

Fig. 8-2. Stable isotope signature of various paleogroundwaters from the Middle East and North Africa. Continental Intercalaire — Gouffanti et al., 1974; Kufra and Sirta Basins — Edmunds and Wright, 1979; Sennag et al., 1979; Nagev — Gat and Dargatzoulis, 1972; Dali Sandstone — Lloyd, 1980; Umm er Radhuma, Saudi Arabia — Moser et al., 1978; Wadi Dawash — Hotzi et al., 1980; Umm er Radhuma, Oman — Clark et al., 1987; Tibesti — Sennag et al., 1979; Southern Sahara — Dray et al., 1983.

## Groundwater Dating with Radiocarbon

Libby discovered radiocarbon in atmospheric  $\text{CO}_2$  in 1946. He determined its half-life to be 5568 years (the Libby half-life) and recognized then its potential as a dating tool. Godwin subsequently refined the determination of its half-life to 5730 years.

Atmospheric  $^{14}\text{C}$  mixes with all living biomass through photosynthesis as well as with meteoric waters and oceans (and carbonates formed in such waters) through  $\text{CO}_2$  exchange reactions. By consequence, any carbon compound derived from atmospheric  $\text{CO}_2$  since the late Pleistocene is potentially eligible for radiocarbon dating. Radiocarbon provides the chronology on which archaeologists have reconstructed our history in the Holocene. It has also provided the basis of climatic reconstructions in the late Pleistocene and Holocene.

As we will see,  $^{14}\text{C}$  is also the leading tool in estimating the age of paleo- and fossil groundwaters. The method is based upon the incorporation of atmospherically derived  $^{14}\text{C}$  from the decay of photosynthetically-fixed carbon in soil. Radiocarbon in the soil can be taken into solution as dissolved inorganic carbon ( $\text{DIC} = \text{CO}_2(\text{aq}) + \text{HCO}_3^- + \text{CO}_3^{2-}$ ) or as dissolved organic carbon (DOC). Neither approach is without complications. Let's first look at the basics of  $^{14}\text{C}$ .

### Decay of $^{14}\text{C}$ as a measure of time

Radiocarbon dating is based on measuring the loss of the parent radionuclide ( $^{14}\text{C}$ ) in a given sample. This assumes two key features of the system. The first is that the initial concentration of the parent is known and has remained constant in the past. The second is that the system is closed to subsequent gains or losses of the parent, except through radioactive decay. If we can be sure of these two conditions, then time is precisely measured by the exponential loss of the parent according to its half-life (which is simply a statistical determination of the relative stability of a given nuclide). This is represented by the decay equation:

$$a_t = a_0 \cdot e^{-\lambda t}$$

where  $a_0$  is the initial activity of the parent nuclide, and  $a_t$  is its activity after some time,  $t$ . The decay constant,  $\lambda$ , is equal to  $\ln 2/t_{1/2}$ . For  $^{14}\text{C}$ ,  $t_{1/2}$  is 5730 years, and this equation simplifies to:

$$t = -8267 \cdot \ln \left( \frac{a_t}{a_0} \right)$$

From this relationship,  $a_t$  is half of  $a_0$  after one half-life, and one quarter of  $a_0$  after two (Fig. 8-3). The usual expression of  $^{14}\text{C}$  activity is as a percent of the initial  $^{14}\text{C}$  activity ( $a_0$ ), i.e. percent modern carbon (pmc; see Chapter 1).

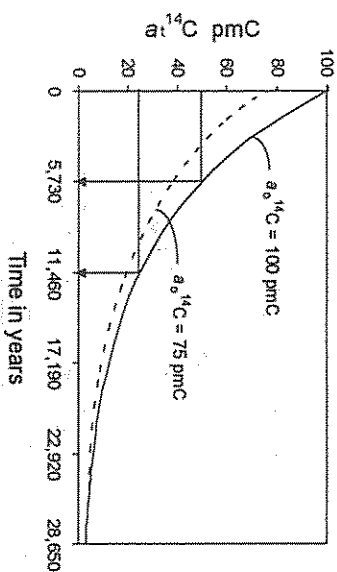


Fig. 8-3. The decay of  $^{14}\text{C}$  and illustration of half-life. Decay shown also for case where  $a_0^{14}\text{C} < 100$  pmC (75 pmC here).

