ABSTRACT

The sources of dissolved carbonate species in ground-water systems must be known in order to correct \( ^{14}C \) measurements to determine true or correct relative ground-water ages. The contributions of the various sources can be estimated from \( C_{13}/C_{12} \) ratios and from total carbonate content measurements on the water.

Atmospheric precipitation generally contains no dissolved carbonate; the initial carbonate dissolved in ground water comes from the soil atmosphere and soil carbonate minerals. Theoretical considerations and field studies in Florida, New York, and Texas show that carbonate dissolved from the soil air has values of \( \delta C_{13} = -25^{\circ}/o \) and \( C_{14} = 100\% \) m.d.n., which are identical with those of plants.

The major source of additional carbonate in deeper portions of a ground-water system is solution of carbonate minerals \( (\delta C_{13} = 0^{\circ}/o; C_{14} = 0\% \) m.d.n.) which apparently takes place freely until an equilibrium is approached between the dissolved and solid phases. In nearly pure carbonate systems, such as the principal Floridan aquifer, this solution about doubles the
content of dissolved carbonate species, and $\delta^{13}C = -12\%$ and
$C_{true} = 2 \times C_{measured}$. Where ionic interaction is affected
by silicate dissolution, cation exchange, or mixing of dissimilar
waters, the dissolved carbonate content can increase further,
and $\delta^{13}C < -12\%$ and $C_{true} > 2 \times C_{measured}$.

Several non-mineral sources may also add dissolved carbonate
to ground water. These include introduction of heavy CO$_2$ by
thermal solutions or of relatively light CO$_2$ through oxidation,
by dissolved oxygen or sulfate reduction, of carbon-bearing
substances in the formation. Such oxidation of peat or lignite
with $\delta^{13}C = -25$ has been observed in Texas and New York and
oxidation of petroleum with $\delta^{13}C < -25$, in Texas.

Regional patterns of water chemistry can suggest how much
additional carbon these sources are adding; $C^{15}/C^{12}$ ratios of
dissolved species help one choose between the various possible
non-mineral sources.

Isotope exchange theoretically could change the $C^{13}/C^{12}$
and $C^{14}/C^{12}$ ratios of the dissolved carbonate towards those of
the aquifer mineral carbonate, but field studies have shown no
evidence that exchange occurs at low temperature. It therefore
does not seem to be a practical problem.

**INTRODUCTION**

The $C^{14}$ content of dissolved carbonate species in ground
water is a function, first, of the time elapsed since the water
was last in contact with a $C^{14}$ source, and, second, of processes
which affect the carbonate chemistry of ground water. Two
fundamentally different approaches are currently in use to
account for the effects of changes in the carbonate chemistry
of water on its $C^{14}$ content.

The first approach was used in early studies of $C^{14}$ in
ground water and is still preferred by many investigators. In
it the carbonate chemistry of the water and particularly the
changes of this chemistry are not treated explicitly. Instead, it is assumed that at time zero, the $^{14}C$ content of the water was less than that of the normal modern standard owing to various reactions which occur in the soil of the recharge zone; commonly a value between 70% and 90% of the modern standard is assumed as an initial C$^{14}$ activity. The considerations on which this approach is based have recently been reviewed by Münich (1968).

The second method explicitly considers chemical interactions involving carbon species which may take place in a particular aquifer system and examines them by thermodynamic and isotopic analysis to determine their effects on C$^{14}$ activity. The principles of this method and examples of its use have been presented (Ingerson and Pearson, 1964; Pearson, 1965; Pearson and White, 1967). Here we briefly review these principles and compare results obtained using them with those which would come from the first approach.

**SOURCES OF C$^{14}$-BEARING DISSOLVED CARBONATE**

The atmosphere contains carbon dioxide at a partial pressure of about $10^{-3.5}$ atmospheres and $\delta C^{13} = -7^\circ/o$\(^1\). Rain and snow falling through the atmosphere can dissolve some of this atmospheric carbon dioxide, but because atmospheric precipitation is strongly acid, the only carbonate species that can exist in precipitation is H$_2$CO$_3$. The concentration of this species will be set by the partial pressure of CO$_2$ in the atmosphere and cannot exceed more than about $2 \times 10^{-5}$ molal. This concentration is insignificant in comparison with the carbonate content of most natural waters.

