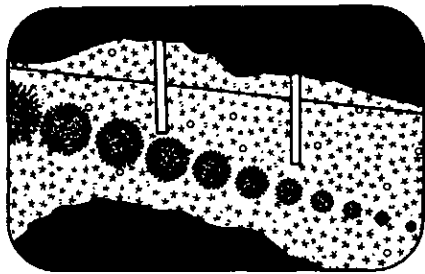


# Articles



## Comments on Carbon-14 Dating of Groundwaters in Crystalline Environments

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### Introduction

There are two principle aspects to all groundwater dating: a) the definition of the age of a water and b) its significance in terms of groundwater flow.

The complexities associated with the first are well recognized and this short note is an attempt to summarize some basic problems of water age determinations based on carbon-14, with special emphasis on water in crystalline environments.

Equally important, however, is the second aspect where the chemical and isotopic geochemistry of a groundwater must be integrated with the hydrology of the flow system. This is often difficult and, for example, becomes the dominant problem if such data are used for the evaluation of potential subsurface disposal sites

suitable for long term containment of toxic materials such as wastes from the nuclear fuel cycle. It has been stated that sites at which young groundwaters are identified should not be considered as potential repositories and that it would be imperative to find localities where old flow systems can be recognized. There is some danger in such reasoning since it neglects to recognize that any *water age reflects the past but not the future*: old water could be discharging to the biosphere in a matter of years whereas very young water might be at the beginning of thousands of years of subsurface history. Therefore, any site evaluation has to include an interpretation of age data in the context of the regional hydrogeology. It cannot be limited to local studies or sampling from isolated wells.

Carbon-14 dating of groundwaters was first introduced about 20 years ago by Münnich (1957) and Brinkmann *et al.* (1959). Since then the reliability of  $^{14}\text{C}$  ages of water samples has been repeatedly questioned, confirmed and denied in a great number of publications. The controversy does not come from the analytical end (although conventional techniques require large samples and great care in handling) but stems from the fact that it is extremely difficult to unravel the geochemical processes which have exerted control on the carbonate geochemical evolution of a groundwater. This is of paramount importance in adjusting raw  $^{14}\text{C}$  ages of groundwater since its aqueous carbon can have several sources, some of which will "contaminate" the original carbon-14 contents. Correction procedures can be proposed, however, if it is possible to characterize and quantify the geochemical processes which have affected the carbon geochemistry of a groundwater.

There are two basic approaches which are taken in the attempt to solve these problems and to "correct" apparent carbon-14 water ages: "the black box models" and the "process oriented models". Each has its merits, and their specific application is usually dependent on the type and quantity of information available.

### Black Box Models

"Black box models" do not attempt to understand the processes which control the geochemical evolution of a groundwater. They assume, that after the initial carbon uptake in the soil zone by infiltrating water, a certain  $^{14}\text{C}$  dilution will occur in the saturated or even in the unsaturated zone through the addition of carbon-14 free carbonate. Thereafter only decay will reduce the  $^{14}\text{C}$  activity of the dissolved aqueous carbon.

In their crudest form, the "black box models" result in the acceptance of an "average" initial value for the  $^{14}\text{C}$  activity of the aqueous carbonate whereby this "initial" value represents the fraction of  $^{14}\text{C}$  after secondary carbon additions. The source of this carbon is not specified. Vogel (1970) found that this "initial  $^{14}\text{C}$  content" of groundwater was  $85 \pm 5$  per cent of the  $^{14}\text{C}$  activity of atmospheric  $\text{CO}_2$  in young waters from both humid and arid climatic regions. He concludes that  $^{14}\text{C}$  ages are probably no more than 20 to 30 per cent too high even under unfavourable conditions. Subsequent analyses of many older groundwaters did not entirely confirm Vogel's observation.

