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CHANGES IN ^{14}C ACTIVITY OVER TIME DURING VACUUM DISTILLATION OF CARBON FROM ROCK PORE WATER

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ABSTRACT. The radiocarbon activity of carbon collected by vacuum distillation from a single partially saturated tuff began to decline after approximately 60% of the water and carbon had been extracted. Disproportionate changes in ^{14}C activity and $\delta^{13}C$ during distillation rule out simple isotopic fractionation as a causative explanation. Additional phenomena such as matrix diffusion and ion exclusion in micropores may play a role in altering the isotopic value of extracted carbon, but neither can fully account for the observed changes. The most plausible explanation is that distillation recovers carbon from an adsorbed phase that is depleted in ^{14}C relative to DIC in the bulk pore water.

INTRODUCTION

Vacuum distillation was first introduced by Davidson (1995) and Davidson et al. (1995) as a method for extracting dissolved inorganic carbon (DIC) from the pores of partially saturated rock for ^{14}C analysis. The distillation method was initially developed in order to obtain DIC from rock pores where the total water content was too low to obtain water by conventional compression or centrifugation methods (Peters et al. 1992). These studies were performed on cores from the Apache Leap Tuff in central Arizona.

The Apache Leap studies compared the ^{14}C activity of DIC collected by distillation of preserved core samples from the Deep Slant Borehole (DSB) with the activity of CO_2 in formation air samples collected from 1-m intervals at the same depth, and from DIC extracted from water collected from adjacent core samples by core compression. The measured ^{14}C activities of samples collected by different methods near the same depths were similar (Figure 1), suggesting that the distillation method could be used to obtain representative samples for ^{14}C analysis.

Minor fractionation of ^{14}C was anticipated during distillation of the DSB cores. Calculated ^{14}C fractionation, based on measured $\delta^{13}C$ fractionation, was less than 4%. This figure was consistent with the differences observed in the measured ^{14}C activities when comparing different methods of extracting carbon (Figure 1).

In the current study, DIC was collected from a preserved core from the Topopah Spring Tuff at Yucca Mountain, Nevada. Analyses of incremental carbon samples collected from the same core over time during the distillation showed a decreasing trend in the ^{14}C activity that was not anticipated based on stable carbon isotope measurements.

METHODS

Distillation of DIC was performed on a single preserved, 3-kg (dry weight) core sample from the Topopah Spring Tuff from borehole UZW-SD-12, Yucca Mountain, Nevada. The core was taken from a densely welded, devitrified, nonlithophysal zone at a depth of 211 m (692 feet). Porosity and initial saturation of the core were approximately 10% and 92%, respectively (Rautman and Engstrom 1996). Preservation had been completed in the field at the time of drilling in July of 1994 by

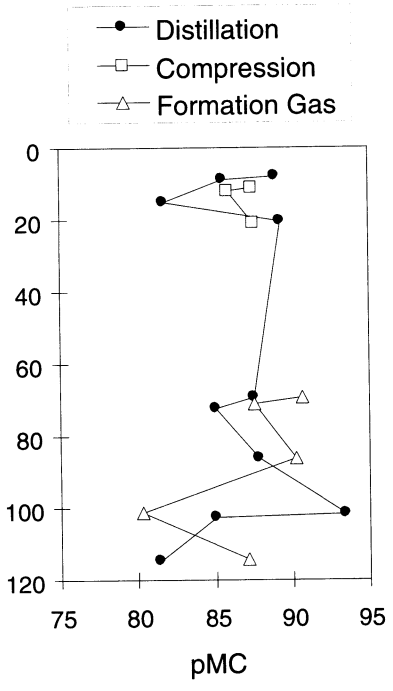


Figure 1 Data from Davidson et al. (1998) showing the measured ^{14}C activity of 1) carbon extracted from rock pores by distillation, 2) DIC from rock pore water collected by core compression, and 3) CO_2 in formation gas collected from 1-m intervals

sealing the core inside a Lexan® liner and then again inside a heat-sealable aluminum laminate (Protec Core®)[1].