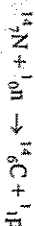
Assuming our two conditions are met ( $a_0^{14}\text{C}$  is known and closed system decay), dating with  $^{14}\text{C}$  is a simple calculation. Since the time of Libby, two independently dated records have helped establish  $a_0^{14}\text{C}$  over the past 30,000 years. These are tree rings and corals. These records of  $a_0^{14}\text{C}$  during the Holocene and late Pleistocene are discussed below. The potential  $^{14}\text{C}$  dating range is then limited only by analytical precision, which now allows measurements to about 10 half-lives or almost 60,000 years. However, the poor preservation and subsequent contamination of old material — our second condition for  $^{14}\text{C}$  dating — makes the effective dating range much shorter. For organic materials such as vegetation and collagen, the effective range is generally less than about 50,000 years. For groundwaters, the range is limited to about 30,000 years, and in most cases to a much shorter time. Reaction and evolution of the carbonate system strongly

dilute the initial  $^{14}\text{C}$  activity in DIC and DOC. The result is an artificial "aging" of groundwaters by dilution of  $^{14}\text{C}$ . Unraveling the relevant processes and distinguishing  $^{14}\text{C}$  decay from  $^{14}\text{C}$  dilution is an engaging geochemical problem.

### Production of $^{14}\text{C}$ in the atmosphere

Before tackling  $^{14}\text{C}$  dilution, let's start with a look at the generation of atmospheric  $^{14}\text{C}$  and the variation of  $\alpha_0^{14}\text{C}$  over the past 30,000 years. Cosmic radiation produces many nucleides in the upper atmosphere, including  $^{14}\text{C}$ . Primary cosmic rays are high-energy particles, electrons and photons from the Sun and beyond, that continually shower Earth (Gregory and Clay, 1988). The lower energy cosmic rays are mainly protons, with other light nuclei present as well. Over 90% of cosmic radiation is attenuated in the atmosphere. Collisions of these high-speed particles with atmospheric gases generate through *spallation* secondary particles of which neutrons are a large component.

Radioactive carbon is produced in the upper atmosphere through one of many nuclear reactions, the bombardment of nitrogen atoms by this secondary neutron flux:



where  $n$  = neutron and  $p$  = proton.

This  $^{14}\text{C}$  then oxidizes to carbon dioxide and mixes with other atmospheric gases, resulting in a constant flux of  $^{14}\text{CO}_2$  to the troposphere where it dissolves in the oceans or is consumed by vegetation during photosynthesis. Decay of vegetation and root respiration return much of the  $^{14}\text{C}$  to the atmosphere. From Table 8-1, the largest storehouse of  $^{14}\text{C}$  is by far the oceans, in the form of  $\text{HCO}_3^-$ . Accumulation in the troposphere and the hydrosphere/biosphere is balanced by radioactive decay and burial. This balance, or "secular equilibrium," is relatively robust over short periods (decades to 100s of years) and amounts to an atmospheric concentration of  $^{14}\text{CO}_2$  on the order of  $10^{-12}$  of the total atmospheric  $\text{CO}_2$ . This  $^{14}\text{C}$  concentration (activity) is defined as "modern"  $^{14}\text{C}$  and is the basis of the radiocarbon standard (see Chapter 1). Thus, not all atmospheric  $\text{CO}_2$  is  $^{14}\text{C}$ -active, only a very small fraction. This secular equilibrium can be altered by both natural processes and man's activities.