A refined version of this black box approach is the "exponential model" introduced by Erikson (1962) and expanded by Geyh (1972). Again, the efforts concentrate on the definition of the "initial"  $^{14}\text{C}$  activity by assuming that any given water mass is a mixture

of recharge from different years. The model permits the mixing of older water with a given proportion of new recharge and allows for decay between recharge periods for each older component. Two basic carbon sources are assumed, soil-CO<sub>2</sub>, which provides the modern carbon component and limestone carbon which is added later and dilutes the original carbon-14 concentrations. This then is the "initial" value used for <sup>14</sup>C dating. Usually, tritium data are used to quantify the addition of the secondary carbon, and, therefore this approach is suitable for young flow systems, (e.g., in Karst). It is possible with this method to evaluate very accurately the "initial" <sup>14</sup>C activity of such a system. It has to be remembered, however, that this "initial" value includes secondary carbonate additions and usually assumes that no further addition or subtraction of carbon can take place. With this assumption these values could be used in other, older flow systems where any further decline in <sup>14</sup>C activity would be attributed to decay and is thus a function of age only.

The decrease in <sup>14</sup>C activity through geochemical reactions can be expressed by a q factor in the decay equation:

$$A_m = qA_0 \exp -\lambda t \quad (1)$$

where  $A_m$  = measured <sup>14</sup>C activity of sample

q = the correction factor which quantifies the <sup>14</sup>C dilution

$A_0$  = is the atmospheric <sup>14</sup>C value at the time of recharge

$A_0 \times q$  = "initial activity"

$\lambda$  = decay constant ( $-\ln 2/t_{1/2}$ )

t = water age

Geyh (1972) summarizes his findings based on exponential model calculations in a number of "characteristic" q-values:

0.65 – 0.75 for Karst systems

0.75 – 0.90 for sediments with fine crystalline carbonate such as loess and 0.90 – 1.00 for crystalline rocks.

The lower q-values emphasize the importance of carbonate reactions in aquifers with abundant carbonate whereas in crystalline rocks with little carbonate, q-values close to 1 are measured.

As indicated above this approach is certainly of value for young waters but

is very problematic if it is applied to older systems. Geochemical reactions are continuously occurring in groundwater and do not stop at any given time. Within a given type of aquifer the actual <sup>14</sup>C dilutions might be much larger (and thus the q-factors smaller) in older systems than in young ones. Thus the q-values determined by Geyh (1972) may reflect more than anything else reaction rates with respect to carbonate dissolution. Water in crystalline rocks may simply take longer to reach equilibrium conditions. Therefore, it would be very instructive to see how many of the samples collected from crystalline rocks and used for these statistics actually reached calcite saturation.

Few groundwater studies have been done in crystalline rocks and little is known about the isotope geochemistry of water in such environments. However, even in crystalline rocks carbonate minerals are not uncommon and occur widespread as fracture coatings. Therefore, one may expect to find in many crystalline "aquifers" q-factors much lower than those quoted above

The results of two studies lend support to this claim: within a joint project between Swedish authorities and the Lawrence Berkeley Laboratory at the University of California a number of <sup>14</sup>C analyses were done on groundwaters encountered in a granitic pluton at Stripa, Sweden (Fritz *et al.*, 1979a). Two samples collected at relatively shallow depth had tritium contents of  $6.8 \pm 1T.U.$  and  $100 \pm 10T.U.$  (Tritium unit = <sup>3</sup>H/10<sup>18</sup> <sup>1</sup>H) with <sup>14</sup>C contents of 53.8 pmC and 89.3 pmC (pmC = per cent modern carbon and referring to the <sup>14</sup>C activity of wood grown during 1950 in a nonpolluted environment) respectively. <sup>14</sup>C decay can thus be neglected. The low tritium levels of the first sample indicates recharge before the main atomic bomb testing period where <sup>14</sup>C in atmospheric CO<sub>2</sub> was still at or only slightly above 100 pmC. Thus the q-factor in this first sample would be between 0.5 and 0.6. In the second case, the atmospheric <sup>14</sup>C-levels must have been much higher, probably between 120 and 130 pmC. The q-factor in this case would be between 0.65 and 0.75.