\(^1\) $^{13}/^{12}$ values are reported in the familiar $\delta$ notation where

$$\delta C^{13} = \left( \frac{C^{13}/C^{12}_{\text{sample}}}{C^{13}/C^{12}_{\text{standard}}} - 1 \right) \times 1000.$$ All $\delta C^{13}$ data in this paper are reported as deviations from the PDB standard (Craig, 1957). On this scale, marine limestones commonly have $\delta C^{13}$ values close to 0$^\circ/o$ and land plants $\delta C^{13}$ values near -25$^\circ/o$.\(^3\)
The partial pressure of CO₂ in the soil of many regions is several orders of magnitude higher than in the atmosphere. Such high CO₂ pressures come from CO₂ produced within the soil by plant root respiration and decay of plant debris. Thus, in a well-developed soil, such as found in non-arid, temperate climates, the soil CO₂ should be isotopically equivalent to that of plants with δC¹³ = -25‰ and C¹⁴ = 100% of modern. The C¹⁴ content of soil air can be slightly greater than modern in soils containing post-bomb plants, or slightly less than modern if soil decay is not rapid and much old plant debris exists; however, these are second order considerations.

Few studies have been made of the chemistry or isotopic composition of soil gas, but inferences can be drawn from numerous studies of the carbonate chemistry of ground water. One such study of particular relevance concerns the carbonate chemistry of water from the Magothy aquifer, Long Island, New York. The Magothy aquifer is an important hydrologic system which supplies water to most of Long Island; it contains essentially no carbonate minerals.

Figure 1 is a cross section through Long Island showing the locations of some of the wells sampled in a study of the island along with the total dissolved carbonate content and δC¹³ value of water from the wells. The Magothy aquifer is recharged in the higher central portion of the island—the right-hand portion of the section in figure 1. Water flows south through the formation and is discharged into the ocean far offshore to the south. The three wells nearest the recharge area have total dissolved carbonate contents of about 3 x 10⁻⁴ molal which corresponds to a Pₐ CO₂ of about 5 x 10⁻³ atmospheres, more than ten times that of the atmosphere itself. Furthermore, the δC¹³ content of the water from these wells is very close to -25‰ for all of them. The same total carbonate content and δC¹³ values are found in other wells in the recharge area of the Magothy aquifer on Long Island. These analyses show that the partial pressure of
FIGURE 1.--Cross-section through Long Island, New York, showing carbonate chemistry of water in the Magothy aquifer.
CO₂ and its stable isotopic composition in the soil are as expected. The results of studies in central Texas and Florida, although they are complicated by other sources of carbonate, also provide evidence that soil-zone CO₂ in temperate, non-arid climates is derived from and isotopically equivalent to plant carbon.

The studies reported here were made in aquifers in temperate regions with recharge areas that have well developed plant growth and soils on them, and the conclusions about soil-air isotopic composition derived from them may not be applicable to all climates. For example, in arid or semi-arid climates, plant activity on and in the soil should be much less than in temperate regions. Thus, the amount of CO₂ produced in the soil could be considerably reduced and might not be enough to overcome the CO₂ partial pressure of the outside atmosphere. Depending on the amount of plant activity, the δC¹³ of the atmospheres of such soils could range from -7 to -25‰ while their C¹⁴ contents would remain about 100% of modern.

Data on soil atmospheres and on water being recharged in arid or semi-arid regions are sparse but suggest that, as a first approximation, a soil air δC¹³ value of -16 to -18‰ may be appropriate. For example, Rightmire (1967) measured the δC¹³ values of soil air CO₂ in arid west Texas and found that they range from about -15 to -19 and average -17‰. Work on carbonate dissolved in ground water in arid regions is complicated by the effect of carbonate in the aquifer. This work, including that of Tamers (1967) in Venezuela and studies by the IAEA (B. R. Payne, personal communication, 1969), also strongly suggests that the soil air δC¹³ in these regions is considerably heavier than -25‰.

For ground-water dating, the zero time datum is the time when the water enters the ground-water system and is coincident with the last C¹⁴ source with which the water is in contact, generally the soil air. To date ground water successfully, one
must be able to determine what proportion of the total carbon present in a ground-water sample was derived from the soil air and, hence, contained C$^{14}$ at time zero.

