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Arthur L. Lange

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CAVES AND KARST

Research in Speleology

Volume 13, Number 3

May/June 1971



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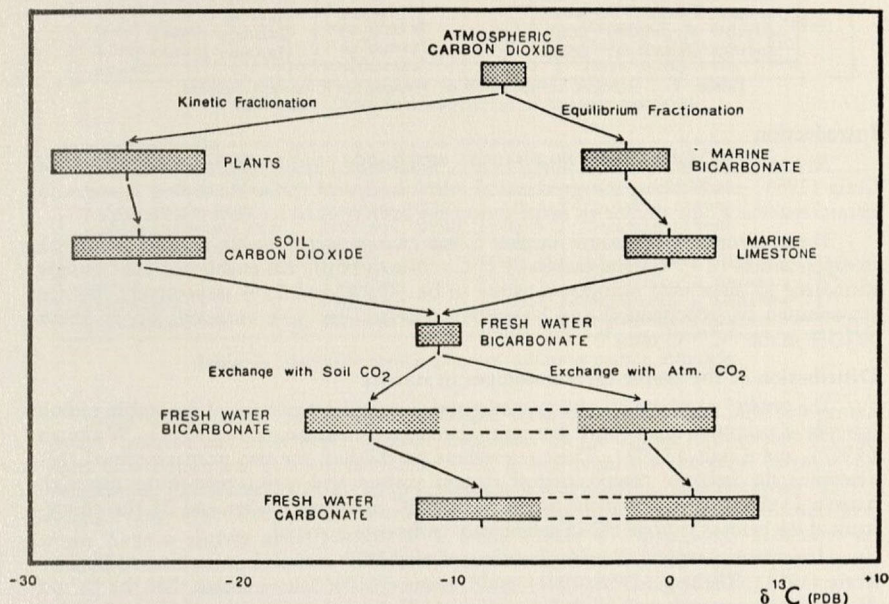


Figure 1. Variations of the stable carbon isotopes in some natural systems relative to the PDB standard of Craig (1953).

THE APPLICATION OF STABLE CARBON ISOTOPE STUDIES TO KARST RESEARCH

PART I: BACKGROUND AND THEORY*

by RUSSELL S. HARMON†

Abstract

The distribution and natural variation of the stable carbon isotopes in the karst environment are reviewed. Isotopic fractionation in the system $\text{CO}_2\text{-H}_2\text{O-CaCO}_3$ is discussed and values for the fractionation factors K_0 , K_1 , and K_3 are recalculated as a function of temperature as follows:

$$1000 \ln K_0 = 0.912 + 0.0063 (1/T^2 \text{ } ^\circ\text{K}),$$

$$1000 \ln K_1 = 4.537 + 1.0985 (1/T^2 \text{ } ^\circ\text{K}),$$

$$1000 \ln K_3 = -3.628 + 1.1941 (1/T^2 \text{ } ^\circ\text{K}).$$

Isotopic models for the "open" and "closed" karst system are presented. At chemical and isotopic equilibrium, carbonate waters in an "open" karst system should have a $\delta^{13}\text{C}$ value of about -16‰ , while those in a "closed" karst system should have values around -12.5‰ , variations depending on P_{CO_2} and temperature.

* Part II will appear in Volume 13, Number 4 of this journal.

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LOCATION	$\delta^{13}\text{C}$	SOURCE
Chicago, Illinois	-8.2	Craig (1953)
Chicago, Illinois	-7.4	Craig (1953)
Yosemite National Park, California	-7.43	Keeling (1958)
Inyo Mountains, California	-6.90	Keeling (1958)
Pacific Ocean (nr California)	-6.94	Keeling (1961)
Assateague Island, Virginia	-7.04	Keeling (1961)
Howard Pocket, Arizona	-7.21	Keeling (1961)
Moscow Province, USSR	-8.4	Galimov (1966)
Moscow Province, USSR	-9.5	Galimov (1966)

Table 1. Isotopic composition of atmospheric carbon dioxide.

Introduction

As a result of the works of Nier (1950), Wickman (1952), and the classic work of Craig (1953) establishing the geochemical relationships of the stable carbon isotopes in natural systems, a new avenue of investigation has been opened for karst researchers.

The element carbon, atomic number 6, has two important stable (non-radioactive) isotopes, carbon-12 (^{12}C) and carbon-13 (^{13}C). Nier (1950) has established the absolute abundance of these two isotopes in nature to be 98.9% and 1.1% respectively. Isotope fractionation by geochemical and biological processes can give variations up to about $\pm 1.5\%$ in the $^{13}\text{C}/^{12}\text{C}$ ratio.¹

Distribution of the stable carbon isotopes in nature

The general geochemical characteristics and distribution patterns of the stable carbon isotopes in natural systems were first investigated by Wickman, et al. (1951), Wickman (1952), and Craig (1953). These researchers established the two primary effects that determine the isotopic composition of natural carbon and carbon-containing material; namely, 1) the enrichment of the lighter isotope ^{12}C in organic matter, and 2) the enrichment of the heavier isotope ^{13}C in sedimentary carbonate material.

