[RADIOCARBON, VOL. 37, NO. 3, 1995, P. 861–874]

EXTRACTION OF ^{14}C FROM PORE WATER IN UNSATURATED ROCK USING VACUUM DISTILLATION

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ABSTRACT. We discuss a vacuum-distillation method for obtaining representative ^{14}C samples from dissolved inorganic carbon in rock pore-waters. Distillation offers four advantages over current centrifugation and compression methods for obtaining pore-water carbon: 1) carbon recovery is possible from rocks that will not yield water by centrifugation or compression; 2) the mass required for ^{14}C analysis can typically be obtained in a single extraction, eliminating the need for storing and combining multiple pore-water collections; 3) water and carbon are extracted and isolated simultaneously, reducing the number of required steps and the potential for contamination; and 4) distillation requires less equipment at lower cost than centrifugation or compression. In this study, isotopic fractionation resulting from incomplete recovery of carbon during distillation was too high for stable isotope applications, but was relatively minor for ^{14}C applications. The lighter isotopes were favored in the recovered phase, resulting in samples depleted in ^{14}C by a maximum of 4%. Mass balance calculations indicate that there may be a significant reservoir of carbon absorbed to mineral surfaces that is only partially removed by this method. Incorporation of adsorbed carbon into the recovered sample did not measurably alter the ^{14}C activity.

INTRODUCTION

Methods used to collect pore water from unsaturated rock include: leaching (Bottrell, Yardley and Buckley 1988), centrifugation (Yang, Davis and Sayre 1990) and compression (Yang *et al.* 1988; Mower, Higgins and Yang 1991; Peters *et al.* 1992). Leaching is the least preferred method for ^{14}C sampling because the leach water may dissolve carbonate minerals if present, and contamination from the leach water itself is difficult to avoid. Centrifugation and compression have the advantage of allowing pore water to be collected without exposure to contaminating air or water. Disadvantages are: 1) water yields are generally small, which requires combining multiple extractions to obtain enough carbon for a ^{14}C analysis; 2) a second step is required to remove the dissolved inorganic carbon (DIC) from the extracted water; 3) the cost of a centrifuge, or of a compression cell and loading frame, can be quite high; and most importantly 4) current centrifugation and compression methods are unable to extract water from some rock types with low water content (Yang, Davis and Sayre 1990; Peters *et al.* 1992; Davidson 1995).

The distillation method reported here was developed to allow ^{14}C sampling of inorganic carbon dissolved in pore waters in variably saturated tuff samples that would not yield water by compression. The results were used in a broader study investigating the occurrence and significance of preferential flow of water through fractures in an unsaturated tuff at the Apache Leap Research Site (ALRS) near Superior, Arizona. Pore water ^{14}C proved to be a useful tool in identifying the importance of fractures in delivering surface runoff to a perched aquifer 146 m below the surface (Bassett *et al.* 1994; Davidson 1995; Davidson *et al.* 1996; Davidson *et al.* in review).

METHODS

Pore-water carbon was extracted from variably saturated tuff core samples obtained from the Deep Slant Borehole (DSB) at the ALRS. Drilling of the DSB was begun at a 45° angle to intersect a series of near-vertical fractures transecting the ALRS. Vertical depths are reported throughout this paper rather than distance along the borehole unless otherwise noted. Atmospheric air was used as the drilling fluid to minimize contamination of pore water in the core. An earlier drilling project in Apache Leap Tuff injected SF_6 into the drilling air as a tracer. Subsequent analyses of pore gases collected by compression of preserved core samples found no SF_6, indicating that penetration of drilling air into the matrix pores of the core was insignificant (Peters *et al.* 1992; I. C. Yang, personal communication 1993).

Size HQ (6.1 cm diameter) core was retrieved from the full 202 m length of the borehole. Upon removal from the core barrel, the core was isolated from the atmosphere by wrapping 50 to 100 cm intervals in Barex® (heavy plastic sheeting), partially sealing each interval in Protec Core® (heat-sealable aluminum/plastic laminate), roughly purging the package of atmospheric gases using high-purity nitrogen, and sealing the package.

The effectiveness of the preservation system for preventing evaporative water loss was documented by weighing preserved core samples over time. Shorter core intervals of 10 to 20 cm were sealed so that packages could be placed on a laboratory mass balance. A total of 15 samples were weighed every 30 to 60 days for a period of nearly 2 yr. Mass losses were less than the limit of detection, which was equivalent to *ca.* 3% of the initial water weight (Davidson 1995).