Distillation followed the method outlined in Davidson et al. (1995). In summary, the preserved core sample was opened and immediately transferred into an argon-filled stainless-steel cell. The cell was mounted on a scale with 1 g resolution and connected to a high-vacuum line. The cell was heated to 180 °C and extracted gases drawn through a series of cryogenic traps to capture water (dry-ice/alcohol traps) and carbon dioxide (liquid nitrogen traps). Total distillation time was 12 h. The mass and isotopic composition of carbon collected over time was monitored by periodically subliming the collected CO_2 into a known volume with a pressure transducer followed by removal for isotopic analysis. Incremental CO_2 samples were analyzed for both $\delta^{13}C$ and ^{14}C. The rate of water removal was monitored by attributing mass loss over time to water loss.

^{14}C results are reported as percent modern carbon (pMC) with an analytical precision of about 1.0% (2σ); $\delta^{13}C$ results are reported as per mil shifts relative to the Vienna Pee Dee Belemnite (VPDB) isotopic standard with an analytical precision of about 0.2‰ (2σ) for all samples.

RESULTS AND DISCUSSION

Figure 2A shows the $\delta^{13}C$ and ^{14}C results for the isotopic composition of each incremental carbon sample. Initial increases in $\delta^{13}C$ over time, representing the first 3 h of distillation and 80% of the total carbon mass recovered, reflect a continuous enrichment of ^{13}C in the aqueous reservoir as ^{12}C

[1]The use of brand/company/trade names is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