**SOURCES OF CARBONATE WITHIN THE AQUIFER**

Mineral sources: Water reacts chemically with its environment, and because carbonate minerals are so widespread in nature, their effect on the carbonate chemistry of water must be considered in some detail. An equation for the reaction between carbon dioxide-containing water with a carbonate mineral is commonly written as:

$$\text{CO}_2 + \text{H}_2\text{O} + \text{CaCO}_3 \rightarrow \text{Ca}^{+2} + 2\text{HCO}_3^-$$

(1)

When equilibrium is obtained between soil air-derived CO$_2$ of $\delta C^{13} = -25\%$ and C$^{14} = 100\%$ modern and marine carbonate minerals of $\delta C^{13} = 0\%$ and C$^{14} = 0$, this reaction would produce a solution with $\delta C^{13} = -12$ and C$^{14} = 50\%$ if the reaction occurred before any significant C$^{14}$ decay had taken place. If the reaction does not go to 100% saturation, either from kinetic effects or due to a paucity of solid carbonate in the aquifer, the dilution by dead carbonate would be between 0 and 50%, and the $\delta C^{13}$ value of the dissolved bicarbonate would be between -25 and -12%. Several schemes have been devised that use the ratio of the carbonate species CO$_2$ (aqueous) and HCO$_3^-$ to determine the extent of this reaction in a given water and so provide a factor to use for dilution by minerals (Ingerson and Pearson, 1964; Tamers, 1967; Wendt and others, 1967). Unfortunately, the behavior of natural systems cannot be satisfactorily represented by such a simple reaction as equation (1), and these schemes tend to be unsatisfactory.

To arrive at more satisfactory results, the carbonate chemistry of water must be considered rigorously. There are many discussions of carbonate equilibria in the geochemical literature, particularly in work by Garrels and Christ (1965);
more than a cursory discussion would be inappropriate here. To suggest where rigorous considerations of carbonate equilibria lead, however, consider equation (2):

$$\frac{a_{H^+} \cdot k_{CaCO_3}}{m_{HCO_3}^2 \cdot \gamma_{Ca^{2+}} \cdot \gamma_{HCO_3} \cdot \gamma_{HCO_3^-}}$$

(2)

This expression is valid for waters with pH of about 6 to 8; and in it, m represents molalities; \( \gamma \), the activity coefficients; \( k \), the dissociation constants for appropriate species; and \( a_{H^+} \), the activity of the hydrogen ion. There are five independent variables in this expression which interact to determine the bicarbonate concentration. They are, first, the temperature which determines the value of \( k_{CaCO_3} \) and \( k_{HCO_3^-} \) and has a secondary effect on the activity of the hydrogen ion and on the activity coefficients of the calcium and bicarbonate ions. The second variable is the term here written \( k_{CaCO_3} \), which is dependent on the composition of the solid carbonate in the system. Only rarely will this composition be stoichiometric \( CaCO_3 \) because natural minerals usually contain significant amounts of other divalent ions, particularly magnesium. The content of ions in solution, other than those explicit in equation (2), is a third variable, important for its effects on the values of the activity coefficients. Finally, the fourth and fifth variables are the pH and the calcium ion concentration, which may be determined in part by reactions with non-carbonate mineral species in the aquifer.

The data needed to treat the carbonate chemistry of water with any rigor come only from rather specialized studies of the geochemistry of both the water and the aquifer material. These data would seldom be available in studies of a reconnaissance nature, and, unfortunately, these are the types of studies in which \( C^{14} \) may prove to be the most useful. However, any scheme for correcting \( C^{14} \) measurements on ground water requires some additional data
which could be obtained during most sampling programs. We are fortunate in that much of our C\textsuperscript{14} work in the United States has been undertaken in conjunction with intensive geochemical studies of ground-water systems. The additional information is not always necessary but does serve to confirm conclusions already drawn from more simple methods.