The second study focussed on shallow groundwaters in the overburden on the Canadian Shield at Chalk River

(Fritz *et al.*, 1978). Such environments could represent the recharge areas for groundwaters in deeper systems within the crystalline rocks and are typically composed of glacial deposits with very little carbonate. Despite this, the geochemical evolution of these groundwaters at Chalk River show that carbonate dissolution is important and a continuous decrease in <sup>14</sup>C activities with depth (i.e., age) is observed. Because tritium occurs throughout the system <sup>14</sup>C decay can again be neglected and geochemical dilutions must account for the observation. The calculated q-factors are close to 0.5 and could even be lower in deeper parts not yet investigated.

Pearson (1965) and Pearson and Hanshaw (1970) attempted to solve the problems associated with the use of such arbitrary "umbrella factors" by introducing a "correction" based on variations in <sup>13</sup>C abundances: Any process that adds, removes or exchanges carbon from the aqueous carbonate reservoir of a groundwater and which thereby alters the <sup>14</sup>C content will also affect the <sup>13</sup>C concentrations. The q-factor was here obtained from a carbon-mass balance where

$$\delta^{13}C_{DIC} = x \delta^{13}C_{soil} + (1 - x) \delta^{13}C_{carb} \quad (2)$$

The basic assumption here is that a certain amount (x) of soil CO<sub>2</sub> with a  $\delta^{13}C_{soil}$  is initially taken up by the water and subsequently carbonate from a second source is added. It is usually assumed that the second source is carbonate minerals (1-x, and  $\delta^{13}C_{carb}$ ) which react with carbonic acid to produce the observed  $\delta^{13}C_{DIC}$  (DIC is Dissolved Inorganic Carbon and corresponds to the sum of all aqueous, inorganic carbonate species). It is implicitly assumed that the addition of the second carbon source occurs in the absence of a soil gas phase, i.e., under closed system conditions. The soil-CO<sub>2</sub> fraction represents the "initial" carbonate content of the water and since q is defined as:

$$q = \text{initial carbonate content} / \text{final carbonate content} = x/x + (1-x) = x \quad (3)$$

(expressing the fact that the difference between initial and final carbonate contents corresponds to the dead carbon contributions)

Combining equations 2 and 3 one obtains

$$q = \frac{\delta^{13}\text{C}_{\text{DIC}} - \delta^{13}\text{C}_{\text{carb}}/\delta^{13}\text{C}_{\text{soil}} - \delta^{13}\text{C}_{\text{carb}}}{\delta^{13}\text{C}_{\text{carb}}} \quad (4)$$

As already mentioned, this equation does not have to specify what carbon is added nor the type of the reaction which must occur. In other words, it is possible that not only carbonate minerals may have dissolved under closed system conditions but that other carbonate sources such as biogenic  $\text{CO}_2$  input may have contributed to the total carbonate budget as well. It is necessary, however, to specify the isotopic composition of this source (or mixture of sources).

The above equation is only correct if the soil- $\text{CO}_2$  is taken up by the water without significant fractionation effects. This is the case in low pH environment where minor isotope fractionation effects occur during the transition from  $\text{CO}_2$  gas to carbonic acid (i.e.,  $\text{CO}_2 + \text{aq} + \text{H}_2\text{CO}_3$ ) whereby the aqueous phase becomes depleted in  $^{13}\text{C}$  by about 0.8 ‰ at usual soil temperatures. At higher pH values in the open system the initial aqueous carbonate in equilibrium with the soil- $\text{CO}_2$  will have much higher  $\delta^{13}\text{C}$  values since then bicarbonate and/or carbonate ions become important and their  $^{13}\text{C}$  enrichment w.r.t. the original soil- $\text{CO}_2$  varies between about 7 and 10 ‰ depending on temperature (see below). The  $\delta^{13}\text{C}_{\text{carb}}$  has to be replaced by a  $\delta^{13}\text{C}_{\text{initial}}$  for which