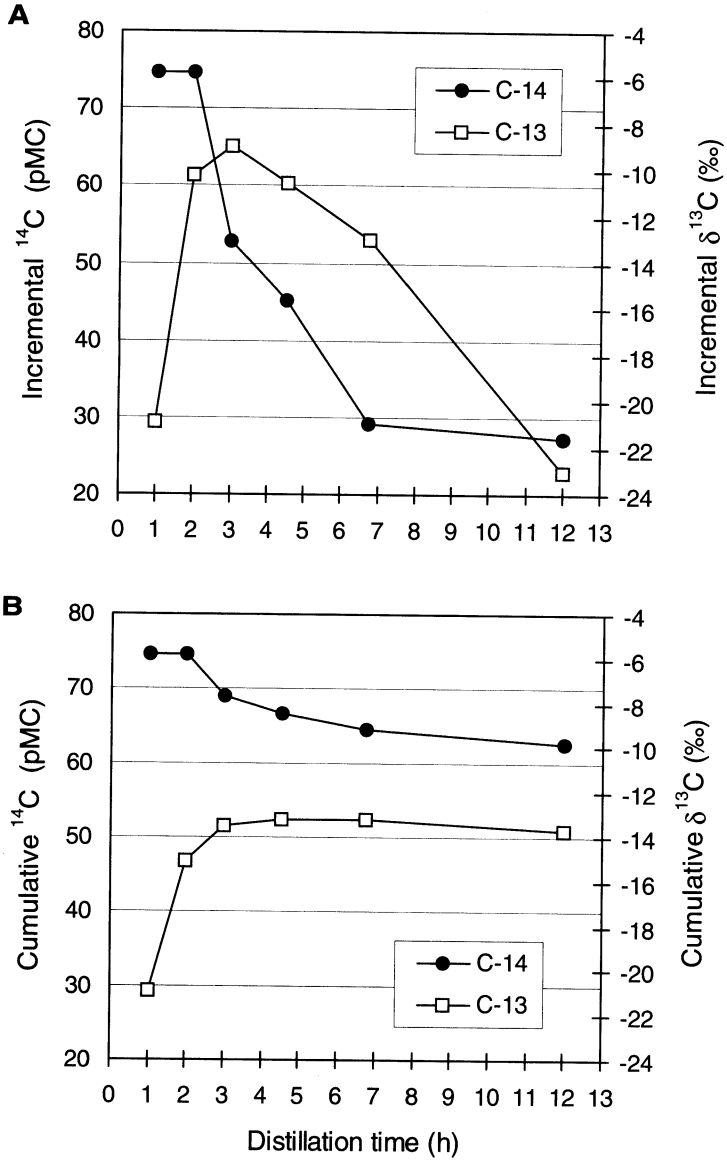


Figure 2. A. Incremental ^{14}C activity and $\delta^{13}C$ of carbon collected by distillation over time. B. Cumulative ^{14}C activity and $\delta^{13}C$ of carbon distilled over time.

is preferentially removed to the gas phase. Subsequent decreases in $\delta^{13}C$ probably reflect competing processes where ^{13}C depletion in the aqueous reservoir, due to calcite precipitation, dominates over continued ^{13}C enrichment of the gas phase through preferential loss of ^{12}C (Davidson et al. 1995). Cumulative results (Figure 2B) show a continuous enrichment of ^{13}C in the extracted phase until more than 90% of the total carbon was recovered. The composite sample was isotopically heavier than the initial incremental sample by 7.2‰. Although extracted carbon becomes enriched in ^{13}C over time, the initial recovery is so depleted in ^{13}C that the final composite sample is typically still isotopically light relative to in situ pore-water DIC (Davidson et al. 1995).

If the isotopic composition of extracted carbon over time is controlled by simple fractionation due to differences in mass, the ^{14}C activity should follow the same general pattern observed in the $\delta^{13}C$ data (that is, changes in $\delta^{13}C$ and ^{14}C should be proportional). Figure 2 shows that the ^{14}C activity followed a distinctly different path. The first 2 incremental samples (Figure 2A), representing the first 2 h of distillation and 60% of the total carbon mass recovered, had a constant activity of 74.6 pMC. Each additional incremental sample decreased in activity to a low of 27.4 pMC after 12 h of distillation. Figure 2B shows a steady depletion of ^{14}C in the cumulative sample, in contrast to the enrichment of ^{13}C shown in the $\delta^{13}C$ data. If the ^{14}C activity were governed by the same processes affecting the stable isotopes, and it is assumed that ^{14}C fractionation is approximately twice that of ^{13}C (relative to ^{12}C), the cumulative ^{14}C should have increased to about 76 pMC.

Three possible processes were considered to explain the decrease in $\delta^{13}C$ and ^{14}C late in the distillation: 1) matrix diffusion, 2) ion exclusion, and 3) adsorption.

Matrix Diffusion

In theory, decreasing ^{14}C activity can result during distillation if carbon begins to be extracted from dead-end micropores in the rock (Neretnieks 1981). This is possible if ^{14}C was depleted in micropores in situ prior to sampling. In a dry rock, advective flow will initially fill dry dead-end micropores with water, but no additional water will enter the pores. As ^{14}C present in the micropores decays, a concentration gradient may be established between the bulk pore-solution and the micropores. Steady-state concentrations will be established as a function of the rate of diffusion of ^{14}C into the micropores and the rate of ^{14}C decay. The steady-state ^{14}C gradient will persist in a preserved core sitting on a shelf, although the overall activity will decline with storage time.

During distillation of a core, the first water and carbon to be sampled is from the larger, more easily accessible pores. Later in the distillation, water and carbon are drawn from smaller pores where the carbon reservoir may be depleted in ^{14}C as described above. At the time when the second incremental carbon sample was collected from the Topopah Spring core, about 56% of the available water had been recovered (Figure 3).

