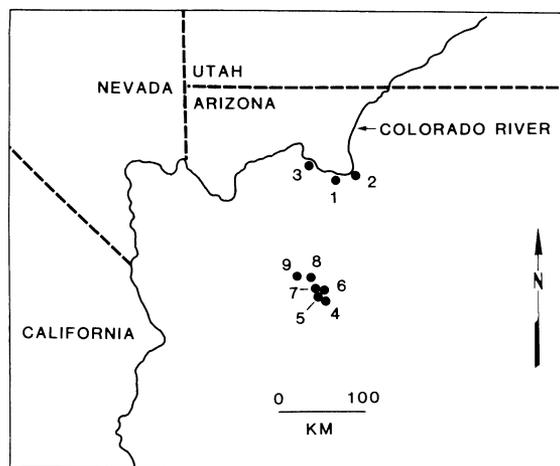
Fig 1. Location map of sampling sites (described in Table 1) in northern Arizona.

Three sites at ca 30km intervals make up the northern transect while 6 sites at less than half that spacing make up the southern one.

At each location, two samples were collected from exposures of the Mooney Falls Member of the Redwall Limestone, one at 0.5m and one at ca 4.5m above the base of this marker bed. Each sample consisted of a block of limestone having a fracture surface with visible signs of alteration from contact with ground water or percolating meteoric water and also having a visibly fresh, unaltered interior. Analyses for ^{13}C were performed on material from both the fracture surface and the interior. In this way, the sampling distances ranged over the following orders of magnitude:

10^{-2} to 10^{-1}m	Interior to exterior samples
10^{0} to 10^{1}m	Upper to lower samples
10^{3} to 10^{4}m	Samples on one transect
10^{5}m	Samples between transects

Description of Sampling Horizon

Throughout most of northern Arizona, the Mississippian-age Redwall Limestone is easily divided into four lithologic members which are, in ascending order, the Whitmore Wash, Thunder Springs, Mooney Falls, and Horseshoe Mesa. The Whitmore Wash and Mooney Falls Members are thick-bedded to massive carbonates deposited in transgressive seaways on the cratonic shelf. The Redwall Limestone forms vertical cliffs up to 60m high which are the most prominent cliffs in the Grand Canyon. The cliffs occur because of the formation's thick bedding, which resulted from sedimentation under low base-level conditions that permitted uniform deposition over an extensive area for long periods of time. Such a sedimentary environment should provide ideal conditions for the uniform deposition of ^{13}C in a carbonate rock.

The Redwall Limestone is remarkably consistent in lithology and gen-

eral form throughout northern Arizona. It is almost certainly originally continuous with the Madison Limestone and Leadville Dolomite which crop out throughout much of the Colorado Plateau, Basin and Range, and Rocky Mountain areas of the western United States. The Redwall Limestone has been exhaustively studied since it was first observed in 1855 (Marcou, 1856) and named (Gilbert, 1875). The definitive work on the Redwall (McKee & Gutschick, 1969) contains 137 measured sections and was used as a guide for selecting sampling locations.

The history of the Redwall Limestone in northern Arizona began in Late Kinderhook time (North American Mississippian State) as waters of the Kaskaskia Sea transgressing into the area from the north, west, and south deposited the Whitmore Wash Member on a surface of low relief. Withdrawal of the Sea is represented by the Thunder Springs Member. At the conclusion of Thunder Springs deposition, an erosional surface of small relief developed from either subaerial or submarine conditions.

The massive beds of the Mooney Falls Member, ca 100m thick in the Grand Canyon area and 50m thick in the Chino Valley area, were deposited on this erosional surface during the second major transgression in late Osage to early Meramec time, ca 330 million years ago. Most of the member is coarse-grained accumulations of intraformational clastic carbonate particles, peloidaloolitic and crinoid and other biogenic fragments. Some amphanitic beds of uniform microcrystalline to cryptocrystalline grains alternate with coarse-grained beds and some dolomite of secondary origin also occurs. The Mooney Falls Member consists of mostly pure limestone and is free of terrigenous material (McKee & Gutschick, 1969).