Regardless of the controls on the solubility of carbonate minerals in a given situation, dissolution of these minerals will do two things to the chemistry of the water. It will (1) increase the total dissolved carbonate species and (2) change the isotopic composition of the dissolved carbonate. Equation (3a) is a general expression relating the stable isotope composition of carbonate dissolved in a water to the amounts (m\textsubscript{c\textsubscript{j}}) and isotopic compositions (\delta C\textsubscript{s\textsubscript{m}}) of various sources of carbonate to the water.

\[
\delta C_{sm}^{13} = \frac{\Sigma m_{c_j} \delta C^{13}_j}{\Sigma m_{c_j}}
\]  

Equation (3b) can be written for the C\textsuperscript{14} activity of the dissolved carbonate.

\[
A_{sm}^{14} = \frac{\Sigma m_{c_j} A_{c_j}^0 e^{-\lambda t_j}}{\Sigma m_{c_j}}
\]

Implicit in equation (3b) is the most difficult problem which arises when using C\textsuperscript{14} in ground-water studies. This is the matter of mixed waters, and in particular, how to relate the apparent C\textsuperscript{14} age of a mixed water to the true average age of its component waters. Unfortunately, there is no general solution to problems of this sort even though mixed waters seem to be the rule rather than the exception. Water table aquifers are particularly likely to be affected by mixing phenomena, and it is probable that many of the difficulties that have been reported in trying to date water from such aquifers are due to mixing rather than to difficulties with correction procedures.
Normally only one source of carbonate dissolved in the water contains radiocarbon. In this case, equation (4) results.

\[
\frac{A_{\text{sample}}}{A_{\text{initial}}} \times \frac{\Xi m_{\text{c}}}{{m_c}_{\text{initial}}} = e^{-\lambda t} \tag{4}
\]

As we have seen, \(A_{\text{initial}}\) will be equal or close to 100% of modern, and the carbonate content, \(m_{\text{c initial}}\), will be that derived from the soil zone.

The expression used by many workers is:

\[
\frac{A_{\text{sample}}}{A^*} = e^{-\lambda t} \tag{5}
\]

where \(A^*\) is taken as some fraction of the modern standard \(A^*\), usually 70 to 90% which is equivalent to a range of 2000 C\(^{14}\) years (Münich, 1968). To avoid this large uncertainty, age differences between points in an aquifer have been used and are obtained from the expression:

\[
\frac{A_B}{A_A} = e^{-\lambda \Delta t} \tag{6}
\]

where \(A_B\) and \(A_A\) are the measured C\(^{14}\) activities of water at points B and A, and \(\Delta t\) is the C\(^{14}\) time difference between A and B. When expanded so as to be similar to equation (4), this becomes:

\[
\frac{A_B}{A_{\text{initial}}} \times \frac{\Xi m_{\text{cB}}}{m_{\text{c initial}}} \times \frac{A_{\text{initial}}}{A_A} \times \frac{\Xi m_{\text{cA}}}{m_{\text{c initial}}} = e^{-\lambda \Delta t} \tag{7}
\]

Those familiar with ground-water chemistry will raise two objections to assuming that equation (6) is equivalent to equation (7). The more serious objection is based on the fact
that the total dissolved carbonate content within an aquifer is generally not constant from place to place. Thus the ratio $\frac{C_{B}}{C_{A}}$ may not be equal to unity. In some cases, of course, simply assuming that this ratio is equal to one introduces no great error, but often we find it to be from 2 to greater than 5, which will introduce errors of from 5600 to greater than 13,000 $C^{14}$ years into the relative ages.

The second objection concerns those aquifers with recharge areas in which several climatic or vegetational regimes may be present or which have been subject to climatic changes in the time span of the water being sampled. In these situations, there is no assurance that $m_{c}$ is the same for all water samples. Extreme changes in $m_{c}$ could occur because of glacial activity near the recharge area, but areal variation of present climates may also be significant.

Figure 2 is an example of the sorts of large, apparently random errors that can appear in rates calculated using equation (6). The data used were taken from a study of the Carrizo sand in south-central Texas. This aquifer has been thoroughly studied by conventional hydrologic techniques, and good estimates of the hydrologic flow rates are available (Pearson and White, 1967). The portion of the aquifer studied has a relatively narrow, climatologically constant recharge area, and thus it seems reasonable to assume a constant value of $m_{c}$ prevails. We have calculated the rates of flow between various pairs of wells based, first, on a simple expression like equation (6) and, second, on an expression similar to equation (7) in which the total carbonate contents of the sampled wells are taken into account. No data other than the measured $C^{14}$ activities and the field-measured total carbonate contents of the wells sampled were used in making the plot in figure 2. It is evident that the rates calculated, taking into account the carbonate chemistry changes of the water, are more self-consistent.
FIGURE 2.-Comparison between flow rates of water in Carrizo sand, Texas, calculated from C$^{14}$ and conventional hydrologic data.
and more nearly represent the hydrologic velocities than do the rates calculated using the measured C\textsuperscript{14} activities alone.