$$\delta^{13}\text{C}_{\text{initial}} = \sum N_j (\delta^{13}\text{C}_{\text{carb},j} + \epsilon_j) \quad (5)$$

where  $N_j$  is the mole fraction of the carbonate species  $j$  and  $(\delta^{13}\text{C}_{\text{carb},j} + \epsilon_j)$  its  $\delta^{13}\text{C}$  value is calculated from  $\delta^{13}\text{C}_{\text{carb}}$  and the isotope enrichment factor between the  $\delta^{13}\text{C}_{\text{carb}}$  and the species  $j$ .  $N_j$  is dependent on pH and temperature and  $\epsilon_j$  only on temperature.

The significance of this effect can be demonstrated with the following example: assume that a water sample with  $\delta^{13}\text{C} = -10$  ‰ and a  $^{14}\text{C}$  activity of 30 pmC (The  $^{13}\text{C}$  contents of natural materials are usually expressed in ‰ values and represent the difference in ‰ from the PDB standard) has been collected. The soil- $\text{CO}_2$  in the recharge area had a  $\delta^{13}\text{C} = -22$  ‰ and the carbonate dissolving under closed system conditions had  $\delta^{13}\text{C} = 0$  ‰ (a

value typical for marine carbonates). If this water had a pH = 4 under open system conditions (during  $\text{CO}_2$  uptake but before carbonate dissolution) then the "corrected" age would be 3140 y B.P. had it, however, a pH = 7 then it would have a "corrected" age of 6440 y B.P.

For most crystalline regions in northern environments, it is reasonable to assume that the low pH conditions in the soils are fulfilled since moss covers and other plant growth will generate high  $\text{pCO}_2$  - low pH systems. The  $\delta^{13}\text{C}$  values of the soil- $\text{CO}_2$  are also fairly well known and will vary between about -20 and -25 ‰. In Northern Canada measured values lie between -21 and -23 ‰. Critical, however, is the composition of the secondary carbon source(s). If the overburden (in Canada generally glacial deposits) contains marine carbonates then values close to 0 ‰ can be anticipated. However, if fracture coatings on the bedrock are dissolved a wide variety of  $\delta^{13}\text{C}$  values appear possible: a few samples collected from fractures on granitic rocks in northern Canada vary between -6 and -9 ‰ and in the Stripa granite fracture calcites with  $\delta^{13}\text{C}$ 's between -15 and +15 ‰ have been found (Fritz *et al.*, 1978, 1979a).

The importance of the knowledge of these values is emphasized in Figure 1 which is a plot of "corrected" ages for a given  $^{13}\text{C}$  and  $^{14}\text{C}$  composition of water sample but assuming variable  $^{13}\text{C}$  contents for the secondary carbon source (e.g., rock carbonate). Note, that with an appropriate choice of  $\delta^{13}\text{C}$  values for this secondary carbon source most measured ages can be reduced to "modern" or "zero-age". Since no reactions are specified, constraints would have to be imposed from geochemical considerations.

Other simplified assumptions regarding the amount of dead carbon added to a groundwater can be derived from a comparison of initial vs. final total carbonate contents (Pearson and Hanshaw, 1970). The  $q$ -factor is then defined as

$$q = \text{initial DIC}/\text{final DIC} \quad (6)$$

where the initial DIC describes the carbonate content of a groundwater before dead carbon additions in closed

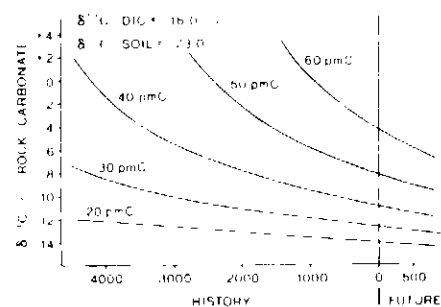
system conditions and the final DIC is the measured carbonate content of the sample. If flow between two points A and B within an aquifer is considered then the initial DIC would correspond to the DIC at point A and the age difference ( $\Delta t$ ) between the two points is

$$A_B = A_A \cdot \text{DIC}_B/\text{DIC}_A \cdot e^{-\lambda \Delta t} \quad (7)$$