The base of the Mooney Falls Member was chosen as the sampling horizon because 1) it is areally extensive, 2) it is not complicated by faulting or folding, 3) outcrops are accessible at the desired intervals, and 4) it is readily identifiable in the field. Three sampling sites were in the Grand Canyon, about two-thirds of the way down from the southern rim. The remaining six sampling sites were located in the Chino Valley near or along the Verde River. The sites are described in Table 1.

Results of Isotopic Analyses

The results of the ^{13}C and ^{18}O analyses on the 36 limestone samples from the Mooney Falls Member are presented in Table 2 and are summarized in Table 3.

Slow reaction rates with acid during sample preparation, typical of impure calcite, were reported[3] for the samples from Kaibab Trail upper horizon interior (1-U-I) and exterior (1-U-E) and from Bass Trail lower horizon exterior (3-L-E). These three samples are appreciably higher in ^{13}C content (average $+0.44\%$) than the overall average (-1.85%). Nevertheless, only the upper samples from the Kaibab Trail were shown by x-ray analysis[4] to be dolomite; the others were essentially calcite. Since these val-

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[3] Isotopic analyses were made at the Laboratoire d'Hydrologie et de Géochimie Isotopique, Université de Paris-Sud, Orsay, France.
[4] X-ray analyses were made at Northern Arizona University, Tempe, Arizona.

TABLE 1
Description of sampling sites

Sampling Site Number and Name	Location	Distance to nearest sampling site (km)	Distance to farthest sampling site (km)	Measured section of McKee and Gutshick (1969)	Description of base of Mooney Falls Member (after McKee & Gutshick, 1969)
Grand Canyon Area					
1. Kaibab Trail	36° 05' 00", 112° 05' 20"	23.3	130	25	Limestone: yellowish-gray, coarse-grained, thick- to very thick-bedded (0.6-6 m); weathers to rough, light-gray surface; forms massive cliff.
2. Old Tanner Trail	36° 03' 55", 111° 49' 55"	23.3	130	22	Limestone: pale-yellow-brown, fine grained; thick-bedded; forms massive cliff.
3. Bass Trail	36° 12' 00", 112° 22' 00"	29.0	130	29	Limestone: dolomitic, pale-red to yellowish-gray, fine grained, very thick-bedded (1.2-6.0 m); contains many tiny fossil casts; weathers rough, dark gray; forms cliff with bench above.
Chino Valley Area					
4. Jerome	34° 45' 20", 112° 22' 00"	7.6	130	90	Limestone: very light-gray, coarse-grained, crinoidal, very thick-bedded, massive; contains numerous fossils; includes zones of solution weathering with red mudstone from infiltration; forms cliff or very steep slope.
5. Bodkin Narrow Gauge Tank	34° 46' 10", 112° 13' 15"	7.6	130	87	Limestone: white to very light-gray, coarse-grained, crinoidal and very thick-bedded (0.9-2.4 m); very fossiliferous; massive.
6. Perkinsville	34° 53' 50", 112° 11' 00"	7.3	120	-	not measured
7. West of Perkinsville	34° 54' 30", 112° 15' 30"	7.3	120	85	Limestone: very light-gray, coarse-grained, crinoidal, very thick-bedded, massive; contains many corals and brachiopods; cliff-forming.
8. Hells Canyon	35° 00' 30", 112° 23' 00"	11.3	120	81	Limestone: very light-gray, coarse-grained, crinoidal, very thick-bedded, massive; fossil traces on weathered surface; forms cliff.
9. Wineglass Canyon	35° 00' 30", 112° 31' 00"	11.3	120	77	Limestone: very light-gray, coarse-grained, crinoidal, very thick-bedded, massive, forms steep slope.

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TABLE 2
Analytical results for carbonate samples