Because it is rarely possible to determine the value for m\textsubscript{c,initial} unequivocally, indirect methods are necessary to find the ratio of total to initial carbonate content. In many aquifers, only two sources of dissolved carbonate are significant. One would be from the soil, and the other, from the mineral carbonate of the aquifer itself. An expression relating the δC\textsubscript{13} content of the two carbon sources to the ratio of the total to the initial carbonate content can be derived from equation (5a). This expression,

\[
\frac{\delta C_{13}^{\text{initial}} - \delta C_{13}^{\text{mineral}}}{\delta C_{13}^{j} - \delta C_{13}^{\text{mineral}}} = \frac{m_{c,j}}{m_{c,\text{initial}}}, \tag{8}
\]

is the equation for a hyperbola in which the parameters measured for each sample, m\textsubscript{c,j} and δC\textsubscript{13}\textsuperscript{j}, are the two variables, and the constant is m\textsubscript{c,initial} x (δC\textsubscript{13}\textsuperscript{initial} - δC\textsubscript{13}\textsuperscript{mineral}). The value of δC\textsubscript{13}\textsuperscript{mineral} for use in equation (8) is generally taken as 0 because rarely will carbonate in an aquifer be of other than marine origin. We have previously discussed reasonable values for δC\textsubscript{13}\textsuperscript{initial} and δC\textsubscript{13}\textsuperscript{initial} of the soil air CO\textsubscript{2} in the recharge zone and have noted that while a typical plant value of -25%o seems adequate in aquifers recharged in non-arid temperate climates, in arid or semi-arid regions, heavier values in the range of -16 to -18%o are perhaps more reasonable.

**Non-mineral sources:** A complication to the use of stable carbon isotopes for determining the proportion of dateable carbon in solution is the fact that sources of carbon other than limestone are commonly present in the aquifer and may add to the total dissolved carbonate content. During our investigations, we have seem the effects of two such sources activated by quite different
aquifer conditions but with about the same effect on the observed isotopic and total carbonate chemistry of the water.

One source comes from lenses or dispersed quantities of ancient plant debris, such as lignite or peat, contained as part of the aquifer framework. Plant material can be oxidized in various ways, such as by oxygen dissolved in the water, and so add to the total carbonate content of the water. Oxidation of plant material can be represented by:

\[
6nO_2 + (C_6H_{10}O_5)_n + nH_2O \rightarrow 6nHCO_3^- + 6nH^+ \quad (9)
\]

Additional carbonate from this reaction contains no C\textsuperscript{14} but has a δC\textsuperscript{13} value similar to that of the soil. This reaction is doubtless occurring in the Magothy aquifer (Figure 1). Although the δC\textsuperscript{13} of the dissolved bicarbonate away from the recharge area remains highly negative, the total carbonate content of the water increases considerably. A mass balance between the increase of carbonate and the loss of dissolved oxygen downgradient coupled with the low pH—as equation (6) suggests--confirms that lignite oxidation is occurring here.

Oxidation of organic material to carbonate species can also take place even if the conditions in the aquifer are strongly reducing. This state of affairs is represented by equation (10):

\[
SO_4^{2-} + CH_4 \rightarrow HS^- + HCO_3^- + H_2O \quad (10)
\]

which shows sulfate reduction coupled with hydrocarbon oxidation. This reaction is known to occur at certain places in the Texas Gulf coastal plain where high bicarbonate waters occur with such light δC\textsuperscript{13} values that they could only be derived from light hydrocarbon oxidation. Waters with anomalously light δC\textsuperscript{13} values and low C\textsuperscript{14} contents produced by oxidation of organic material and hydrocarbons have also been reported from Germany (Matthess and others, 1969).
It is also possible that gaseous CO₂ could be introduced into a water by migration from surrounding formations. The CO₂ could be that often found in thermal areas or that associated with natural gas or petroleum. Thermal CO₂ is likely to be relatively enriched in C¹³ and thus may not be as easily recognizable in solution as the light, plant-derived CO₂ from lignite or hydrocarbon oxidation. The regional geology of the area of interest and anomalous carbonate chemistry of the water should suggest whether migrating carbon dioxide is likely to be present.