These models do not permit the precipitation of calcite or incongruent dissolution of dolomite (Smith *et al.*, 1975; Wigley, 1978) nor can exchange between aqueous carbonate and carbonate minerals of the aquifer (Thilo and Münnich, 1970) be accounted for. They thus permit at best rough estimates of possible  $^{14}\text{C}$  dilutions and more refined approaches are needed for many aquifer systems. This applies also to crystalline environments and is discussed below in more detail.

### Process Oriented Models

The correction models described above consider both  $\delta^{13}\text{C}$  and chemistry of the groundwater and, therefore, are neither pure "black box" models nor are they fully developed "process oriented" models. If, however, some geochemical information is available this approach can be expanded and is then particularly well suited for model calculations. For example, chemical data can be treated with the U.S.G.S. WATEQ programme and thus the correct partitioning of different aqueous carbonate species can be determined. A variety of  $q$ -factors can then be calculated from a matrix of assumed



**Figure 1**

The dissolution of carbonate minerals under closed system conditions influences the carbon isotopic composition of the dissolved inorganic carbon. This figure shows that an appropriate choice of rock carbonate values is necessary in order to define "corrected"  $^{14}\text{C}$  ages from measured carbon-14 activities.

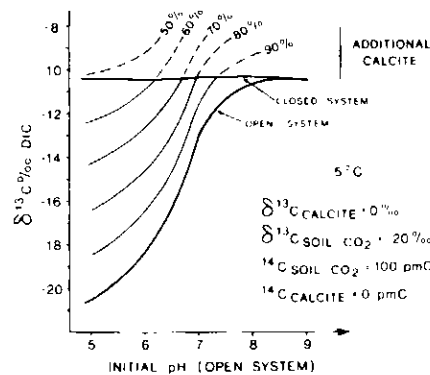
input conditions (in which recharge pH and the pCO<sub>2</sub> of the soil atmosphere are the variables) and comparisons with the measured carbonate concentrations of the ground water. With these, "corrected" <sup>14</sup>C ages can be determined. Parallel to it the δ<sup>13</sup>C of the water is calculated for each computed age, based on the assumed δ<sup>13</sup>C values for rock-carbonate and soil-CO<sub>2</sub>. A match between the calculated and measured δ<sup>13</sup>C -DIC values corresponds to a potential evolutionary path and represents an isotopically consistent age determination for the water. Similar calculations are possible using a chemical mass balance based on Ca and Mg as indicators for the amount of mineral carbonate dissolved and ½(Na<sup>+</sup> - Cl<sup>-</sup>) as a measure of exchanged Ca-ions on Na-clays, provided the geochemistry of the groundwaters permits discussions on the origin and geochemical history of these ions.

Process oriented models thus attempt to integrate the geochemical reactions which have occurred in a groundwater system with the evolution of the carbon contents in it. In addition these models are not limited to a description of the environmental conditions existing during carbonate dissolution but can also include subsequent isotope exchange with gas and/or solid phases (Thilo and Münnich, 1970) as well as carbonate removal through secondary calcite precipitation (Smith *et al.*, 1975; Wigley, 1978). The terms "open" and "closed" system are thereby frequently used and merit some explanation.