Site:		1	2	3	4	5	6	7	8	9	$\bar{x}+s^{**}_x$
UPPER δ¹³C (‰ PDB)	Interior:	+0.28*	-0.92	-0.73	-2.37	-2.97	-3.20	-2.71	-2.63	-2.37	-1.96+1.2
	I-E:	-0.20	-0.12	-0.17	+1.47	+0.52	-3.17	-1.65	-0.61	+0.85	-0.34+1.4
	Exterior:	+0.48*	-0.80	-0.55	-3.84	-3.49	-0.03	-1.06	-2.02	-3.22	-1.67+1.6
	ave:	+0.38	-0.86	-0.64	-3.10	-3.23	1.58	-1.88	-2.32	-2.80	-1.78+1.4
LOWER	Interior:	-2.24	+0.17	-1.25	-3.61	-3.46	-2.03	-2.01	-2.88	-3.00	-2.29+1.1
	I-E:	-0.35	+0.07	-1.85	-1.82	-0.53	-0.38	-4.45	-0.12	+0.56	-0.82+1.5
	Exterior:	-1.85	+0.10	+0.57	-3.08	-2.91	-2.37	+2.44	-2.76	-3.56	-1.48+2.1
	ave:	-2.04	+0.14	+0.14	-0.34	-3.34	-2.20	+0.22	.2.82	-3.28	-1.87+1.7
UPPER δ¹⁸O (‰ PDB)	Interior:	-4.04	-5.55	-5.93	-4.33	-5.36	-6.24	-5.24	-2.63	-5.19	-4.94+1.1
	I-E:	-0.08	+0.46	+1.15	+2.45	+5.96	+1.87	+1.14	-2.63	+0.93	-1.83+1.8
	Exterior:	-3.96	-6.01	-7.12	-6.78	-11.32	-8.07	-6.26	-5.26	-6.12	-6.76+2.1
	ave:	-4.00	-5.78	-6.52	-5.55	-8.34	-7.16	-5.75	-3.94	+5.66	-5.86+1.9
LOWER	Interior:	-6.69	-5.08	-7.56	-5.17	-5.58	-4.65	-5.82	-5.97	-6.51	-5.89+0.9
	I-E:	-0.18	+0.32	-3.52	+0.41	-0.02	+0.10	-0.33	+1.24	+0.13	-0.20+1.3
	Exterior:	-6.51	-5.40	-4.02	-5.31	-5.56	-4.75	-5.49	-7.21	-6.64	-5.65+1.0
	ave:	-6.60	-5.24	-5.79	-5.24	-5.57	-4.70	-5.66	-6.59	-6.58	-5.77+0.7

* X-ray diffraction data shows sample to be dolomite.

** Uncertainties are one standard deviation of the sample.

TABLE 3
Summary of analytical results for carbonate samples (n = 36)

	Mean ± standard deviation	
	$\delta^{13}C$ (‰ PDB)	$\delta^{18}O$ (‰ PDB)
OVERALL:	−1.85 ± 1.5	−5.81 ± 1.4
Interior:	−2.11 ± 1.2	−5.42 ± 1.1
Exterior:	−1.55 ± 1.9	−6.20 ± 1.7
Upper:	−1.78 ± 1.4	−5.86 ± 1.9
Lower:	−1.87 ± 1.7	−5.77 ± 0.7
Maximum:	+2.44(7-L-E)	−2.67(8-U-I)
Minimum:	−3.84(4-U-E)	−11.32(5-U-E)

ues are by far not the most positive in the data set (see 7-L-E, value confirmed by the laboratory), they were not treated differently from the others.

No statistically significant differences in ^{13}C content can be detected between (1) interior and exterior samples, either overall or within the upper or the lower horizon samples; (2) upper and lower horizon samples, either overall or within the interior or the exterior samples.

The 12 samples from the northern transect appear to have significantly higher ^{13}C contents (−0.56 ± 0.9)‰[5] than those from the southern transect (−2.46 ± 1.3)‰. The entire data set varied from a minimum of −3.84‰ to a maximum of +2.44‰. This range of 6.28‰ is larger than would be expected for a single limestone formation. Rather it is comparable to the 5.7‰ range found by Craig (1953) in his classic study for 21 marine carbonates dating from the Cambrian to the Pleistocene from around the world.

The $\delta^{13}C$ values of the interior samples are plotted against those of the exterior samples in Figure 2. Points would lie on the dashed line if interior and exterior $\delta^{13}C$ values were equal. The magnitude of the differences in pairs of interior/exterior data is clear from the length of the connecting lines. Although northern and southern transect samples are somewhat clustered, no general trend is apparent. A few large (>3‰) differences between interior and exterior samples can be seen.