Atmospheric carbon dioxide: In terms of the PDB standard—a marine mollusk—Craig (1953), Keeling (1958, 1961), and Galimov (1966) have shown that the carbon dioxide in the atmosphere is slightly enriched in ^{12}C , having a $\delta^{13}\text{C}$ value of about -7‰ (Table 1).

Organic Material: Craig (1953), Broecker and Walton (1959), and Park and Epstein (1960) have determined that plant material is very much enriched in ^{12}C with an average $\delta^{13}\text{C}$ value of -25‰ . Similarly, Craig (1953) and Oana & Deevey (1960) have shown that organic-rich sediments are also enriched in ^{12}C and have a $\delta^{13}\text{C}$ value very close to that of the plants (Table 2).

Soil-zone carbon dioxide: In the soil zone, carbon is present mostly as carbon dioxide resulting primarily from organic processes, such as plant respiration and the decay of organic material. Galimov (1966) and Rightmire & Hanshaw (1971) have indicated that this carbon dioxide is very much enriched in ^{13}C , having $\delta^{13}\text{C}$ values near -22‰ (Table 3). This value may of course be higher where direct exchange of carbon dioxide occurs between the soil zone and the atmosphere.

¹ Conventionally, the $^{13}\text{C}/^{12}\text{C}$ ratio is expressed in terms of delta carbon-13 per mil ($\delta^{13}\text{C}$ ‰) values where

$$\delta^{13}\text{C} \text{ in } \text{‰} = \left(\frac{^{13}\text{C}/^{12}\text{C}_{\text{sample}} - ^{13}\text{C}/^{12}\text{C}_{\text{standard}}}{^{13}\text{C}/^{12}\text{C}_{\text{standard}}} \right) \times 10^3$$

Using this notation, a negative $\delta^{13}\text{C}$ value indicates that a sample contains less ^{13}C than the standard and is thus isotopically "lighter." Similarly, a positive $\delta^{13}\text{C}$ value indicates that a sample contains more ^{13}C than the standard and is thus isotopically "heavier." It should be remembered throughout this paper that isotopic variations expressed in per mil differences to a standard represent only relative abundance variations. By convention, the standard used for reporting carbon isotope variations is the Chicago PDB standard of Craig (1953), a Cretaceous belemnite from the Pee Dee formation of South Carolina.

MATERIAL	LOCATION	$\delta^{13}\text{C}$	SOURCE
clover	Wyoming	-25.6	Craig (1953)
spruce wood	California	-25.0	Broecker & Walton (1959)
marine algae	Florida	-15.3	Craig (1953)
cyprus wood	Egypt	-22.4	Craig (1953)
fresh water algae	Nevada	-22.7	Broecker & Walton (1959)
organic mud	Connecticut	-27.9	Oana & Deevey (1960)
organic mud	Connecticut	-30.9	Oana & Deevey (1960)
organic mud	Florida	-14.0	Craig (1953)
tree leaves	New York	-23.6	Broecker & Walton (1959)
lichen	California	-21.1	Park & Epstein (1960)
grass	California	-28.3	Park & Epstein (1960)

Table 2. Isotopic composition of organic material.

ENVIRONMENT	LOCATION	$\delta^{13}\text{C}$	SOURCE
forest podzolic loam	Moscow, USSR	-23.4	Galimov (1966)
soddy-sandy loam	Moscow, USSR	-23.5	Galimov (1966)
soddy-carbonate soil	Moscow, USSR	-24.6	Galimov (1966)
peaty-clay soil	Moscow, USSR	-26.5	Galimov (1966)
forest	Florida	-20.4	Rightmire & Hanshaw (1971)
forest	Florida	-21.3	Rightmire & Hanshaw (1971)
grassland	Florida	-15.2	Rightmire & Hanshaw (1971)
grassland	Florida	-19.0	Rightmire & Hanshaw (1971)

Table 3. Isotopic composition of soil-zone carbon dioxide.

Sedimentary rocks: Sedimentary carbonate rocks can be divided into two general groups: marine and fresh water. Marine carbonates are formed in equilibrium with sea water bicarbonate and thus are enriched in ^{13}C to approximately the same extent as the bicarbonate. According to Craig (1953), Keith & Weber (1964), and Friedman (1970), among many others, marine limestones have a $\delta^{13}\text{C}$ value of about 0‰. Dolomites generally have a slightly more positive $\delta^{13}\text{C}$ value (Table 4). Freshwater carbonates are formed in isotopic equilibrium with fresh-water bicarbonate and subsequently are less enriched in ^{13}C than the marine carbonates. Vogel (1959), Gross (1964), Galimov & Grinenko (1965), Land (1970), and others have indicated that the average $\delta^{13}\text{C}$ value for the fresh-water carbonates should be about -8‰ (Table 5).