Multiple packages representing the full length of the borehole were later opened and examined for carbonate minerals. Identification methods for both fracture and matrix minerals included visual examination, acid testing, X-ray diffraction on powdered samples, and scanning electron microprobe analyses on intact surfaces. No carbonate minerals were detected.

The distillation cell was a 100 cm long, 6.5 cm diameter, stainless-steel cylinder with an O-ring sealed face plate at one end for loading and removing core (Fig. 1). A 9 mm O.D. port was positioned at each end, one for introducing argon and the other for extracting sample gas. The entire length of the cell was wrapped with heating tape and fiberglass insulation. Total cost for materials and fabrication of the distillation cell and for adaptations to a high-vacuum line (primarily large volume 100–500-ml capacity cold traps) was less than $1000 U.S.

Before placing core segments inside the cell, the face plate was removed, the cell was placed on end with the opening at the top, and the cell was purged of atmospheric gases using ultra-high purity argon introduced through the bottom port. The argon was reduced to a slight positive flow rate and 50–100 cm of rock core was dropped into the cell. The cell was immediately sealed, placed back in a horizontal position, and connected to a high-vacuum line.

The cell was opened directly to a roughing pump bypassing the traps for the first 20–30 sec until the pressure dropped to *ca.* 20 torr. Extracted gases were then directed through a series of water traps immersed in dry ice and isopropyl alcohol, and CO_2 traps immersed in liquid nitrogen. No heat was applied during the first 15–60 min due to high initial water flux rates. The temperature of the cell was then raised to 150–180°C for the remainder of the extraction. Distillation times for 19 samples ranged from 4 to 15 h per sample. The progress of the distillation was monitored for three of the distillations by isolating the CO_2 traps periodically, sublimating the CO_2 into a known volume, measuring the pressure and temperature, and freezing the CO_2 into a sample vessel. At the end of each distillation, the cell was filled with argon and allowed to cool. The core was removed, weighed and transferred into new Protec Core® packages.

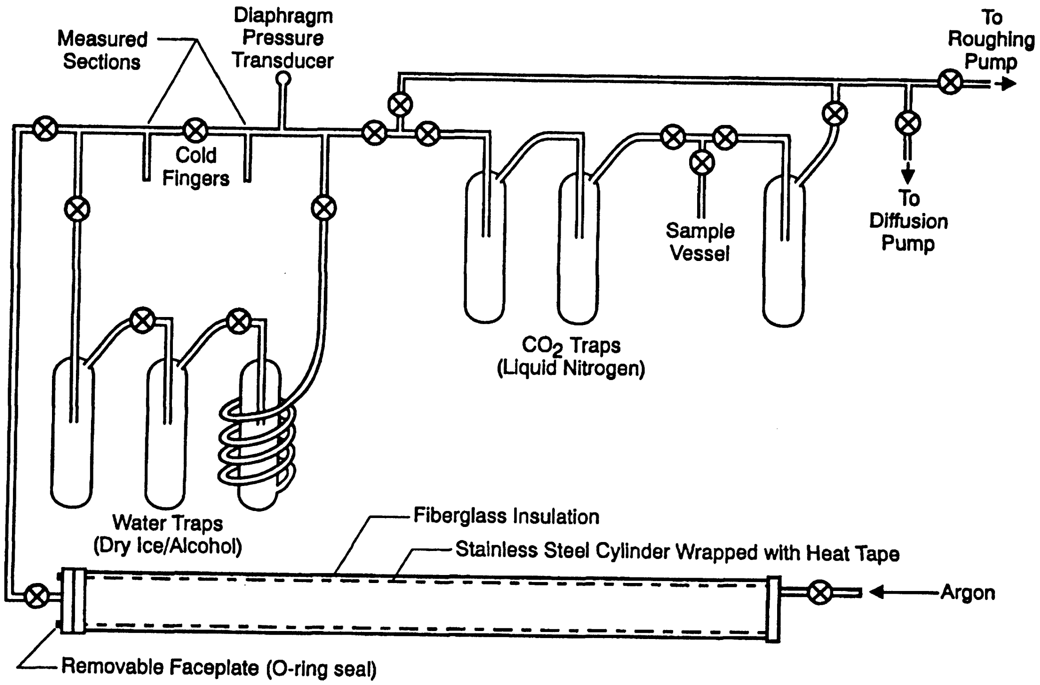

Fig. 1. Schematic diagram of the distillation cell, high-vacuum line and cyrogenic traps used to collect carbon and water from the pores of unsaturated rock core samples