^{18}O contents of marine carbonate can be used as an indicator of recrystallization under non-marine conditions since their original isotopic composition, which reflects isotopic equilibrium with sea water and subsequent diagenetic alteration, undergoes a characteristic depletion when the carbonate is recrystallized from lighter meteoric water. A shift of >2‰ in $\delta^{13}C$ was considered an indication of such a recrystallization.

The upper samples from the Jerome, Bodkin Tank and Wineglass Canyon sites (Sites 4, 5 and 9) show depletions of this magnitude in the exterior samples with respect to those of the interior. Note that these samples were not suspected of containing any minerals other than calcite and do not have anomalous $\delta^{13}C$ values, as would be expected if complete

[5] All uncertainties are reported as ±1 σ. The analytical uncertainties of 0.1‰ of each analysis are not reflected in these values.
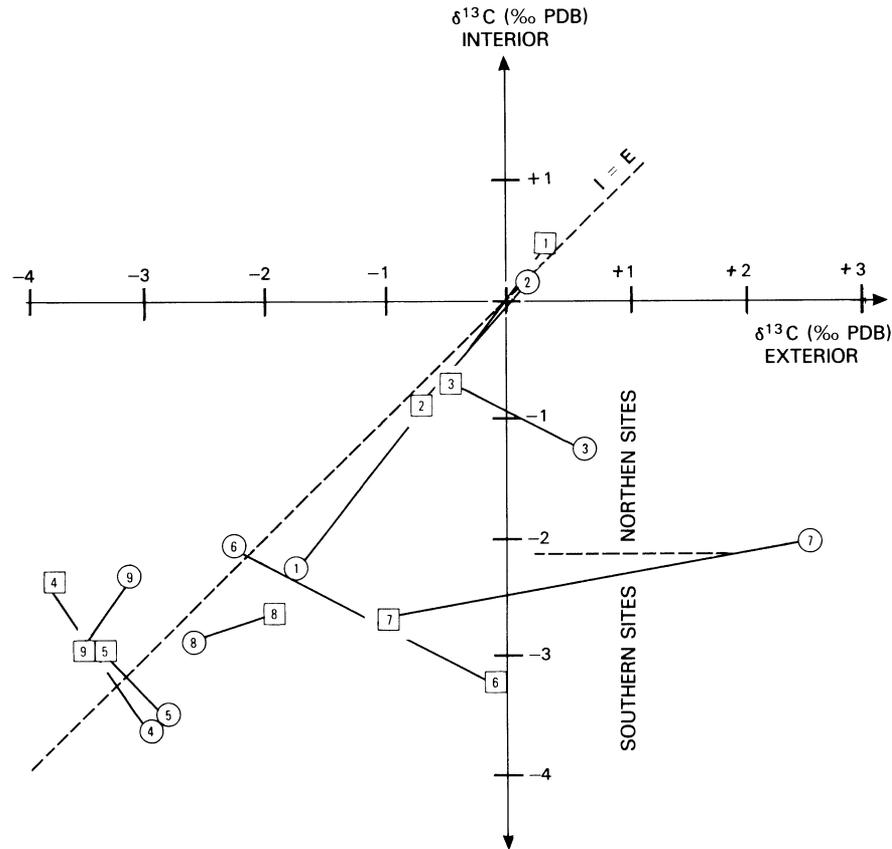
Fig 2. $\delta^{13}C$ (‰ PDB) of internal *vs* external samples. □ = upper samples; ○ = lower samples. Site numbers appear within the symbols.

recrystallization of dissolved marine calcite occurred. Thus the effect would be the same whether $\delta^{13}C$ data from such samples or data from unaltered specimens were used.

MODELING STUDY

Description of Models

Models of A_o generally take the form

$$A_o = F A_g + (1 - F) A_m \tag{1}$$

where A_g and A_m are the ^{14}C contents of the soil gas and mineral carbonate reservoirs respectively (in pmc) and F is the fraction of aqueous carbonate (TDIC) originating from the gaseous reservoir. For the old marine limestone in this study, $A_m = 0$. The groundwater "age" is then estimated from

$$T = -8270 \ln \frac{A_s}{A_o} \tag{2}$$

where T is the "age" of the water sample and A_s is the measured activity of the water sample.