Carbon in aqueous systems: In aqueous systems inorganic carbon is present as either molecular carbonic acid (H_2CO_3^0) or ionic carbonate species (HCO_3^- and CO_3^{2-}) due to the dissociation of the carbonic acid. Within the rather limited chemical conditions of most natural waters, the bicarbonate ion (HCO_3^-) is the most important of these carbon-bearing species.

Craig (1954), Mook (1968), and Deuser & Hunt (1969) have indicated that sea-water bicarbonate is enriched in ^{13}C relative to atmospheric carbon dioxide by about +8‰ (Table 6). For fresh waters this value is much lower, reflecting an organic source for a portion of the bicarbonate. Broecker & Walton (1959), Vogel (1959), Oana &

DESCRIPTION	LOCATION	$\delta^{13}\text{C}$	SOURCE
limestone	Harz, Germany	+0.08	Keith & Weber (1964)
limestone	Texas	+0.86	Keith & Weber (1964)
limestone	South Dakota	-0.40	Keith & Weber (1964)
limestone	Eigg, Scotland	-0.04	Keith & Weber (1964)
limestone	Tennessee	+0.30	Craig (1953)
limestone	Nevada	-2.5	Craig (1953)
limestone	Indiana	+2.4	Craig (1953)
dolomite	New York	+2.7	Craig (1953)
dolomite	Michigan	+1.2	Craig (1953)
dolomite	Wyoming	+1.3	Friedman (1970)

Table 4. Isotopic composition of marine carbonates.

DESCRIPTION	LOCATION	$\delta^{13}\text{C}$	SOURCE
stalactite	Wisconsin	-8.9	Craig (1953)
travertine	Utah	-10.1	Craig (1954)
calcite vein	Bermuda	-8.4	Gross (1964)
stalactite	Bermuda	-7.8	Gross (1964)
stalactite	Bermuda	-3.6	Gross (1964)
stalactite	Bermuda	-10.9	Gross (1964)
stalactite	Bermuda	-9.9	Land (1970)
flowstone	Jamaica	-4.5	Land & Epstein (1970)
dripstone	Crimea, USSR	-7.0	Galimov & Grinenko (1965)
dripstone	Crimea, USSR	-4.9	Galimov & Grinenko (1965)
dripstone	Crimea, USSR	-10.6	Galimov & Grinenko (1965)
dripstone	Crimea, USSR	-11.3	Galimov & Grinenko (1965)
dripstone	Crimea, USSR	-9.1	Galimov & Grinenko (1965)
dripstone	Crimea, USSR	-5.5	Galimov & Grinenko (1965)
limestone	Utah	-11.40	Keith & Weber (1964)
limestone	Quebec, Canada	-10.46	Keith & Weber (1964)
limestone	Colorado	-6.39	Keith & Weber (1964)
dolomite	West Virginia	-8.88	Keith & Weber (1964)
stalagmite	Jura, Germany	-7.4	Vogel (1959)
stalactite	New Zealand	-7.3	Hendy (1970)
stalactite	New Zealand	-5.6	Hendy (1970)
stalagmite	New Zealand	-4.0	Hendy (1970)
stalagmite	New Zealand	-9.0	Hendy (1970)

Table 5. Isotopic composition of fresh water carbonates.

LOCATION	$\delta^{13}\text{C}$	SOURCE
North Atlantic Ocean	-2.5	Craig (1954)
Mediterranean Sea	-2.0	Craig (1954)
North Sea	+1.1	Mook (1968)
South Atlantic Ocean	+0.1	Deuser & Hunt (1969)
North Atlantic Ocean	-1.0	Deuser & Hunt (1969)

Table 6. Isotopic composition of marine-dissolved carbon.

LOCATION	$\delta^{13}\text{C}$	SOURCE
Pyramid Lake, Nevada	-5.9	Broecker & Walton (1959)
Linsley Pond, Connecticut	-13.9	Oana & Deevey (1960)
Wononscopomuc Lake, Connecticut	-11.5	Oana & Deevey (1960)
Rhine River, Netherlands	-12.6	Mook (1968)
groundwater, Netherlands	-15.4	Mook (1968)
Vecht River, Netherlands	-13.4	Mook (1968)
groundwater, Netherlands	+1.2	Mook (1968)
groundwater, Florida	-13.6	Rightmire & Hanshaw (1971)
groundwater, Florida	-12.2	Rightmire & Hanshaw (1971)
Rio Bueno, Jamaica	-9.5	Land & Epstein (1970)
groundwater, Jamaica	-12.7	Land & Epstein (1970)
groundwater, Germany	-10.7	Vogel (1959)
groundwater, Germany	-13.2	Vogel (1959)
groundwater, Florida	-8.3	Pearson & Hanshaw (1970)
groundwater, Florida	-11.5	Pearson & Hanshaw (1970)
dripstone water, New Zealand	-12.5	Hendy (1970)

Table 7. Isotopic composition of fresh water-dissolved carbon.