Table 8-1 Terrestrial carbon reservoirs

Form	Mass ( $10^9$ g)	Living biomass equivalent
$^{14}\text{C}$ -free		
Marine Carbonates	60,000	107,000
Sedimentary Hydrocarbon	15,000	26,800
Recoverable Coal, Oil and Gas	4	7.1
$^{14}\text{C}$ -active		
Oceanic DIC	42	75
Dead Vegetation	3	5.4
Atmospheric $\text{CO}_2$	0.72	1.3
Life on Earth	0.56	1

(From Berner and Lasaga, 1989.)

Neutron fluxes in the subsurface from the spontaneous fission of uranium and other elements can produce hypogenic  $^{14}\text{C}$  by neutron activation of  $^{14}\text{N}$  or neutron capture by  $^{17}\text{O}$  and  $\alpha$  decay.

In zones of exceptionally high neutron fluxes, hypogenic  $^{14}\text{C}$  be important. Calculations of *in situ* neutron fluxes and  $^{14}\text{C}$  production were made for the ore zone in the Cigar Lake uranium deposit in Saskatchewan. Secular equilibrium for groundwater in rocks with 40 weight percent U was determined to be 29 pMC. With over 50 weight percent U, this rose to over 200 pMC (Fabryka-Martin et al., 1994). However, the subsurface neutron flux in most rocks is very low. When considered with the large reservoir of carbon for dilution in the subsurface, hypogenic production is a negligible source of  $^{14}\text{C}$  in groundwaters.

### Natural variations in atmospheric $^{14}\text{C}$

A constant production and stable concentration of atmospheric  $^{14}\text{C}$  would require that the secondary neutron flux from cosmic radiation has been constant. In fact, it has not. Dendrochronology studies show strong variations in the  $^{14}\text{C}$  activity of atmospheric  $\text{CO}_2$  during the Holocene. Counting rings provides a firm chronology (1 in the dating equation). Measurement of  $\alpha^{14}\text{C}$  in tree rings by AMS, then provides a measure of  $\alpha_0^{14}\text{C}$  through time. Fig. 8-4 shows that  $^{14}\text{C}$  activity in the atmosphere has varied by over 10% during the Holocene. This record has been extended into the late Pleistocene by measuring the  $^{14}\text{C}$  content of corals (Bard et al., 1990). A reliable chronology of the corals was provided by U/Th disequilibrium dating by TIMS (thermal ionization mass spectrometry). This work shows that atmospheric  $^{14}\text{C}$  was a whopping 40% higher during the last glacial maximum. In addition to this systematic decrease since ca. 30,000 years ago are second-order excursions, the so-called "Suess wiggles" with ca. 200-year period (Suess, 1980). There is even an 11-year cycle to  $^{14}\text{C}$  production that matches the sunspot cycles.

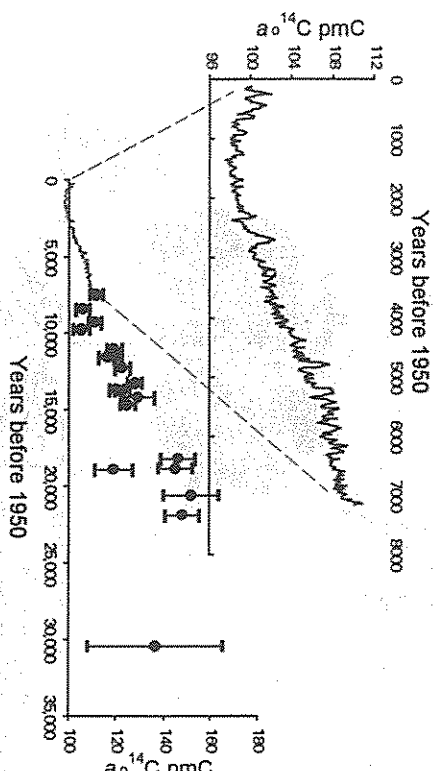


Fig. 8-4 Composite of atmospheric  $^{14}\text{C}$  activity from tree rings, determined using their dendrochronological age (from Pearson et al., 1986), and from shallow marine corals, based on their U/Th ages (from Bard et al., 1993). Holocene data show the ca. 200-year period Suess variations that are related to changes in solar output. The strong decrease from ca. 30,000 years BP to present are related to changes in the Earth's geomagnetic field.