Assume precipitation infiltrates through a soil horizon and migrates through the unsaturated zone towards the water table. This water will dissolve soil-CO<sub>2</sub>, until isotopic equilibrium between the soil-gas and the aqueous carbonate species is reached. The latter will be composed of CO<sub>2</sub>, H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>=</sup> and any bicarbonate or carbonate ion pairs or complexes that may be of importance. The relative abundance of these species will depend on the pH and total chemistry of the water - which may or may not be controlled by the carbonate dissolution reactions alone. Such a system which is open to exchange with the soil-gas is usually called "open" and the δ<sup>13</sup>C of the aqueous carbonate (DIC) will depend on the pH of the water and the temperature dependent carbon

isotope fractionation factors between soil-CO<sub>2</sub> and the different aqueous carbonate species (eqn.5). Figure 2 depicts the predicted δ<sup>13</sup>C-DIC for an open system neglecting ion pairs and complexes for which fractionation factors are at present unknown. It also shows that the <sup>14</sup>C-activity of such waters is always very close to the soil-CO<sub>2</sub> and thus to atmospheric <sup>14</sup>C activities (q ≈ 1). One also should note that carbonate minerals can be dissolved under open system conditions and that even calcite saturation may be achieved. This would have little or no influence on the <sup>13</sup>C or <sup>14</sup>C content of the aqueous carbonate which still would remain in isotopic equilibrium with the soil-CO<sub>2</sub>, regardless of whether these carbonates carry <sup>14</sup>C or not (Reardon *et al.*, in prep).

The same applies if such calcite-saturated water were moved into the subsurface (where the pH could change through non-carbonate reactions), since as long as the aqueous carbonate reservoir in the groundwater remains intact, <sup>14</sup>C decay will be the only mechanism to remove it from the water. The situation is different if water not saturated with respect to carbonate minerals is moved from the open system into closed system conditions.

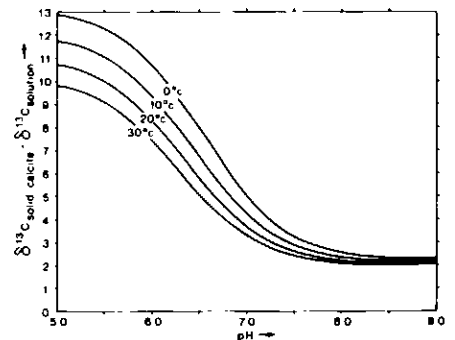


**Figure 2**

The effects of the CO<sub>2</sub>-DIC equilibria on δ<sup>13</sup>C at various pH values is shown (open system). If such water dissolves rock carbonate under closed system conditions the δ<sup>13</sup>C and carbon-14 contents are affected. The "closed system" line represent the δ<sup>13</sup>C values achieved after all carbonic acid present in an initial water with variable initial pH values has been used for carbonate mineral dissolution. If additional proton donors are available the <sup>14</sup>C dilutions caused by calcite dissolution can exceed those of a pure H<sub>2</sub>CO<sub>3</sub>-calcite system.

Then dissolution of carbonate minerals could substantially change both <sup>14</sup>C and <sup>13</sup>C compositions in the absence of an open system CO<sub>2</sub>-gas reservoir. Assuming a pure carbonate system it is possible to evaluate for a given initial (open system) pH value a final δ<sup>13</sup>C composition provided the δ<sup>13</sup>C's of the soil-CO<sub>2</sub> and mineral carbonates are known. This is also shown in Figure 3, along with the effects of such closed system reactions on the <sup>14</sup>C-activity of the water. It turns out that if recharge occurs at low pH and if all carbonic acid formed is used for the dissolution of carbonate minerals (top line in fig. 2) then the maximum <sup>14</sup>C dilution if 50% (q = 0.5) which corresponds to a maximum correction of the measured <sup>14</sup>C ages by one half life (5730 y).

Data accumulated in numerous studies show, however, that in many groundwaters considerably greater dilutions occur. Processes responsible for this may be carbonate dissolution where proton donors other than carbonic acid are active, isotopic exchange with carbonate minerals (less likely in crystalline rocks but especially important in aquifers with fine grained carbonates such as the chalk, Smith *et al.*, 1975; Wigley, 1978), addition of bacterial CO<sub>2</sub> (Barker *et al.*, 1978) or carbon originating from the oxidation of organic matter (Winograd and Farlekas, 1974), precipitation of carbonate minerals (Smith *et al.*, 1975; Wigley, 1978) and addition of volcanic CO<sub>2</sub> (Fritz *et al.*, 1979b). There may be other reactions and in any system where