Isotope exchange: In theory, exchange reactions between mineral and dissolved carbonate could so modify the isotopic composition of the latter that C¹⁴ work in ground-water systems would give no meaningful results. Because the possible effects of such exchange are well known and have recently been summarized (Hünnich, 1968), they need not be discussed here. Rather, we would point out how the results of our work agree with those of others in showing that in natural systems at low temperatures the effects of such exchange, if any, cannot be detected.

Massive exchange would cause the δC¹³ value of the dissolved carbonate to approach that of the aquifer carbonate minerals without a change in the total dissolved carbonate content. That is, in a ground-water system in which equation (8) should be valid, there would be an imbalance between the two sides of the equation which would increase regularly with flow time and distance. The results of the Texas study, referred to below, show no such imbalance even in waters with temperatures of greater than 65°C and with ages in excess of 30,000 years.

It is possible that exchange could lower the C¹⁴ content of the dissolved carbonate without detectably changing its δC¹³ value and so lead to falsely old ages and low flow rate values. We see no evidence of this process either, for both in Florida and Texas, C¹⁴ ages are in agreement with those predicted from excellent conventional hydrologic data.
Recent determinations of diffusion rates of carbon in carbonate minerals (Anderson, 1969) provide theoretical grounds for expecting minimum exchange. These results reinforce our conclusion from field studies that exchange is not generally a factor affecting the isotopic composition of carbonate in ground-water systems.

FIELD EXAMPLES OF THE USE OF ADJUSTMENT EQUATIONS

Florida limestone system: We have been studying the principal artesian aquifer of Florida as a complex hydrogeochemical system for the past eight years. A complete discussion of the geology, mineralogy, hydrology, and isotopic chemistry of the rocks and water is not needed here. However, for complete discussions of these topics, the interested reader is referred to Back and Hanshaw (in press) and Hanshaw, Back, and Deike (in press) and to the references listed in those two papers.

The area of principal recharge in the Floridan aquifer occupies a major portion of the west-central part of the state, an area of about 25,000 km$^2$. In such an area there are bound to be many different microclimates; for example, there are areas covered with sand dunes into which rainfall infiltrates rapidly as well as extensive areas of lakes and swamps with large quantities of organic dieback. There are also areas which can almost be characterized as semi-arid. Such a great variety of soil types gives rise to large variations in the carbonate content of the ground water. In the recharge area, it ranges from as low as 0.9 mM (millimoles) per liter to 4 mM per liter, while in the deeper, confined portion of the aquifer system, it varies from approximately 2 mM per liter to more than 6 mM per liter. Therefore it is not surprising that corrections made using equation (4) or (7) assuming a constant $m_{\text{initial}}$ are not successful here.
The $^{13}C$ adjustment equation (8), on the other hand, has proven successful in the Floridan aquifer system. Of the 72 wells chosen for carbon isotope analysis, 65 have $^{13}C$ contents of between -8.3 and 14.9°/oo, while the remaining 7 have $^{13}C$ contents more positive than -8.0°/oo. The wells with more positive $^{13}C$ values are either in areas of salt water encroachment or wells in which hydrogen sulfide is present and therefore perhaps have had additional carbonate added from hydrocarbon oxidation accompanying sulfate reduction. The average $^{13}C$ of the 65 wells is -10.8°/oo.

In general, the lighter $^{13}C$ values correspond to samples from wells in or near the recharge area and represent incomplete equilibrium between soil zone CO$_2$ and the aquifer carbonate. Chemical equilibrium studies (Back and Hanshaw, in press) show that in this area, the saturation of the water with respect to calcite, the dominant mineral in the aquifer, ranges between 60 and 110%. In the deeper, confined portion of the system, the $^{13}C$ values are generally somewhat heavier, and the calcite saturation of the water may achieve values as high as 160%; that is, the waters here may be as much as 60% supersaturated. This explains the slightly heavier than average $^{13}C$ values for these wells.