Why the variations? The short-term cycles have been related to variations in solar output (Stuiver and Quay, 1980; Damon et al., 1989). Satellite measurements of solar output since 1979 document variations that follow the 11-year sunspot cycle (Floyd et al., 1992). Historical records of sunspot activity also show strong correlation with atmospheric  $^{14}\text{C}$ . However, they are

weak compared to the long-term evolution in atmospheric  $^{14}\text{C}$ . This is due to the changing structure of the Earth's geomagnetic field (Danton et al., 1989), which shields the Earth from much of the incoming flux of charged particles. This field is internally generated by the dynamo of the rotating/convecting Fe-Ni liquid outer core. Subtle variations in its dipole affect the flux of solar rays into the atmosphere and by consequence the production of  $^{14}\text{C}$ . These huge variations in  $a_0^{14}\text{C}$  will affect the calculated age of a radiocarbon-dated sample. If the standard 100 pMC is categorically used, one expresses the age in *radiocarbon years* rather than calendar years.

### Anthropogenic impacts on atmospheric $^{14}\text{C}$

While evidence now suggests that the variation of atmospheric  $^{14}\text{C}$  has varied between at least 97 and 140 pMC, anthropogenic effects over the past century have been even greater. The combustion of fossil fuel has pumped over 70 pmmv of dead carbon into the atmosphere (now at ~360 pmmv), diluting  $^{14}\text{C}$  by 25%. The record of this contribution in Vostok ice is clear from both the net increase in  $\text{CO}_2$  and by the shifting isotopic signature from a high pre-industrial  $\delta^{13}\text{C}$  value of the atmosphere (-6.4‰) towards that of fossil fuel (-26‰) (Friedli et al., 1986).

While the industrial age has been diluting atmospheric  $^{14}\text{C}$ , the nuclear age has been creating it. Since the 1950s, atmospheric weapons testing and nuclear power plants have been releasing additional radiocarbon to the atmosphere and biosphere (Fig. 8-5). The high neutron flux generated by thermonuclear bomb testing (see Chapter 7) activated  $^{14}\text{N}$  to produce  $^{14}\text{C}$ . The result was a considerable increase (a doubling at the peak in 1963) of the  $^{14}\text{C}$  activity of atmospheric  $\text{CO}_2$  that has subsequently been attenuation by exchange with the oceans. This peak is a very useful tracer to examine air sea transfers of  $\text{CO}_2$  and ocean mixing. Like tritium, it can be a useful indicator of modern recharge to aquifers. Although thermonuclear bomb tests were global in impact, local increases in  $a^{14}\text{C}$  are observed in the vicinity of nuclear power stations.