Deevey (1960), and Mook (1968), among others, have shown that the $\delta^{13}\text{C}$ for fresh water bicarbonate may vary between -17‰ and $+2\text{‰}$, depending on the presence or absence and relative amounts of organically derived carbon dioxide and carbonate rock available to participate in the dissolution process (Table 7).

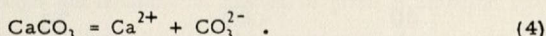
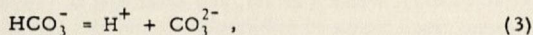
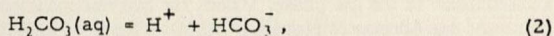
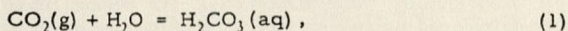
The natural variations in the stable carbon isotopic composition of the materials and systems discussed above are illustrated in Figure 1.

CALCULATED VALUE	EXPERIMENTAL VALUE	TEMP. °C	SOURCE
0.9990	0.99951	22.	Vogel (1962)
0.99905	0.99883	0.	Vogel, et al. (1970)
0.99907	0.99887	10.	Vogel, et al. (1970)
0.99910	0.99892	20.	Vogel, et al. (1970)
0.99913	0.99895	30.	Vogel, et al. (1970)
	0.99899	40.	Vogel, et al. (1970)
	0.99903	50.	Vogel, et al. (1970)
	0.99908	60.	Vogel, et al. (1970)
0.9992		0.	Thode, et al. (1965)
0.9992		20.	Thode, et al. (1965)
0.9993		40.	Thode, et al. (1965)
0.9993		60.	Thode, et al. (1965)
	0.99944	7.	Wendt (1968)
1.0005		0.	Deuser & Degens (1967)

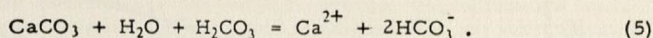
Table 8. Fractionation equilibria for carbon dioxide-carbonic acid.

Chemical equilibria

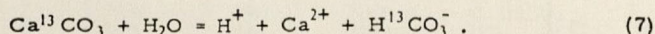
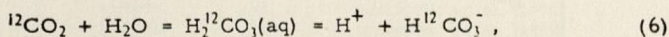
The chemical equilibria for the system $\text{CO}_2\text{-H}_2\text{O-CaCO}_3$ are well known and have been clearly illustrated by Garrels & Christ (1965) among many others. The important equilibrium equations are given in Equations 1-4 for calcium carbonate (CaCO_3), but have the same basic form for any other carbonate mineral:



From these equilibria it is seen that the solution or precipitation of calcium carbonate can be described by the equation



The stoichiometry of this reaction requires that one bicarbonate ion be contributed by the dissociation of the aqueous carbon dioxide and the other by the solution of the calcium carbonate. Thus, disregarding any isotopic fractionation, it would be expected from Equations 6 and 7 that the isotopic composition of the bicarbonate in solution would lie midway between that of the carbon dioxide and calcium carbonate sources:



Isotopic equilibria

Isotopic fractionation occurs between each of the different carbon-bearing species involved in the solution equilibria. The extent of this fractionation at isotopic equilibrium depends solely on the temperature. This fractionation can likewise be characterized by certain equilibrium constants. These are listed in Equations 8-11 relative to gaseous carbon dioxide:

$$K_O = {}^{12}\text{CO}_2(\text{g}) / {}^{13}\text{CO}_2(\text{g}) \Big/ \text{H}_2^{12}\text{CO}_3 / \text{H}_2^{13}\text{CO}_3, \quad (8)$$

$$K_1 = {}^{12}\text{CO}_2(\text{g}) / {}^{13}\text{CO}_2(\text{g}) / \text{H}^{12}\text{CO}_3^- / \text{H}^{13}\text{CO}_3^- , \quad (9)$$

$$K_2 = {}^{12}\text{CO}_2(\text{g}) / {}^{13}\text{CO}_2(\text{g}) / {}^{12}\text{CO}_3^{2-} / {}^{13}\text{CO}_3^{2-} , \quad (10)$$

$$K_3 = {}^{12}\text{CO}_2(\text{g}) / {}^{13}\text{CO}_2(\text{g}) / \text{Ca}^{12}\text{CO}_3 / \text{Ca}^{13}\text{CO}_3 . \quad (11)$$

The computed and experimentally determined fractionation factors for these equilibria are listed in Tables 8-12 and are discussed in more detail in the paragraphs that follow.