Although the total carbonate concentration varies throughout the aquifer, in what at first appearance seems to be an unsystematic manner, this variation turns out to be simply a function of local conditions in the recharge area. This is shown by the $^{13}C$ values. If the solution of calcite goes to 100% saturation according to equation (1), then the $^{13}C$ values will equal one-half of $^{13}C$ in the soil zone if the $^{13}C$ values of the material being dissolved are close to zero. If the waters are slightly undersaturated, the $^{13}C$ of the bicarbonate will be slightly lighter than that predicted by the above relationship, and if they are slightly supersaturated, the dissolved carbonate species will be somewhat heavier. Because supersaturation of
ground water with respect to calcite is common, sample $\delta^{13}$C values more positive than -12 or -10‰ are not unusual and should cause no disaview.

The theoretical relationship between percent calcite saturation and $\delta^{13}$C for various values of soil $\delta^{13}$C is shown in figure 3. Also shown are the measured percent calcite saturation and $\delta^{13}$C values of several Florida wells. Various other data on these wells are also given in table I. From these data, it is clear that no simple relationship between sample $\delta^{13}$C values and total dissolved carbonate contents exists—a result in keeping with the heterogeneity in the area of recharge to the system. However, the relationship between calcite saturation and $\delta^{13}$C (Figure 3) is close to the theoretical relationship, and so $\delta^{13}$C values are suitable for estimating the amount of C$^{14}$ dilution by limestone. By inspection of figure 3, it appears that -22‰ is an appropriate value of $\delta^{13}$C initial to use in the correction equation (8).

The wells shown in table I were also analyzed for their tritium content. The first three wells on the table are from the principal recharge area, and all contain thermonuclear tritium. Weeki Wachee No. 11 had 103 TU in 1966; the average tritium content in rainfall in central Florida that year was 114 TU, although in the years immediately preceding, it had been somewhat higher. The Lecanto wells also contained measurable tritium and are located somewhat downgradient from Weeki Wachee No. 11. The water from all three wells is clearly a mixture of fairly recent and somewhat older water, with the amount of recent water greatest in the Weeki Wachee well. The remaining three wells are farther downgradient in the confined portion of the aquifer and contain essentially no tritium.

Using the data in table I, two sets of adjusted C$^{14}$ ages have been calculated for these wells. The first set was made using equation (5) and a value for $A^\alpha_0=50$% of modern. These
FIGURE 3.--Relationship between \( \delta^{13}C \) values and percent calcite saturation of wells in the Floridan aquifer.
TABLE 1:—Comparison between two age adjustment methods

<table>
<thead>
<tr>
<th>Location</th>
<th>( A_{\text{meas.}} ) (% Mdn)</th>
<th>( \text{C}^{14} ) age (years)</th>
<th>( \delta^{13} \text{C} ) (PDB) (%)</th>
<th>( \Sigma \text{C} ) (mM/l)</th>
<th>Calcite saturation (%)</th>
<th>Adjusted age 1 (years)</th>
<th>Adjusted age 2 (years)</th>
<th>Tritium (TU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weeki</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wachee #11</td>
<td>62.4</td>
<td>3,790</td>
<td>-13.7</td>
<td>1.74</td>
<td>62</td>
<td>125%</td>
<td>90</td>
<td>103*10</td>
</tr>
<tr>
<td>Lecanto #5</td>
<td>50.0</td>
<td>5,570</td>
<td>-11.5</td>
<td>1.57</td>
<td>85</td>
<td>100%</td>
<td>510</td>
<td>36*4</td>
</tr>
<tr>
<td>Lecanto #6</td>
<td>51.1</td>
<td>5,390</td>
<td>-11.8</td>
<td>1.48</td>
<td>74</td>
<td>102%</td>
<td>540</td>
<td>15*2</td>
</tr>
<tr>
<td>Frostproof</td>
<td>6.7</td>
<td>21,800</td>
<td>-9.2</td>
<td>3.02</td>
<td>103</td>
<td>16,100</td>
<td>14,980</td>
<td>0*1</td>
</tr>
<tr>
<td>Holopaw</td>
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<td>23,780</td>
<td>-9.6</td>
<td>4.06</td>
<td>132</td>
<td>18,200</td>
<td>17,300</td>
<td>1*1</td>
</tr>
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<td>Arcadia</td>
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<td>28,300</td>
<td>-8.3</td>
<td>3.38</td>
<td>148</td>
<td>22,600</td>
<td>20,600</td>
<td>0*1</td>
</tr>
</tbody>
</table>

Adjusted age 1 calculated from \( \frac{A_{\text{meas.}}}{0.50} = e^{-\lambda t} \)