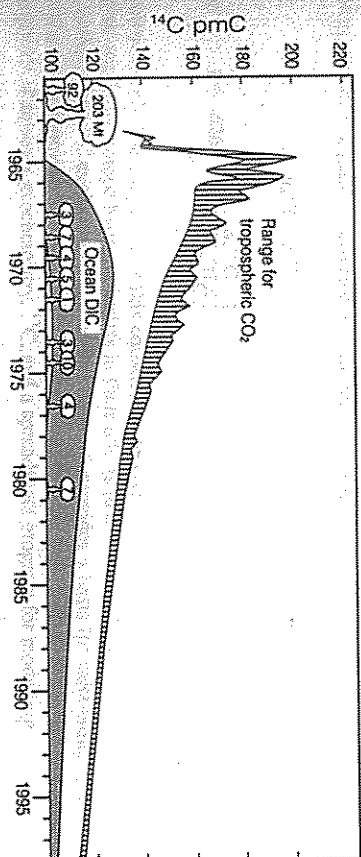


Fig. 8-5 Ranges for radiocarbon in tropospheric  $\text{CO}_2$  and the DIC in near-surface seawater. The data show for the northern hemisphere an almost twofold increase in  $^{14}\text{C}$  contents during the mid-1960s as a consequence of the atmospheric testing of thermonuclear bombs (omni total testing given in megatons). In the southern hemisphere the increase was lower, but since about 1970 the concentrations have been very similar around the globe. Oceanic  $^{14}\text{C}$  increased through the uptake of atmospheric  $^{14}\text{C}$ . Based on data to 1979 from IAEA (1983) and extrapolated to 1996. Bomb test data from Rath (1988).

Anthropogenic effects are of little relevance for paleogroundwater but such carbon is found in young systems. In modern groundwaters, radiocarbon activities above 100 pMC are often

measured. This addition of radiocarbon assists in the recognition of very young groundwaters. It also is useful in establishing dilution by carbonate dissolution in groundwater recharge areas.

### The $^{14}\text{C}$ pathway to groundwater in the recharge environment

Although rainwater contains some  $^{14}\text{CO}_2$  from the atmosphere, it is the soil zone that gives recharging groundwater its radiocarbon signal. Atmospheric  $^{14}\text{C}$  is incorporated into vegetation by photosynthesis and later released in the soil by decay and root respiration. The result is a huge reservoir of  $^{14}\text{C}$  in the soil zone. Fig. 8-6 shows the pathway for atmospheric  $^{14}\text{C}$  through the soil zone and into groundwater. Shown also is the fractionation experienced by  $^{13}\text{C}$  along this pathway. Recall that the radiocarbon standard of 100 pMC is calibrated to wood grown in 1890 and has  $\delta^{13}\text{C} = -25\text{‰}$ . The  $\delta^{13}\text{C}$  value of atmospheric  $\text{CO}_2$  (prior to significant contributions from fossil fuel) was about -6.4‰. This is 18.6‰ enriched over the value for vegetation of about -25‰. The strong fractionation during photosynthesis that causes this depletion of  $^{13}\text{C}$  will also affect the  $^{14}\text{C}$ . Saliege and Fomes (1984) determined that there is a  $-2.3 \times$  mass effect for  $^{14}\text{C}$  with respect to  $^{13}\text{C}$  fractionation. This means that unpolluted atmospheric  $\text{CO}_2$  was 42.5‰ or 4.3‰ enriched over the standard 100 pMC.

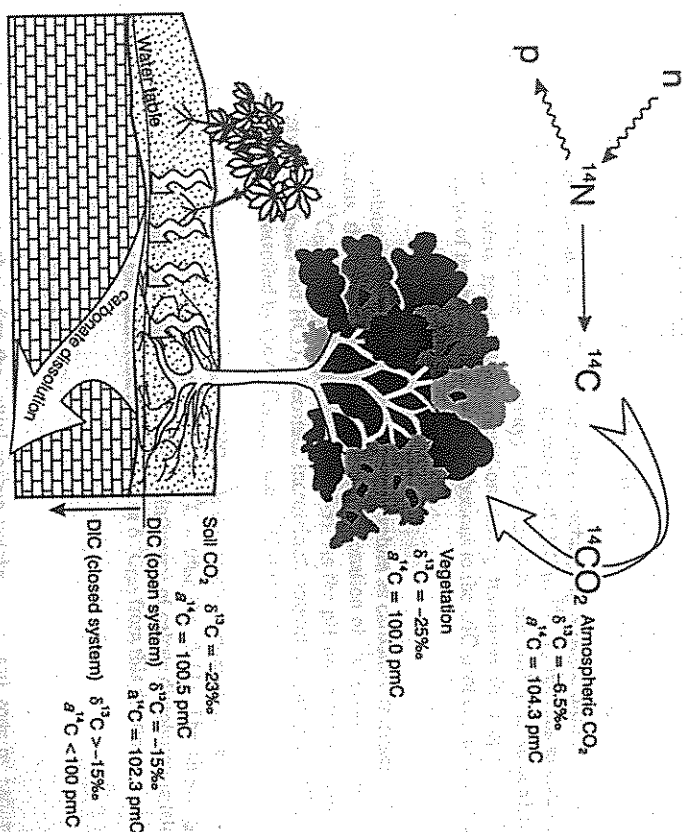


Fig. 8-6 The pathway and associated fractionation of  $^{14}\text{C}$  and  $^{13}\text{C}$  in  $\text{CO}_2$  during photosynthesis, respiration in soils, and dissolution by groundwaters.