Steady-state flux of ^{14}C from the bulk solution into micropores can be modeled using a one-dimensional transport equation with a first-order reaction term:

$$-D\frac{d^2A(x)}{dx^2} + kA(x) = 0 \ , \tag{1}$$

where D is the diffusion coefficient (1.185×10^{-9} m^2s^{-1} for HCO_3^- in water; (Lide 1997, p 5–99), k is the decay constant for ^{14}C (3.836×10^{-12} s^{-1}), and $A(x)$ is the activity at distance x into a micropore. The diffusion coefficient for HCO_3^- is used because it is the predominant form of DIC in pore water samples obtained from related cores. If the boundary conditions for Equation (1) are set such that there is a constant activity at the mouth of the pore (A_o) and no flux is allowed at the extreme end of the pore ($x = L$), the solution is (Bird et al. 1960, p 532–3):

$$A(x) = A_o\left[\frac{\cosh\left(\sqrt{\frac{k}{D}}\,[L-x]\right)}{\cosh\left(\sqrt{\frac{k}{D}}\,[L]\right)}\right] . \tag{2}$$

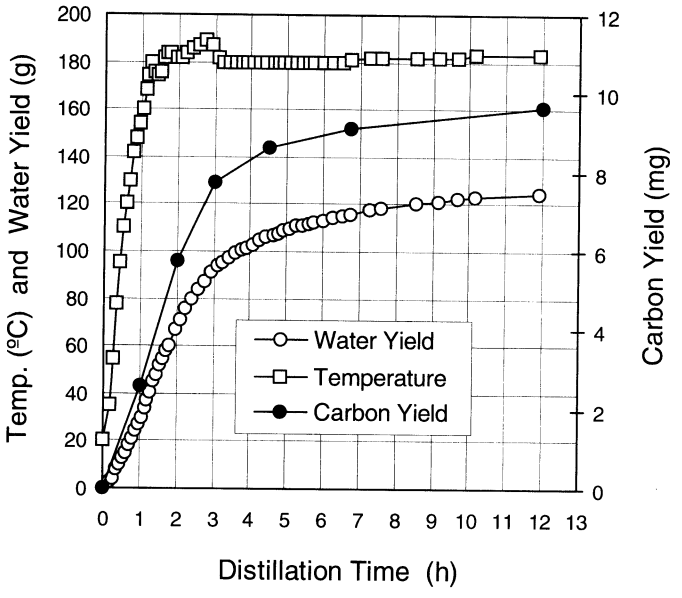


Figure 3. Temperature and cumulative water and carbon yield during distillation

If it is assumed that the final carbon drawn from the distilled rock came from the extreme ends of micropores, the ^{14}C activity of the last incremental carbon sample can be represented by $A(x) = 27.4$ pMC where $x = L$. If it is further assumed that the first 60% of the carbon recovered represents the composition of the bulk pore-solution, then $A_o = 74.6$ pMC. Solving for L then gives an unrealistic mean pore length of 29 m. This model is imperfect because carbon distilled from micropores near the surface of the core and from the bulk solution closer to the center of the core may be recovered simultaneously. Such mixing, however, would elevate the activity of the later samples, requiring even longer pore lengths to account for the lower activity of the carbon coming from the micropores alone.

The model is also imperfect because it assumes that the pores were fully saturated. The degree of saturation in the sampled core was about 92% (Rautman and Engstrom 1996). This means that water in some of the micropores in situ may have been separated from the bulk solution by air pockets. Significant depletion of ^{14}C in these micropores relative to hydraulically connected micropores is unlikely, however, because isotopic exchange readily occurs between gaseous CO_2 and aqueous DIC (Mook et al. 1974), and diffusion of CO_2 in air is more rapid than diffusion of HCO_3^- in water (Lide 1997, p 5-99 and 6-218).

Ion Exclusion

The isotopic composition of DIC in the smallest pores could be altered by interactions between charged DIC species and mineral surfaces. In this model, DIC anions (HCO_3^- and CO_3^{2-}) are inhibited from passage into the smallest pores, resulting in an enrichment of the uncharged species (H_2CO_3) in the micropores. This will result in a depletion of ^{13}C in the DIC within the micropores relative to the bulk solution, assuming equilibrium isotopic fractionation between the three DIC species (Deines et al. 1974). Samples collected late in the distillation may reflect collection of this isotopically depleted reservoir.