The mass and $\delta^{13}C$ of unrecovered carbon was also determined for several distillations. Following distillation, six samples were crushed using equipment that had been washed with dilute HCl (0.001 N), rinsed with distilled deionized water and dried with pressurized air. Crushed samples were divided into homogeneous splits of *ca.* 500 g each. Split samples were acidified using dilute HNO_3 (0.1 N) under vacuum. Evolved CO_2 was captured using the traps described above (Fig. 1). Replicate extractions were performed on up to five splits from each sample.

The compression method described by Peters *et al.* (1992) was used to obtain pore water from core samples taken from the uppermost 21 m of the tuff. Several dozen attempts were made to extract pore water from core below 21 m, but only two attempts produced water. In both successful attempts below 21 m, the yield provided insufficient carbon for isotopic analysis. Core segments 8–12 cm long were compressed in 36 MPa increments up to a maximum pressure of 552 MPa. Maximum pressure was achieved in about 90 min and then held constant for an additional 20–30 min (Davidson 1995). Pore waters collected from several adjacent core samples were composited to obtain enough carbon for each ^{14}C and $\delta^{13}C$ analysis. DIC was collected from the extracted pore water by acidifying under vacuum and trapping the evolved CO_2 as described above.

Stable carbon isotopes were analyzed by the Isotope Geochemistry Lab at The University of Arizona; results are reported as per mil shifts relative to the PDB isotopic standard (Craig 1957) with an analytical precision of *ca.* 0.2‰ (2 σ). ^{14}C was analyzed by the NSF-Arizona Accelerator Mass Spectrometer (AMS) facility at The University of Arizona; results are reported as percent modern carbon (PMC) with an analytical precision of *ca.* 1.0% (2 σ) (Donahue, Jull and Toolin 1990).

RESULTS AND DISCUSSION

Representative ^{14}C and $\delta^{13}C$ samples can be obtained from pore water by distillation provided that one of the following conditions is met: 1) recovery of carbon from the pore water is complete; 2) partial recovery of carbon does not result in significant isotopic fractionation; 3) isotopic fractionation resulting from partial recovery is consistent, allowing accurate corrections to be applied; or 4) if no initial carbonate mineral is present in the rock matrix or pores, the mass and isotopic composition of carbon in the precipitated solid phase can be measured along with the distilled phase to reconstruct the original composition of the pore water.

The first three conditions assume that any carbonate mineral (typically calcite) initially present in the rock does not contribute to the distilled carbon mass. If calcite is present in pores, the pore water should be in chemical equilibrium with respect to calcite. During distillation, calcite should not dissolve because all the changes occurring over time favor precipitation. Evacuation of air from the cell lowers the P_{CO_2} resulting in degassing of CO_2 from the pore water. This drives the pore-water pH upward, which decreases the solubility of calcite. Elevating the temperature also results in lower calcite solubility. Finally, precipitation is further encouraged by the concentration of solutes through the selective removal of water during distillation. It is possible that calcite solubility may increase late in a distillation when solute concentrations are very high. If this occurs, the first solids to dissolve should be those most recently precipitated from the pore water, thus delaying the possibility of incorporating pre-existing mineral carbon into the distilled sample.

While this reasoning suggests that distillation will not draw carbon from a pre-existing solid phase, it also implies that the first condition may not be met, *i.e.*, recovery of DIC may be incomplete. If calcite is initially absent in pores, and pore water is undersaturated with respect to calcite, the distillation process should eventually produce saturated conditions resulting in loss of DIC to the solid phase.

Recovery by distillation was determined by comparing the carbon mass extracted by distillation with the mass left behind in the pores. The mass of residual carbon was determined for six of the distillations by crushing the exhausted core and acid leaching sub-samples as described in the methods section. Replicate determinations using multiple sub-samples from the same distillation gave reproducible results. Distilled carbon recoveries for the six different distillations, however, were highly variable. Recoveries ranged from as low as 15% to as high as 60% of the total available carbon (Table 1). No correlation was observed between recovery and any physical characteristic of the distillation, such as distillation time or heating history. The cause of the variability is uncertain.