The four A_o models examined in this study have been described in detail by Fontes (1983) and are not elaborated here. Sensitivity analysis was performed on F for each model, using the following expressions for F:

Simple Isotopic Mixing Model (or Pearson model; eg, Pearson & Hanshaw, 1970).

$$F = (\delta_s - \delta_m)/(\delta_g - \delta_m) \tag{3}$$

where δ_s is the $\delta^{13}C$ of the groundwater sample. This is a linear mixing model between gaseous and mineral ^{13}C reservoirs.

Isotopic Mixing Model with fractionation approximation (or modified Gonfiantini model; eg, Gonfiantini, 1972).

$$F = (\delta_s - \delta_m - \epsilon_{bm})/ (\delta_g + \epsilon_{bg} - \delta_m - \epsilon_{bm}) \tag{4}$$

where ϵ_{bm} and ϵ_{bg} are the fractionation factors (in ‰) between aqueous bicarbonate and mineral carbonate and between aqueous bicarbonate and CO_2 gas, respectively. The models in the sensitivity analysis below used the temperature functions (after Vogel, Grootes & Mook, 1970; Mook, Bommerson & Staverman, 1974):

$$\epsilon_{bm} = -15.1 + 4232/(t + 273.15)$$

$$\epsilon_{bg} = -23.89 + 9483/(t + 273.15) \tag{5}$$

Isotope Mixing Model with CO_2 exchange in closed system (or Mook model; eg, Mook, 1976). The simplified version of this model (Mook, 1980; Eq 28) was used here:

$$F = \frac{a}{\Sigma} + 0.5\frac{b}{\Sigma} + \frac{\delta_s - \left(\frac{a}{\Sigma} + 0.5\frac{b}{\Sigma}\right)\delta_g - 0.5\frac{b}{\Sigma}\delta_m}{\delta_g - \delta_m + 2\epsilon_{bg}} \tag{6}$$

where a/Σ and b/Σ are the mole fractions of aqueous carbon in the form of dissolved CO_2 and bicarbonate ion, respectively. The model in the sensitivity analysis used the temperature functions (Harned & Davis, 1943; Harned & Scholes, 1941; after Mook, 1976):

$$pK_1 = 3404.71/(t + 273.15) + 0.032786\ (t + 273.15) - 14.8435$$

$$pK_2 = 2902.39/(t + 273.15) + 0.02379\ (t + 273.15) - 6.4980 \tag{7}$$

for the first and second apparent dissociation constants of carbonic acid. Thus, a/Σ and b/Σ were calculable from

$$a/\Sigma = [H^+]^2/([H^+]^2 + [H^+]K_1 + K_1K_2)$$

$$b/\Sigma = [H^+]\ K_1/([H^+]^2 + [H^+]K_1 + K_1K_2) \tag{8}$$

where $[H^+]$ is the activity of hydrogen ion $(=10^{-pH})$.

Global Exchange-Mixing Model in closed systems (or Fontes model; Fontes & Garnier, 1979).

$$F = k + \frac{a}{\Sigma} + 0.5\frac{b}{\Sigma} + \frac{\delta_s - \left(\frac{a}{\Sigma} + 0.5\frac{b}{\Sigma}\right)\delta_g - 0.5\frac{b}{\Sigma}\delta_m}{\delta_g - \delta_m - \epsilon_{bm} + \epsilon_{bg}} \qquad (9)$$

In addition to setting $A_m = 0$, the model used in the sensitivity analysis set $k = 0$ where

$$k = 0.2\,(\epsilon_{bg} - \epsilon_{bm})\,\frac{\delta_s - \left(\frac{a}{\Sigma} + 0.5\frac{b}{\Sigma}\right)\delta_g - 0.5\frac{b}{\Sigma}\delta_m}{\delta_g - \delta_m + \epsilon_{bm} - \epsilon_{bg}} \qquad (10)$$

since at expected values of the independent parameters, this term is very small compared to the other terms in Equation 9. Further, the following equivalences were made with the C_M and C_T terms (molal TDIC and molal concentration of carbon of mineral origin):

$$C_T = \Sigma = a + b$$

$$C_M = 0.5\,b \qquad (11)$$

These equivalences permit a clearer comparison of the last two models and are well justified in most practical cases (Mook, 1980).