Bacterial degradation of organic litter, as well as organic substances released by living plants, pumps an enormous amount of  $\text{CO}_2$  into soils. While the atmosphere today contains about 360 ppmv  $\text{CO}_2$  ( $P_{\text{CO}_2} \sim 10^{-3.4}$ ), soils contain between 3000 to 30,000 ppmv ( $P_{\text{CO}_2} \sim 10^{-2.5}$  to  $10^{-1.5}$ ). The amount of carbon dioxide that can dissolve will depend on the geochemistry of the recharge environment: the temperature, the pH of the water, the partial pressure of  $\text{CO}_2$ , and the weathering reactions that take place in the soil. Consequently, as groundwaters recharge through soils, they gain levels of  $^{14}\text{C}$ -active DIC that are much higher than that provided by direct dissolution of atmospheric  $\text{CO}_2$ . The  $^{13}\text{C}$  and  $^{14}\text{C}$  in soil  $\text{CO}_2$  are marginally enriched over the vegetation due to diffusion of lighter  $\text{CO}_2$  from the soil to the atmosphere.

If the  $^{14}\text{C}$  gained in the soils remains with the groundwater along the flow path, without subsequent dilution, its decay can be used as a measure of age. As this is rarely the case, dilution and loss by geochemical reactions both within the soil and along the flow path must first be addressed.

The most typical reactions include:

1. Calcite (limestone) dissolution, beginning in the recharge area
2. Dolomite dissolution
3. Exchange with the aquifer matrix
4. Oxidation of "old" organics found within the aquifer and other biochemical reactions
5. Diffusion of  $^{14}\text{C}$  into the aquifer matrix

The dilution of  $^{14}\text{C}$  through reaction is accounted for in the decay equation by the dilution factor or fraction,  $q$ . The  $^{14}\text{C}$ -activity of DIC in the groundwater recharge environment following calcite dissolution ( $a^{14}\text{C}_{\text{rechl}}$ ) is equal to the modern  $^{14}\text{C}$  in the soil ( $a_0^{14}\text{C}$ ) times the dilution factor:

$$a^{14}\text{C}_{\text{rechl}} = q \cdot a_0^{14}\text{C}$$

Thus, the decay equation corrected for dilution becomes:

$$a^{14}\text{C} = q \cdot a_0^{14}\text{C} \cdot e^{-\lambda t}$$

$$\text{or } t = -8267 \cdot \ln \left( \frac{a^{14}\text{C}}{q \cdot a_0^{14}\text{C}} \right)$$

Unfortunately, the simplicity of this equation is deceiving. The dilution factor,  $q$ , is the elusive grain sought by isotope hydrogeologists in their efforts to date groundwater. The development of carbonate and  $^{13}\text{C}$  evolution presented in Chapter 5 provides a basis for calculating  $q$ . Here we will explore approaches to tracing  $^{14}\text{C}$  evolution and correcting radiocarbon ages through using a tool kit of aqueous geochemistry,  $^{13}\text{C}$ , and a spreadsheet program for modelling.

## Correction for Carbonate Dissolution

The approaches to correct apparent  $^{14}\text{C}$  water ages have evolved over the past 30 years from "statistical models" and "mixing models," to "process-oriented models." The following discussion presents a few of the published models. These are followed by the development of algorithms useful for correcting the various dilution processes. Calculations require some

familiarity with alkalinity and aqueous geochemistry. A brief review was given in Chapter 5. References for further reading include such texts as Garrels and Christ (1965), Freeze and Cherry (1979), Stumm and Morgan (1996) and Drever (1997).