Adjusted age 2 calculated from \( \frac{A_{\text{meas.}}}{1} x \frac{(-22)}{(\delta^{13} \text{C} + 0.5)} = e^{-\lambda t} \)
adjusted ages are in harmony with the tritium results and with the hydrology of the region, but to get this agreement, it was necessary to use a value for \( A^* \) of 50\%, which is outside the range normally used in this adjustment equation. The second column of adjusted ages was calculated using a combination of expressions (4) and (8). $\delta C^{13}$ values of -22 and +0.5\%/oo were used for the initial carbonate and the mineral carbonate in the aquifer, respectively; the former was taken from figure 3, and the latter is the measured $\delta C^{13}$ value of the aquifer material. These ages also are in agreement with the tritium results and with the regional hydrology. However, to calculate them required no unusual assumptions, whereas to produce a good agreement using the first calculation method, the assumption of a rather unusual value for $A^*$ was needed.

**Carrizo sand, Texas:** Although much of the work on the Carrizo sand has already been reported (Pearson and White, 1967), the chemistry of the system has some interesting features which are worth recalling here. Unlike the Floridan aquifer, the recharge area to the portion of the Carrizo sand studied is quite narrow and climatically homogeneous. Thus both the stable carbon isotope ratios and the total initial carbonate content in the soil zone should be constant from place to place, and if the only source of carbonate in the formation is carbonate minerals, all wells should fall on a line defined by equation (8). A plot of this sort of the Carrizo data is shown in figure 4. Rough boundaries of various water types are also shown on this figure. Waters in the lower right are of the calcium bicarbonate type; that is, waters in which the predominant cation, in chemical equivalents, is calcium and the predominant anion is bicarbonate. These are similar to the Floridan waters in that the primary change taking place in them as they move downdip is the solution of mineral carbonate. Waters in the next zone with $\delta C^{13}$ values ranging from about -9 to about -12\%/oo are either
Figure 4: Relationship between $\delta C^{13}$ values and total dissolved carbonate contents of wells in Carrizo sand, Texas.
oversaturated with calcium carbonate or are those in which a sodium or calcium exchange with clay minerals has occurred. When this exchange takes place, calcium is removed from the solution, and thus a great deal more carbonate can dissolve without the solution reaching saturation or great supersaturation with respect to calcite. Continuing sodium for calcium exchange produces the high bicarbonate waters in the upper portion of the diagram and, if no other reactions are occurring, produces waters which continue to follow the theoretical line drawn. Of the samples of this water type shown in figure 4, only one is a result of natural softening alone.

The δC¹³ values of the other four wells are much too light to have been derived solely from marine carbonate. The source of carbonate in these wells clearly must be one of the non-mineral sources previously mentioned, such as CO₂ produced by oxidation of organic or petroliferous material within the formation. Addition of plant CO₂ by lignite oxidation would permit solution of equal molar quantities of mineral carbonate in the formation and thus would increase the total carbonate content in solution while maintaining the δC¹³ value at about -10 to -12‰. Three of the samples seemed to fit this scheme, while that of the fourth is rather light. In this sample either lignite could be producing CO₂ faster than equivalent quantities of carbonate are being dissolved, in which case it represents a calcite-undersaturated water, or the CO₂ introduced could have a lighter C¹³ content due perhaps to oxidation of light hydrocarbons rather than of lignite. Whatever the source of down-dip carbonate in these waters, it is clear that the initial dateable carbon content of all of them is essentially the same. Thus C¹⁴ ages calculated using equation (4) should truly reflect the water age as indeed we have found them to do.
CONCLUSIONS

$^{14}C$-bearing carbonate dissolved in ground water has its source in the soil zone of the recharge area. Within the ground-water system, $^{14}C$ is lost by radioactive decay and may also be diluted by solution of $^{14}C$-free carbonate from various sources in the aquifer but apparently is not affected by isotope exchange. In systems in which no significant mixing of waters of different histories occurs, total dissolved carbonate contents and $^{6}C^{13}$ values can be used to estimate the amounts and generally to identify the sources of the diluting carbonate. These estimates can be used to adjust measured $^{14}C$ values to give proper ground-water ages and flow rates. $^{14}C$ values so adjusted are generally more self-consistent and in better agreement with hydrologic data than those adjusted using methods that do not explicitly take into account changes of chemistry within the ground-water system.
REFERENCES