Sensitivity Analysis

The inherent numerical instability of the A_o models described above arises as the denominator terms in the F-functions (Equations 3, 4, 6 and 9) approach zero. Division by zero occurs when (Muller, 1977):

Eq 3: $\quad 0 = \delta_g - \delta_m$

Eq 4: $\quad 0 = \delta_g - \delta_m - \epsilon_{bm} + \epsilon_{bg}$

Eq 6: $\quad 0 = \delta_g - \delta_m + 2\epsilon_{bg}$

Eq 9: $\quad 0 = \delta_g - \delta_m - \epsilon_{bm} + \epsilon_{bg} \qquad (12)$

Note that the denominator of the $\delta^{13}C$ dependent term in Equations 5 and 10 are zero under the same conditions, but the rate at which F approaches infinity (*ie*, the shape of the curve) will differ because the other terms in the two equations are not equal. Moreover, secondary differences arise when the additive k-term (Eq 10) is not set to zero.

Four representative cases of the multivariate sensitivity performed are presented in Table 4. The first two reflect conditions which could be expected in temperate environments while the latter two may occur in some semi-arid environments.

In order to facilitate the comparison of effects due only to changes in δ_m, F-values were calculated rather than A_o-values (eliminating A_g and A_m as independent parameters). Further, Equation 8 was used to calculate consistent carbonate chemistry data, dependent upon only pH (and temperature). Figure 3 presents the results of the sensitivity analysis of each model as the deviation of F from the base case *vs* δ_m. The base case is the value of F (multiplied by 100 so as to express it as a percentage) at $\delta_m = 0\%_0$ PDB. The

TABLE 4
Conditions and results of sensitivity analysis

	Case 1	Case 2	Case 3	Case 4
Conditions				
δ_s (‰ PDB)	−15	−12	−12	−9
δ_g (‰ PDB)	−25	−25	−18	−18
t (°C)	15	15	25	25
pH	7.5	7.5	6.5	7.5
Results				
"Tamers" model	*54*	*54*	*71*	*54*
"Pearson" model	*60*	*48*	*67*	*50*
	11	**15**	**14**	**11**
'Gonfiantini" model	*94*	*74*	*121*	*88*
	3	**13**	**21**	**12**
"Mook" model	*76*	*33*	*37*	*26*
	38	**108**	**170**	**200**
"Fontes" model	*58*	*49*	*68*	*51*
	8	**9**	**8**	**13**

In the Results section, the numbers in bold face represent the range in F-values (multiplied by 100 so as to be expressed as percent) resulting from using the observed range of δ_m values (−3.8 to +2.4‰) from the Mooney Falls. The numbers in italics are the A_o values calculated under the same conditions with $A_g = 100$ pmc, $A_m = 0$ pmc and $\delta_m = 0$‰ PDB.

base case values of F thus expressed appear in italics in Table 4 and are equivalent to A_o under the given conditions if A_g were 100 pmc and A_m were 0 pmc.

The reduction of pH to 6.5 in Case 3 was necessary to prevent the "Mook" model from calculating unreasonably high A_o values (*ie*, A_o 100 pmc). This could not be avoided in the modified "Gonfiantini" model in the same case. These examples serve to illustrate that the various models should not be applied systematically and indiscriminately to all groundwater dating problems. Rather, *each model is intended to describe a specific geochemical process under specific conditions and should be applied only when the situation being modeled is known to be appropriate.* The reasonable and relatively stable results of the "Mook" model in Case 1, for which it is most suited (Mook, 1976), compared to the very low and unstable results in the other three cases illustrates this well. In this paper, the models are being applied to common sets of parameters simply to determine their numerical response under comparable conditions to expected variations in δ_m and not in an attempt to evaluate actual groundwater "ages."