Figure 2 plots the carbon mass yield as a function of time for three different distillations. Figure 3 provides the heating history of each sample. Detailed records of water recovery with time were not made, but anticipated water yields were achieved or exceeded for all samples, including two with distillation times of only 4.7 and 5.0 h. Figure 4 plots the water content of DSB core as a function of depth. Water content was determined gravimetrically by weighing core samples before and after drying at 105°C for >10 d (Geddis 1994), and *via* distillation by measuring the distilled water yield and the mass of the rock sample. Most of the distilled samples plot on the gravimetric analysis line, with a few samples plotting at higher water contents.

Although water removal was essentially complete within the first 5 h, carbon removal continued at a diminishing but significant rate until the termination of each distillation as much as 9 h later (Fig. 2). A comparison between the mass of recovered carbon and water suggests that a reservoir of carbon exists in the rock pores in addition to the DIC reservoir, perhaps as CO_2 adsorbed to mineral surfaces. DIC concentrations were calculated for 18 of the distillations by dividing the mass of recovered carbon by the mass of recovered water. One sample was not included because the distilled water was lost before being measured. Calculated DIC concentrations for the remaining 18 samples range from 17 to 124 mg liter^{-1} with a mean of 50 ± 30 mg liter^{-1} (1 σ) (Fig. 5C). Concentrations measured directly from 5 pore-water samples obtained by compression were significantly lower, with a range of 12 to 20 mg liter^{-1} and a mean of 16.6 ± 3.6 (1 σ). The mean distilled-DIC concentration is greater than the most concentrated compression sample by a factor of 2.5 (Table 2).

TABLE 1. Carbon recovery for six distillations using DSB core samples. Recovery is defined as the mass of carbon recovered by distillation divided by the total mass of carbon recovered by both distillation and acid leaching. Core samples were initially free of carbonate minerals. Multiple entries represent replicate measurements using *ca.* 500 g sub-samples from the same distilled core.

Sample depth (m)	Distillation time (h)	Distilled C/rock (mg kg^{-1})	Leached C/rock (mg kg^{-1})	Distilled recovery (%)	Mean recovery (%)
9	5.0	1.02	2.31	30.7	30.0
			2.58	28.4	
			2.88	26.2	
			2.50	29.0	
			1.84	35.7	
15	13.8	1.97	2.20	47.2	47.2
20.5	13.3	3.37	2.16	61.0	61.3
			2.16	61.6	
69.3	14.8	0.64	3.67	14.8	15.2
			3.46	15.5	
150	12.2	1.71	3.59	32.3	32.9
			3.41	33.4	
155.4	13.5	1.95	4.78	29.0	29.6
			4.52	30.2	

This value becomes even larger if the unrecovered carbon fraction is added to the DIC calculation. Using the total carbon mass measured from the six distilled and leached samples, calculated DIC concentrations range from 60–180 mg liter^{-1} with a mean of 121 ± 60 mg liter^{-1} (1 σ). The mean of these six samples is greater than the most concentrated compression sample by a factor of 6 (Table 2).

The additional mass of carbon appears high, but is consistent with the results of soil-CO_2 studies by Striegl (1988) and Striegl and Armstrong (1990). These investigations reported an apparent adsorbed carbon reservoir on glacial and eolian sediments from Illinois that exceeded the mass of carbon dissolved in the sediment pore-water by 8 to 17 times. These authors speculated that iron oxides may play a significant role in CO_2 adsorption. Although the adsorption mechanism is not known, iron and manganese oxides in the Apache Leap Tuff may also play a significant role in CO_2 adsorption.