Preferential passage of H_2CO_3 has been observed in hyperfiltration experiments where DIC solutions were forced through smectite clay (Fritz et al. 1987). The results of hyperfiltration are not directly analogous to diffusion into micropores, however, because the driving forces are not the same. Fritz et al. (1987) attributed initial transient increases in DIC and enrichment of ^{13}C in the filtrate to advectively driven processes: conversion of HCO_3^- to H_2CO_3 at the upstream clay–solution interface, allowing easier passage of DIC through the clay, and differential back-diffusion of the isotopes from the concentrated clay-solution layer to the bulk feed solution.

Ion exclusion effects may contribute to the decline in the incremental $\delta^{13}C$ values late in the distillation, but they do not adequately account for the decrease in ^{14}C activity. Fractionation induced solely by ion exclusion at the micropore level should be proportional for ^{13}C and ^{14}C, resulting in a much smaller decline in ^{14}C than observed.

Adsorption

A more plausible possibility is that carbon sampled later in the distillation begins to draw from a secondary source of carbon, such as an adsorbed phase. If exchange between DIC and adsorbed carbon is slow, ^{14}C in the adsorbed phase will not be readily replenished as it decays. The activity of the adsorbed phase will continue to decline until the exchange rate with the bulk solution is equal to the decay rate. In this model, carbon recovered in the early stages of distillation represents DIC degassed from the bulk solution. Later in the distillation, carbon becomes increasingly derived from the ^{14}C-depleted adsorbed phase.

The existence of a sizeable reservoir of adsorbed inorganic carbon on mineral surfaces has been suggested to explain high uptake of CO_2 on experimental soils (Striegl 1988; Striegl and Armstrong 1990), and high recovery of carbon from distilled tuff cores from Superior, Arizona (Davidson et al. 1995). In these studies, the mass of carbon removed by soils or recovered from cores ranged from 3 to 17 times higher than the mass of DIC in the pore water of the samples. The existence of an adsorbed phase in the present study can only be approximately evaluated because there was no way to directly measure the original mass of DIC in the pore water of the distilled core. The total water content was too low to obtain pore water samples by typical compression or centrifugation methods.

Simply dividing the total mass of carbon recovered (9.64 mg) by the total mass of water distilled (0.125 L) gives a C concentration of 77 mg/L (391 mg/L HCO_3^-). This represents only a portion of the available carbon in the rock pores because some of the original mass is left behind as precipitated carbonate during the distillation. An earlier study investigating the recovery efficiency of the distillation method found that 40% to 85% of the available carbon in 6 tuff samples was left behind following distillation (Davidson et al. 1995). No DIC concentration data are available from the Topopah Spring Tuff, but concentrations of pore water obtained by compression from adjacent units (Calico Hills and Prow Pass Tuff) range from 114 to 323 mg/L HCO_3^-, with pH values of 8.7 and 8.3, respectively (Yang et al. 1998). The partial mass of carbon collected from the distilled Topopah Spring sample exceeds the highest total DIC concentration measured in the Calico Hills and Prow Pass samples by more than 20%. Comparison with adjacent units is speculative, but the high carbon yield is consistent with the hypothesis that carbon has been drawn from an adsorbed phase. The high yield cannot be accounted for by atmospheric leakage into the distillation cell because a leak would result in an increase in the ^{14}C activity with time rather than the observed decline.