A simple chemical mixing model (labeled "Tamers" model; eg, Ingerson & Pearson, 1964; Tamers, 1967) which is independent of δ_m has been included in Table 4 for comparison. The principal conclusions which can be drawn from Table 4 and Figure 3 about sensitivity of the models to changes in δ_m are 1) the modified "Gonfiantini," "Mook" and "Fontes" models are more unstable under "semi-arid" conditions than under "tem-
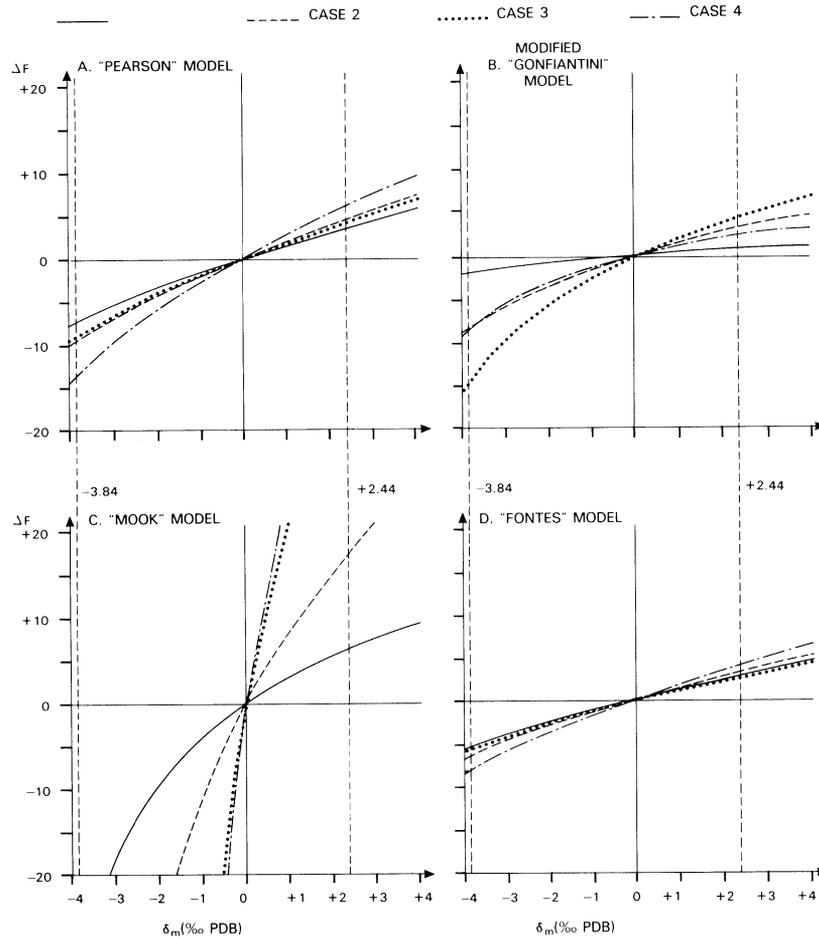
Fig 3. A. "Pearson," B. modified "Gonfiantini," C. "Mook" and D. "Fontes" model sensitivity analysis results. Deviation of F (in %) from base case plotted *vs* δ_m (‰ PDB).

perate" ones; 2) the "Mook" model is appreciably less stable than the other models, even under the best of conditions; and 3) the "Fontes" and "Pearson" models are generally the most stable.

Stability in no way implies accuracy, since the complex mixture history and evolution of ground waters preclude a single "accurate" result for A_o. Stability has no bearing on the suitability of the model, but simply emphasizes the degree to which δ_m should be characterized to minimize uncertainties resulting from its estimation.

CONCLUSIONS

The observed range of δ_m (6.28‰) was appreciably greater than expected for the formation studied. Assumptions about δ_m should be exper-

imentally verified on as large a scale as possible in groundwater dating studies in order to avoid the effects of unexpectedly large variations.

Table 4 shows that a variation of at least $\pm5\%$ (*ie,* ±5 pmc under base case conditions) can be routinely expected when the models are applied over the range of δ_m observed in the field study. For a calculated A_o value of 60 pmc from any of the models studied and for a sample with $A_s = 40$ pmc, this variation would result in an uncertainty in the "age" of 20% (or 3400 $\pm$ 700 yr) exclusively due to δ_m variations. Such sensitivity of δ_m variations is significant and should be quantified when the models are applied.

More generally, the usefulness of the A_o models discussed in this paper seems limited to cases for which they were specifically designed and to studies with insufficient geochemical, isotopic, and hydrologic data available to model the detailed geochemical evolution of the groundwater system (eg, Wigley, Plummer & Pearson, 1978).

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