CO₂-H₂CO₃ (aq) fractionation (K₀): The isotopic fractionation between gaseous and dissolved carbon dioxide is quite small, with the lighter isotope concentrated in the aqueous species. Values for this fractionation have been calculated by Vogel (1962), Thode, et al. (1955), Deuser & Degens (1967), and Vogel, et al. (1970). Experimental determinations have been made by Vogel (1962), Deuser & Degens (1967), Wendt (1968) and Vogel, et al. (1970). These data are listed in Table 8. Using experimental and calculated data, values of K₀ were determined as a function of temperature, using a simple linear regression analysis. The calculated straight-line equation for this K₀ is given in Equation 12 and shown in Figure 2.

$$1000 \ln K_0 = 0.912 + 0.0063 (1/T^{2^\circ\text{K}}) . \quad (12)$$

CO₂(g)-HCO₃⁻ fractionation (K₁): The isotopic fractionation between gaseous carbon dioxide and dissolved bicarbonate is of intermediate magnitude, with the lighter isotope concentrated in the gas phase. Values for this fractionation have been experimentally determined by Abelson & Hoering (1960), Vogel (1962), Wendt, et al. (1963), Thode, et al. (1965), Wendt (1968), and Emrich, et al. (1970). These data, listed in Table 9,

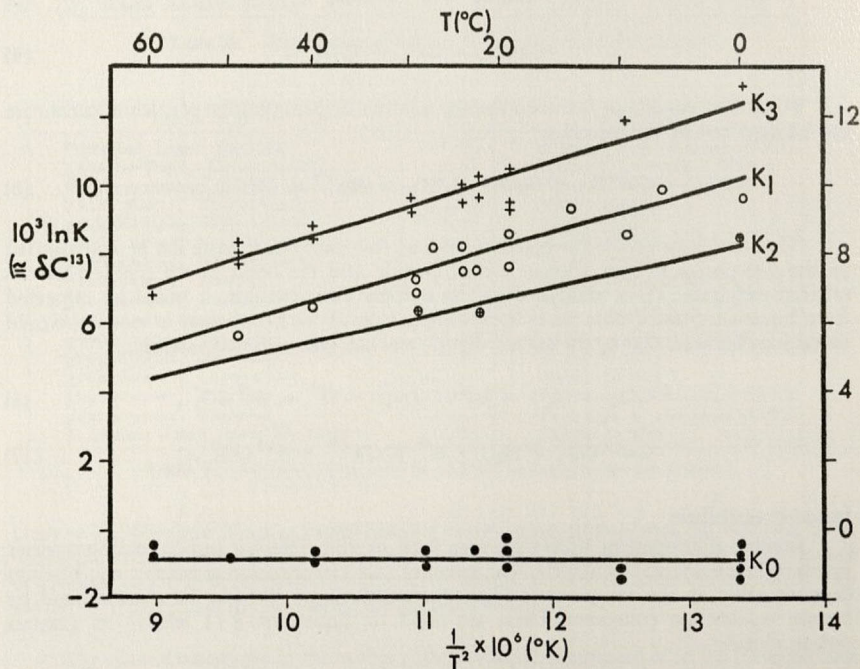


Figure 2. Isotopic fractionation in the system CO₂-H₂O-CaCO₃ as a function of temperature.

EXPERIMENTAL VALUE	TEMP. °C	SOURCE
1.00940	14.	Wendt (1968)
1.00845	28.	Wendt (1968)
1.00968	7.	Wendt, et al. (1963)
1.00771	22.	Vogel (1962)
1.0083	25.	Abelson & Hoering (1961)
1.0093	0.	Deuser & Degens (1967)
1.0084	10.	Deuser & Degens (1967)
1.0076	20.	Deuser & Degens (1967)
1.0069	30.	Deuser & Degens (1967)
1.00838	20.	Emrich, et al. (1970)
1.00721	30.	Emrich, et al. (1970)
1.00649	40.	Emrich, et al. (1970)
1.00555	50.	Emrich, et al. (1970)
1.00439	60.	Emrich, et al. (1970)
1.0077	25.	Thode, et al. (1965)
1.0040	98.	Malinin, et al. (1967)
1.0034	103.	Malinin, et al. (1967)

Table 9. Fractionation equilibria for carbon dioxide-dissolved bicarbonate.

CALCULATED VALUE	EXPERIMENTAL VALUE	TEMP. °C	SOURCE
1.0042	---	0.	McCrea (1950)
1.0038	---	25.	McCrea (1950)
---	1.0029	32.	McCrea (1950)

Table 10. Fractionation equilibria for dissolved carbon-calcium carbonate.

were used to determine values of K_1 as a function of temperature by simple linear regression analysis. The calculated straight-line equation for this K_1 is given in Equation 13 and shown in Figure 2:

$$1000 \ln K_1 = -4.537 + 1.0985(1/T^{\circ}K). \quad (13)$$

$CO_2(g)$ - CO_3^{2-} fractionation (K_2): The fractionation between gaseous carbon dioxide and dissolved carbonate should be less than that of K_1 and K_3 . This fractionation has received little attention, and thus its value is not well established. The only values reported to date are those calculated by Thode, et al. (1965), which appear to be unusually large. Because of this, values for K_2 were determined indirectly by using the data of McCrea (1950) for the fractionation between $CaCO_3$ and CO_3^{2-} listed in Table 10. The straight-line equation derived from this calculation is shown in Figure 2.