The possibility of an undetected leak in the extraction line was ruled out as a possible source of the additional carbon, because the mass and isotopic composition of the recovered samples are not consistent with a leak. Incorporation of atmospheric carbon should result in a correlation between ^{14}C, $\delta^{13}C$ and carbon/water recovery results with extraction time. Longer distillations should produce carbon with elevated ^{14}C activities, heavier (less negative) $\delta^{13}C$ values, and higher carbon/water

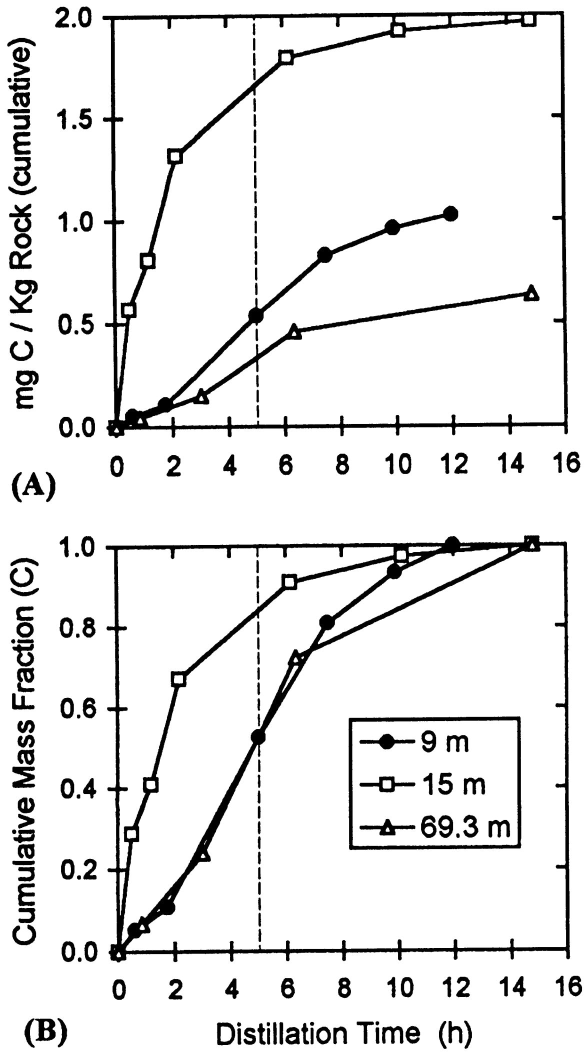

Fig. 2. A. Cumulative mass of extracted carbon per kilogram rock during distillation of three DSB core samples. B. Cumulative mass-fraction of carbon collected during distillation of three DSB core samples. --- identifies the approximate time by which water recovery was essentially complete.

recovery ratios. Figure 5 plots each of these with respect to time to demonstrate that no correlations exist. The sample with the highest ^{14}C activity may be individually suspect because it also has an anomalously high recovered carbon/water ratio, but the $\delta^{13}C$ is consistent with the other distillations (Fig. 5). Incorporation of a large mass of atmospheric carbon should have raised the $\delta^{13}C$ value closer to an atmospheric value of *ca.* -8‰.

The carbon/water ratio could appear falsely high if water recovery during distillation was incomplete or if evaporative losses occurred during storage. Figure 4, however, documents that distilled water yields were equal to or higher than anticipated based on gravimetrically determined water content measurements on core from similar depths. Weight records of monitored core packages also document that the preservation method was effective in preventing significant evaporative losses during storage (Davidson 1995).

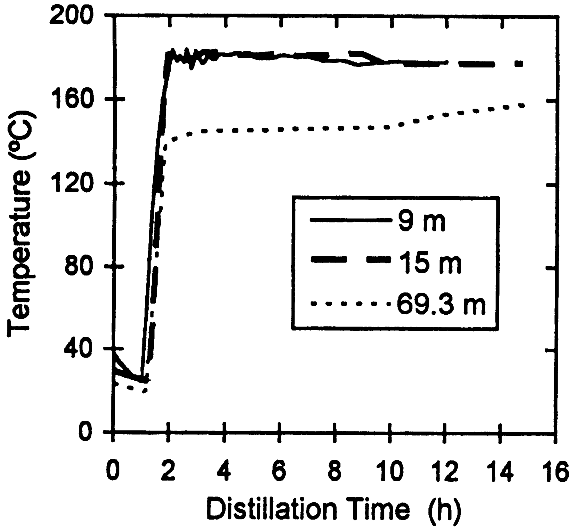

Fig. 3. Temperature of the stainless-steel cell during distillation of three DSB core samples