The continued decline in $\delta^{13}C$ during the final stages of distillation is also consistent with adsorption-induced fractionation observed by others. Yang et al. (1985) collected CO_2 from a subsurface formation by pumping borehole gas through a molecular sieve (MS) packed with a silicate substrate

and through a solution of potassium hydroxide (KOH). The $\delta^{13}C$ values of the MS samples were 5‰ to 6‰ lighter than the KOH samples, suggesting preferential adsorption of $^{12}CO_2$ over $^{13}CO_2$ by the MS. Preferential adsorption of $^{12}CO_2$ is also routinely observed by colleagues at the University of Mississippi during gas chromatography experiments (Jon Parcher, unpublished data). The substrates in both the MS and chromatography experiments are not the same as in the tuff sample, however, so further investigation is warranted to measure the fractionation associated with adsorption on specific minerals found in the tuff.

The rate of carbon and water collection over time was analyzed to determine whether recovery of an adsorbed carbon phase late in the distillation would result in an increasing ratio of recovered carbon/water (Figure 4). The opposite trend was actually observed; the ratio of recovered carbon/water decreased during the later stages of distillation. There are at least two possible explanations. First, DIC removal may be more efficient than water removal under conditions of low pressure and elevated temperature. Under these conditions, a disproportionate mass of DIC may degas early in the distillation, resulting in a diminished supply of carbon as water continues to vaporize slowly. Second, lower carbon/water yields may be expected if the later stages of distillation draw water from ion-deficient micropores (Peters et al. 1992).

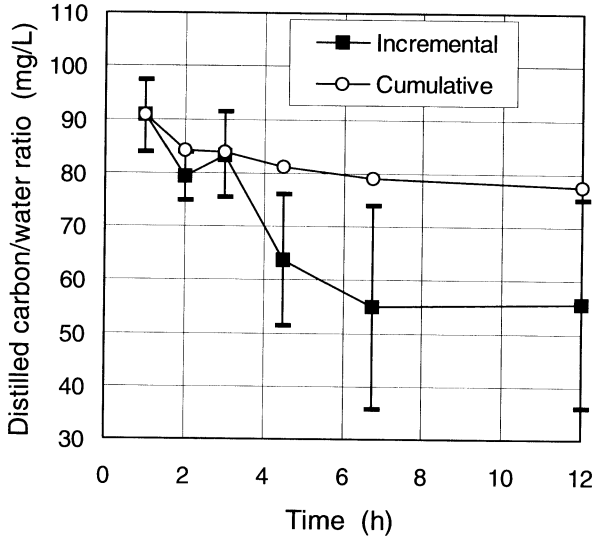


Figure 4. The ratio of carbon/water recovered during distillation. Error bars are left off the cumulative data to avoid cluttering the figure, but are of the same magnitude as the corresponding incremental data.

CONCLUSION

The ^{14}C activity of carbon distilled from a tuff core began to decline after approximately 60% of the water and carbon was extracted. This phenomenon cannot be attributed to simple isotopic fractionation because changes in the ^{14}C activity and $\delta^{13}C$ of recovered carbon over time followed distinctly different pathways. Matrix diffusion and ion exclusion may be active in situ processes, but neither can account for the observed decline in ^{14}C activity. Matrix diffusion into dead-end micropores requires unrealistic pore lengths to account for the final ^{14}C activities. Ion exclusion may contribute to the late-stage decline in $\delta^{13}C$, but does not account for the disproportionate decline in ^{14}C. The

most plausible explanation is that distillation recovers carbon from an adsorbed phase that is depleted in ^{14}C relative to DIC in the bulk pore water. Depletion of ^{14}C may result from slow in situ exchange between the adsorbed phase and the bulk pore water.

Viewed in isolation, these results would suggest that the distillation method will not provide carbon with representative ^{14}C activity because the cumulative activity changed by 12 pMC over the course of the distillation. Comparisons, however, between different methods of extracting carbon from tuff have shown that the activities of distilled samples are reasonably close to those of samples obtained from adjacent depths by other methods (Figure 1). It is probable that distillation produces carbon with a ^{14}C composition representative of pore-water DIC within a finite range of accuracy. The range is probably less than ±10%, but additional work is needed to refine this estimate.

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