CALCULATED VALUE	EXPERIMENTAL VALUE	TEMP. °C	SOURCE
---	1.0094	20.	Emrich, et al. (1970)
---	1.0096	30.	Emrich, et al. (1970)
---	1.0087	40.	Emrich, et al. (1970)
---	1.0082	50.	Emrich, et al. (1970)
---	1.010	25.	Baertschi (1957)
---	1.008	63.	Baertschi (1957)
---	1.0093	22.	Vogel (1962)
1.0094	---	22.	Stranks & Harris (1953)
1.0130	---	0.	Bottinga (1968)
1.0118	---	10.	Bottinga (1968)
1.0107	1.0093	20.	Bottinga (1968)
1.0096	---	30.	Bottinga (1968)
1.0086	---	40.	Bottinga (1968)
1.0077	1.0084	50.	Bottinga (1968)
1.0069	---	60.	Bottinga (1968)
1.0101	---	25.	Bottinga (1968)

Table 11. Fractionation equilibria for carbon dioxide-calcium carbonate.

FRACTIONATION FACTOR	0°C	10°C	20°C	30°C
K_0^*	0.99906	0.99907	0.99908	0.99910
K_1^*	1.0112	1.0102	1.0091	1.0082
K_2^*	0.99812	0.99821	0.99831	0.99872
K_3^*	1.0040	1.0038	1.0035	1.0033

Table 12. Fractionation equilibria between individual aqueous carbon species.

$CO_2(g)$ - $CaCO_3$ fractionation (K_3): The isotopic fractionation between gaseous carbon dioxide and solid calcium carbonate is the largest of the four fractionations. It received much attention due to its importance in determining the isotopic composition of calcium carbonate precipitated from aqueous solution. Values for K_3 have been calculated by Stranks & Harris (1953) and Bottinga (1968). Experimental determinations have been made by Baertschi (1957), Vogel (1962), and Emrich, et al. (1970). The data of these workers are listed in Table 11. Once again, values for this fractionation were determined using a simple linear regression analysis. The calculated straight-line equation for this K_3 is given in Equation 14 and shown in Figure 2:

$$1000 \ln K_3 = -3.628 + 1.1941 (1/T^2 - 1/K) \quad (14)$$

The carbon isotope equilibria can also be written in terms of fractionation between the individual carbon-bearing species in solution, as follows:

$$K_0^* = {}^{12}CO_2(g) / {}^{13}CO_2 \bigg/ H_2{}^{12}CO_3 / H_2{}^{13}CO_3 \quad (15)$$

$$K_1^* = H_2{}^{12}CO_3 / H_2{}^{13}CO_3 \bigg/ H^{12}CO_3^- / H^{13}CO_3^- \quad (16)$$

$$K_2^* = H^{12}CO_3^- / H^{13}CO_3^- \bigg/ {}^{12}CO_3^{2-} / {}^{13}CO_3^{2-} \quad (17)$$

$$K_3^* = {}^{12}CO_3^{2-} / {}^{13}CO_3^{2-} \bigg/ Ca^{12}CO_3 / Ca^{13}CO_3 \quad (18)$$

The equilibrium constants for this second set of equilibria can then be determined from the first set by the relationships

$$K_0^* = K_0 \quad (19)$$

$$K_1^* = K_1 / K_0 \quad (20)$$

$$K_2^* = K_2 / K_1 \quad (21)$$

$$K_3^* = K_3 / K_2 \quad (22)$$

Values for these fractionation equilibria were calculated using the values for K_0 - K_3 previously derived; the results are listed in Table 12.

The equilibria equations 19-22, however, do not entirely describe the magnitude of the isotopic fractionation between the carbon-bearing species in solution, because the distribution of these species is a function of pH (THODE ET AL., 1965; DEUSER & DEGENS, 1967). This distribution has been illustrated by Mook (1968) and is shown in Figure 3.

Thus, as shown in Equation 23, the isotopic composition of a solution is the sum of the isotopic compositions of each of the dissolved carbonate species present in the solution.