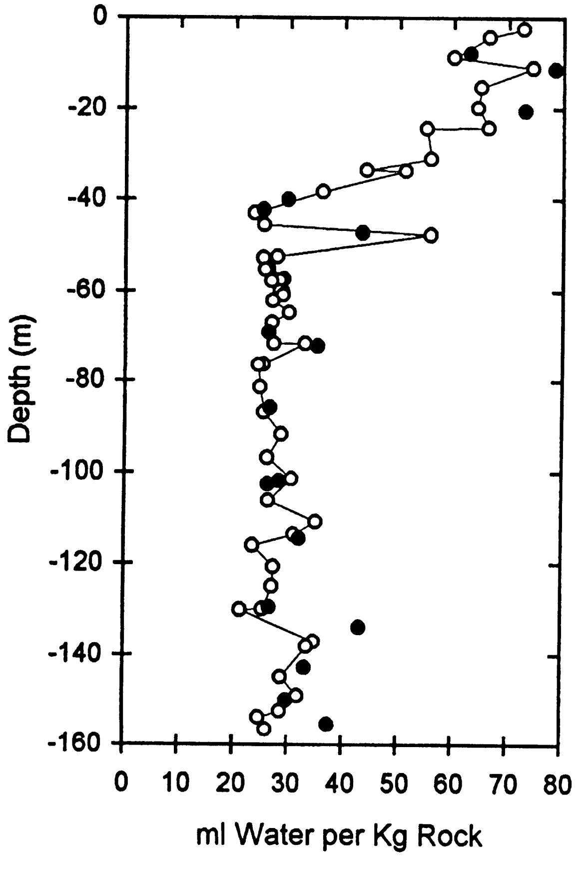

Fig. 4. Water content of DSB core measured by gravimetric analysis (○ , Geddis 1994) and by distillation (●, Davidson 1995). The two filled circles nearest the surface are the samples distilled for the shortest period of time.