**Figure 3**

Carbon isotope fractionation effects between solid calcite precipitated from a solution with given δ<sup>13</sup>C. The effects increase with decreasing pH because of the increasing importance of H<sub>2</sub>CO<sub>3</sub> which has less <sup>13</sup>C than HCO<sub>3</sub><sup>-</sup> or CO<sub>3</sub><sup>=</sup>. (after Wigley *et al.* 1978; Barker, in prep).

such processes are suspected, detailed geochemical and hydrologic investigations are required. Emphasis has to be placed on the description of the geochemical evolution of the groundwaters especially as it affects the carbonate equilibria. Thus, it has to be emphasized again that a meaningful  $^{14}\text{C}$ -age cannot be obtained from analysis of a single well within a groundwater system. Rather, the isotope geochemistry programme has to be integrated with studies in regional hydrology and geochemistry.

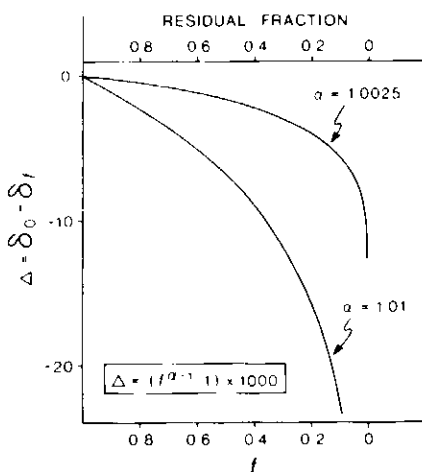
Fortunately, in general, no more than a few interferences come together in one flow system and an assessment of the geologic situation will permit the exclusion of certain processes. In crystalline environments several reactions may be important: a) the dissolution of calcites which can be totally or partially independent of the presence of carbonic acid, b) the precipitation of calcite (as evidenced by the common carbonate coatings on fracture surfaces) and c) biogenic  $\text{CO}_2$  production which might locally be important.

If calcite dissolution occurs under closed system conditions then it can be corrected for through matrix calculations based on chemical and isotopic mass-balances if the carbonate contents and pH of the water, the carbon isotopic composition, the dissolving minerals and the  $\delta^{13}\text{C}$  soil are known (Reardon and Fritz, 1978; Fontes and Garnier, 1978). The  $\delta^{13}\text{C}$ -carbonate content correction (eqn. 4) outlined above will suffice to assess the dead carbon contributions if recharge occurred in a low pH environment and calcite dissolution proceeded only under closed system conditions.

The precipitation of calcites from groundwaters is usually discussed only in the context of the incongruent dissolution of dolomites, i.e., a situation where precipitation and dissolution occur simultaneously. Because of the absence of dolomite this is not possible in crystalline environments. However, geochemical data obtained from the Stripa groundwaters indicates that precipitation of calcite does occur in these systems. There the total dissolved inorganic carbon content decreases from about  $10^{-3}$  moles/l in the shallow groundwaters to about  $10^{-4}$  moles/l in the deepest waters. Calcite saturation is maintained be-

cause the pH rises continuously and at depth reaches values above 9.5. This simple removal of carbonate from solution causes some isotope fractionation whereby the residual aqueous carbon will be depleted in heavy isotopes. The change in isotopic composition will follow a Rayleigh distillation model where the isotope effects will depend on the pH of the water at which this precipitation occurs. These fractionation effects are shown in Figure 3 and are close to 2.5‰ for waters whose pH is greater than 7.5 but may exceed 10‰ at lower pH-values. Figure 4 shows that the effects of this removal on the residual carbonate are small if less than 50 per cent of the original carbon are removed but may become significant thereafter. The  $^{13}\text{C}$  data would thereby be much more sensitive and little effect on the  $^{14}\text{C}$  would be expected because a 10‰ shift in  $\delta^{13}\text{C}$  would correspond to only two per cent shift in  $^{14}\text{C}$ .