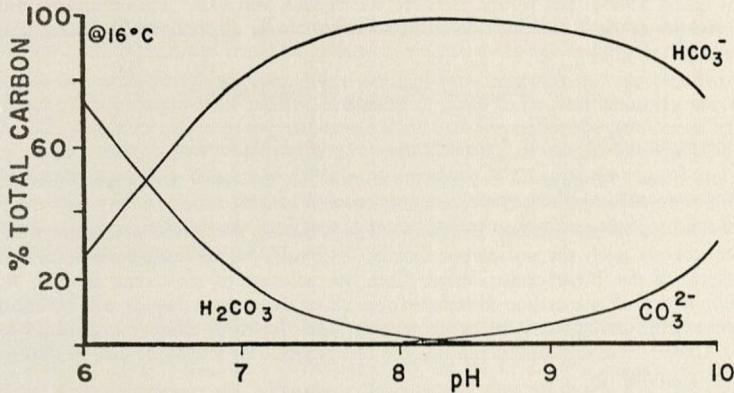


Figure 3. Distribution of dissolved carbonate species in the system $\text{CO}_2\text{-H}_2\text{O-CaCO}_3$ as a function of pH at 16°C .

This is, in fact, the isotopic composition that one measures when analyzing a water sample, and not just the bicarbonate isotopic composition as indicated by most workers:

$$\delta^{13}\text{C}_{\Sigma\text{CO}_3^{2-}} = \frac{(\delta^{13}\text{C}_{\text{H}_2\text{CO}_3})(\% \text{H}_2\text{CO}_3) + (\delta^{13}\text{C}_{\text{HCO}_3^-})(\% \text{HCO}_3^-) + (\delta^{13}\text{C}_{\text{CO}_3^{2-}})(\% \text{CO}_3^{2-})}{(\% \text{H}_2\text{CO}_3) + (\% \text{HCO}_3^-) + (\% \text{CO}_3^{2-})} \quad (23)$$

As indicated by this equation, isotopic fractionation between a solution and a precipitated calcium carbonate will be smaller at high pH values where the dissolved carbonate is primarily CO_3^{2-} than at low neutral pH values, where it is primarily HCO_3^- . Similarly, the fractionation between the dissolved carbonate and the gas phase should increase with increased pH due to the predominance of HCO_3^- and CO_3^{2-} over $\text{CO}_2(\text{aq})$.

It should be recalled, however, that isotopic fractionation is also a direct function of temperature, since fractionation generally increases with decreasing temperature. Therefore, either of these two factors can act to add to or subtract from the fractionation effect of the other, depending upon the pH and temperature of the solution.

Discussion

Although the stoichiometry of the chemical equilibria for the system $\text{CO}_2\text{-H}_2\text{O-CaCO}_3$ indicates that there should be a one-to-one relationship between carbon derived from solution of carbon dioxide and that derived from solution of calcium carbonate, it has been shown that isotopic exchange can alter this relationship. The extent of this alteration is directly related to the hydrogeologic setting in which the solution occurs.

The open karst system: In the open karst system, it is presumed that downward percolating waters are able to dissolve carbonate rock in the presence of an excess of carbon dioxide gas provided by the soil-zone reservoir. Thus, providing for sufficient residence time, isotopic exchange between the aqueous carbon-bearing species and the soil-zone carbon dioxide gas should maintain a state of equilibrium. Because the amount of carbon dioxide gas in the soil zone is assumed to be in excess and exchangeable with the carbon dioxide species in solution, the carbonate derived from dissolution of the limestone must be quite small compared with the total carbon-bearing species in solution. Under these circumstances, the isotopic composition can be determined from the relationship

$$\delta^{13}\text{C}_{\Sigma} = \frac{[(\delta^{13}\text{C}_{\text{CO}_2(\text{g})} + K_0)(\% \text{H}_2\text{CO}_3)] + [(\delta^{13}\text{C}_{\text{CO}_2(\text{g})} + K_1)(\% \text{HCO}_3^-)] + [(\delta^{13}\text{C}_{\text{CO}_2(\text{g})} + K_2)(\% \text{CO}_3^{2-})]}{\% \text{H}_2\text{CO}_3 + \% \text{HCO}_3^- + \% \text{CO}_3^{2-}} \quad (24)$$

At nearly neutral pH values, however, the H_2CO_3 and CO_3^{2-} concentrations are negligible and the isotopic composition of the solution can be approximately described by the relationship

$$\delta^{13}\text{C}_{\Sigma_0} \approx \delta^{13}\text{C}_{\text{CO}_2(\text{g})} + (K_0^*)(K_1^*), \quad (25)$$

remembering that K_0^* and K_1^* are temperature- and pH-dependent.

Thus, for example, at 10°C a solution of pH 7.5 in contact with a gas phase of $\delta^{13}\text{C} = -25\text{‰}$ should have an isotopic composition of -16‰ .