In the approaches presented here, the diluting source of carbon is presumed to be  $^{14}\text{C}$ -free. This is certainly the case with marine limestone, which is generally millions of years old. On the other hand, some soil carbonates may have measurable  $^{14}\text{C}$  activities. Conversely, the oxidation of old carbon in soils can generate soil  $\text{CO}_2$  with  $a^{14}\text{C}$  that is slightly less than modern. In such cases, the correction factor must be modified accordingly.

Recall from Chapter 5, that the carbonate evolution of many groundwaters involves the dissolution of soil  $\text{CO}_2$  with the subsequent dissolution of carbonate:



Two sources of DIC then dominate in recharge environments — the  $^{14}\text{C}$ -active component from the soil used to date the water, and a (generally)  $^{14}\text{C}$ -free carbonate which dilutes  $^{14}\text{C}_{\text{soil}}$ . This dilution is characteristic of non-carbonate aquifers as well. In sandy aquifers or tills, calcite is often present as a component of the matrix or as secondary cement and calcrete. In crystalline environments, fracture calcite is often available.

Under closed system conditions, the stoichiometry of calcite dissolution by carbonic acid imparts about a 50% dilution to the initial  $^{14}\text{C}$ :



Under open system conditions, the DIC is continuously exchanging with the infinite reservoir of  $^{14}\text{C}$ -active soil  $\text{CO}_2$ . In this case, the initial  $^{14}\text{C}$  activity of DIC ( $a_0^{14}\text{C}_{\text{DIC}}$ ) remains unchanged at 100 pMC (or at the current initial  $^{14}\text{C}$  activity). Unfortunately, the reality is somewhere in between. Most groundwaters reach calcite saturation during transition from open to closed conditions. The openness of the system and the contributions to the DIC pool can be reflected by the  $\delta^{13}\text{C}$  of the DIC.

Fig. 5-6 shows the evolution of  $\delta^{13}\text{C}_{\text{DIC}}$  towards enriched values as carbonate is dissolved. Under open system conditions, this is due to the increase in fractionation of  $^{13}\text{C}$  between soil gas and DIC as the pH rises ( $\delta^{13}\text{C}_{\text{DIC-CO}_2} \approx 9\text{‰}$  @ 25°C, Fig. 5-5). As the pH increases, the strong  $^{13}\text{C}$  enrichment between  $\text{CO}_{2(\text{soil})}$  and  $\text{HCO}_3^-$  becomes increasingly important and the  $\delta^{13}\text{C}_{\text{DIC}}$  goes up. However, it is still controlled by the  $\delta^{13}\text{C}_{\text{CO}_{2(\text{soil})}}$  and  $a^{14}\text{C}$  is still 100 pMC.

Under fully closed conditions, the increase in  $\delta^{13}\text{C}_{\text{DIC}}$  is due solely to mixing between DIC from soil ( $\delta^{13}\text{C} \approx -12$  to  $-20\text{‰}$ ) and marine carbonate ( $\delta^{13}\text{C} \approx 0\text{‰}$ ; Fig. 5-12). The closed system evolution of  $\delta^{13}\text{C}_{\text{DIC}}$  is more dramatic because here the influence of calcite dissolution is felt. We can calculate  $^{14}\text{C}$  dilution by the additional enrichment in  $\delta^{13}\text{C}_{\text{DIC}}$  from this dilution.

### Statistical correction (STAT model)

Statistical models assume that after the initial carbon uptake in the soil zone by infiltrating water, some  $^{14}\text{C}$  dilution will occur through the addition of  $^{14}\text{C}$ -free carbon. Statistical evaluations are possible if geochemical evolution can be averaged over the recharge area to estimate an "initial" value for the  $^{14}\text{C}$  activity of the aqueous carbonate. This initial value