Studies in Northern Canada have shown that methane producing bacteria are not uncommon and that "contamination" of groundwaters with biogenic  $\text{CO}_2$  can be expected where they are active (Barker, in prep.). Such contributions are immediately reflected in the  $^{13}\text{C}$  contents, and  $\delta^{13}\text{C}$  values as high as +16‰ have been measured



**Figure 4**

This figure shows the carbon isotope effects as they can occur during precipitation of calcite from a finite carbon reservoir (DIC).  $\delta$  is the  $^{13}\text{C}$  factor between aqueous and solid carbonate. At  $\text{pH} \approx 8$  this value is close to = 1.0025 but increases rapidly at lower pH values to a maximum of close to = 1.01. "f" is the residual fraction of aqueous carbonate.

at pH greater than 8. If such water precipitated calcite similar high  $\delta^{13}\text{C}$  values would be noticeable in the precipitates. Such is the case for some fracture calcites in the Stripa granite and  $\delta^{13}\text{C}$  values close to +15‰ have been measured (Fritz *et al.*, 1978a). The effects of biogenic carbonate on the  $^{14}\text{C}$  content will depend on the food source and in crystalline environments this should be either organic or inorganic carbon in the groundwater because the aquifer rocks do not contain organic matter. If organic carbon were decomposed, it would have approximately the age of the groundwater, whereas the inorganic carbon would have a mixed origin. Therefore, in the latter case no additional  $^{14}\text{C}$  contamination takes place, whereas the biogenic  $\text{CO}_2$  would partially reset the  $^{14}\text{C}$  clock, i.e., increase the  $^{14}\text{C}$  of the aqueous carbonate in the water. No  $^{14}\text{C}$  data are yet available on methane contaminated systems but work is in progress and corrections can be proposed for systems in which a quantification of these processes is possible (Barker *et al.*, 1978). This has to be done by studying the geochemical evolution of a groundwater body whereas the correction procedures are essentially mass balance considerations.

## Conclusions

Carbon-14 dating of groundwaters is not a tool that can be used with ease unless one can demonstrate that the geochemical evolution of a groundwater follows simple processes whose influence on the carbon budget can be assessed. An integration of carbon isotope investigations with geochemical and hydrogeological studies is not only recommended but usually necessary.

In the foregoing an attempt was made to summarize the geochemical interferences which may influence the carbon geochemistry and thus the  $^{14}\text{C}$  budget of groundwaters in crystalline environments. It is evident that no simple correction formula can be proposed and it is impossible to provide an unique solution. For example, it was demonstrated that the choice of the carbon-13 contents of carbonate minerals dissolving in the subsurface can reduce many measured ages to modern values.

In order to carry any discussion beyond a general level will require very detailed geochemical data, i.e., a knowledge of the nature of geochemical reactions and associated mass-transfers are a prerequisite for a comprehensive evaluation of the possible magnitude of  $^{14}\text{C}$  dilutions. Wigley *et al.* (1978) summarized this and showed that the latter can vary over a very wide range.

To apply such considerations however, it is necessary to know a priori which processes are dominant in the system under consideration. This is usually not the case and simplified model considerations will have to be used to eliminate those reactions which are impossible or unlikely. This task is facilitated in crystalline rocks because – on the basis of the data available to us – one can show that the most complicating process, namely the incongruent dissolution of dolomite and/or magnesium calcites, is of little importance. This, however, does not eliminate the need for detailed investigations relating to the geochemical evolution of a groundwater before acceptable model consideration will provide us with appropriate  $^{14}\text{C}$  corrections.

Finally it has to be emphasized again, that environmental isotope studies on waters from crystalline environments can only help to elucidate the hydrology and geochemistry of flow systems. They may be a key element in the assessment of groundwater flows and water ages but the final analyses should include investigations of the regional hydrogeology utilizing the tools of classical hydrology and mathematical modelling.

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MS received October 27, 1978