The "closed" karst system: If downward percolating meteoritic waters are unable to maintain contact with the soil-carbon dioxide reservoir, the resulting equilibrium isotopic composition of the bicarbonate derived from the solution of the carbon dioxide will be very close to that of the carbon dioxide because all of the carbon dioxide will be consumed during the solution process as replenishment, and thus also isotopic exchanges are restricted. Under these conditions the isotopic composition of a solution can be determined from the relationship

$$\delta^{13}\text{C} = \frac{[(\delta^{13}\text{C}_{\text{CO}_2(\text{g})})(\% \text{C}_{\Sigma\text{CO}_2(\text{K})})] + [(\delta^{13}\text{C}_{\text{CaCO}_3})(\% \text{C}_{\Sigma\text{CaCO}_3})]}{\% \text{C}_{\Sigma\text{CO}_2(\text{g})} + \% \text{C}_{\Sigma\text{CaCO}_3}} \quad (26)$$

where $\% \text{C}_{\Sigma\text{CO}_2(\text{g})}$ and $\% \text{C}_{\Sigma\text{CaCO}_3}$ are the amounts of the carbon-bearing species in solution derived from the soil-zone carbon dioxide and carbonate rock, respectively. Thus for example, at a temperature of 10°C a calcite-saturated solution of pH 7.5, having passed through a soil zone with carbon dioxide gas of a $\delta^{13}\text{C}$ value of -25‰ and having dissolved a carbonate rock with a $\delta^{13}\text{C}$ value of 0‰ , should have an isotopic composition of -12.5‰ .

Additional changes in the isotopic composition of a solution may occur through isotopic exchange with the atmospheric carbon dioxide. In this case, the isotopic composition of a solution should become less negative because the atmospheric carbon dioxide is isotopically heavier than the dissolved carbonate species. The result should be a solution with an equilibrium isotopic composition between -9‰ and -7‰ .

Thus, it has been shown that, based upon physical, chemical, isotopic fractionation, and isotopic exchange considerations, the $\delta^{13}\text{C}$ variations for low-temperature carbonate waters at equilibrium should be large, ranging from possibly -16‰ to -7‰ .

Application to karst research

From the preceding discussion, it is obvious that stable carbon isotope studies can be important factors in the study of carbonate solution or precipitation. Although little use has been made of such studies to date, their potential is nonetheless significant, as illustrated by the following brief examples.

The most widespread use of stable carbon isotope studies to date has been in conjunction with radiocarbon hydrogeologic age-dating studies to identify the sources of dissolved carbonate species in a particular carbonate groundwater system (PEARSON & HANSHAW, 1970; MÜNNICH & VOGEL, 1959). In studying the principal artesian aquifer of the Florida peninsula, Pearson & Hanshaw (1970) were able to show that well waters with $\delta^{13}\text{C}$ values more negative than that predicted from equilibrium relationships at saturation were concentrated near the recharge area and represented incomplete chemical and isotopic equilibrium between the gas phase and the carbonate rock. Similarly, well waters with more positive values than that expected at equilibrium were a result of supersaturation in the deeper, more confined portions of the aquifer.

A second application of such studies has been illustrated by Galimov & Grinenko (1965), who were able to date paleoclimates in a karst area in the Soviet Union. Their $\delta^{13}\text{C}$ measurements on cave dripstones from the Crimean Uplands indicated that the cave

deposits were more enriched in ^{12}C than the country rock, and that a sharp division of the $\delta^{13}\text{C}$ values in stalactite rings could be related to a climatic change during Tertiary time.

Extension of these studies into other areas of karst research is very possible. With good stratigraphic control and careful sampling of both water and bedrock, one might identify the source rock for a given carbonate water and determine the amount of solution actively occurring within any or all units of a carbonate rock sequence. The applications of such information to karst denudation studies are obvious. It also appears likely that stable carbon isotope studies can be fruitfully extended to include studies of solution kinetics, rates, and equilibria in karst systems; groundwater pollution studies; and, to some extent, hydrogeologic investigations of karst aquifers.

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CORRIGENDUM

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Page 12: Complete final paragraph as follows:

The very limited results of the test are depicted in Figure 2. Measurements were made by placing the seismometer directly on the marble of the surface; hence, exposed to some wind noise. After completing the east side of the traverse a wind arose that prevented further readings during the remaining time available. The general nature of the background noise at the east end of the line could be described as "white noise"; the sound above the stream contained definite irregular "thumps and plunks" superimposed on a level of white noise higher than background.

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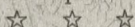
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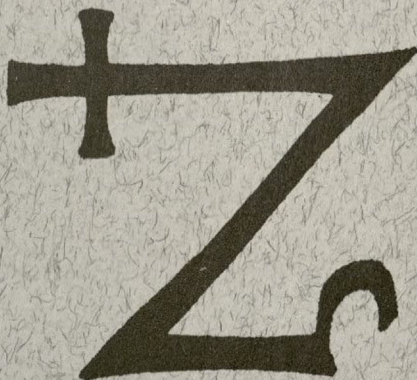
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