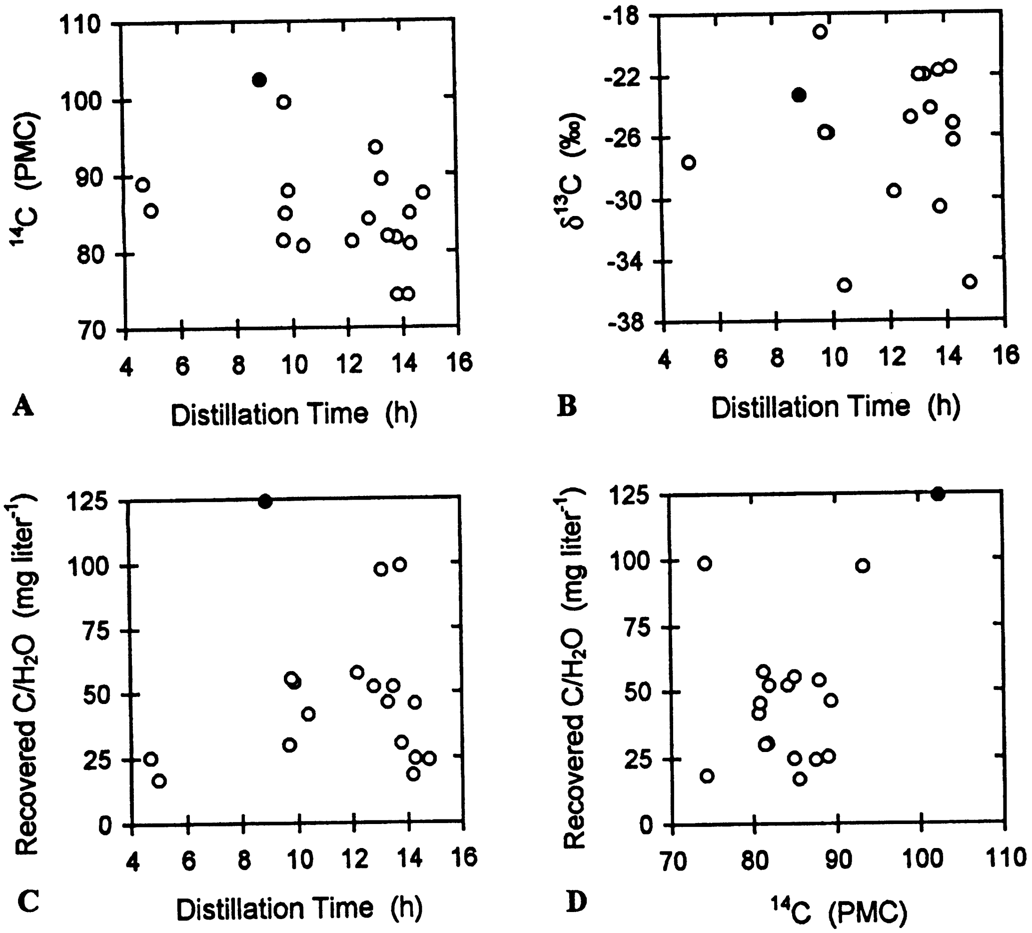

Fig. 5. Total distillation time *vs.* A. ^{14}C activity, B. δ^{13}C, and C. carbon mass recovered per volume of water recovered from DSB core samples. D. compares ^{14}C activity with the carbon/water recovery data from C. In A–D, the sample with the highest ^{14}C activity is shown as ●. All samples represent cumulative carbon recovery at the end of distillation.

Both incomplete carbon recovery and partial incorporation of adsorbed carbon into the recovered phase can potentially result in isotopically fractionated samples. We investigated the degree of fractionation over time by measuring the δ^{13}C for each extraction stage shown in Figure 2. Figure 6 plots changes in δ^{13}C over time. Gas/aqueous exchanges favor ^{12}C in the gas phase, leaving behind an aqueous phase enriched in ^{13}C (Friedman and O'Neil 1977). The low initial δ^{13}C values plotted in Figure 6 reflect this phenomenon. Subsequent carbon transferred to the gas phase continues to be isotopically lighter than the aqueous phase but, as the aqueous reservoir becomes increasingly heavy, degassing carbon also trends heavier with time.

At some point following the increase in temperature, calcite saturation is reached and precipitation begins. The heavier isotope is favored in the solid phase resulting in a depletion of ^{13}C in the aqueous phase (Friedman and O'Neil 1977). The decrease in distilled δ^{13}C values after 2 to 3 h (Fig. 6A) suggests that the rate of precipitation eventually exceeds the rate of degassing by a factor large enough to cause a net depletion of ^{13}C from the aqueous phase.

TABLE 2. Calculated and measured DIC concentrations in pore water from DSB core samples. Distilled DIC concentrations are calculated from the mass of carbon and water recovered by distillation alone. Distilled and leached DIC concentrations are calculated from the mass of carbon recovered by both distillation and acid leaching, and the mass of water recovered by distillation. DIC concentrations in pore waters obtained by compression were measured directly.

	DIC concentrations determined from:		
Sample depth (m)	Distillation only (mg liter^{-1})	Distillation and leaching (mg liter^{-1})	Compression (mg liter^{-1})
7.8	25	--	--
8.5	--	--	14
9	17	60	--
11	--	--	20
12	--	--	20
15	30	64	--
15.6	--	--	--
20.5	46	76	--
21	--	--	12
39.9	42	--	--
42.2	99	--	--
47.1	52	--	--
69.3	24	171	--
72.3	25	--	--
86	54	--	--
101.8	97	--	--
102.5	55	--	--
114.6	30	--	--
129.4	124	--	--
133.8	18	--	--
142.7	46	--	--
150	57	177	--
152.8	--	--	24
155.4	52	180	--

After the bulk of the water was distilled from the pores, carbon continued to be removed. If ^{13}C is favored in an adsorbed phase relative to the gas phase, the $\delta^{13}C$ of recovered carbon should begin to increase as residual absorbed carbon becomes enriched in ^{13}C, but this expected trend was not observed. The continued decrease in the $\delta^{13}C$ of time series samples beyond the first 5 h suggests that factors other than simple molecular kinetic energy determine isotopic preference in the adsorbed phase (Fig. 6A).

High initial $\delta^{13}C$ variability between core samples was diminished as more carbon was collected. The final values in Figure 6B are within a 6‰ range compared to initial differences of nearly 20‰. Table 3 compares the cumulative $\delta^{13}C$ of carbon collected by distillation with carbon extracted from pore waters obtained by compressing the core. Comparisons were only possible in the top 21 m of the formation because the compression method would not yield sufficient water from core deeper than 21 m. The distilled samples have $\delta^{13}C$ values significantly lower than the compression samples.

The results also appear too variable to allow a simple correction to be applied, so the second and third conditions stated at the beginning are not met for stable carbon isotopic applications. The $\delta^{13}C$ of all distilled samples ranged from −19.2 to −35.7‰ with a mean of −25.9 ± 4.6‰ (1 σ) (Fig. 5B).

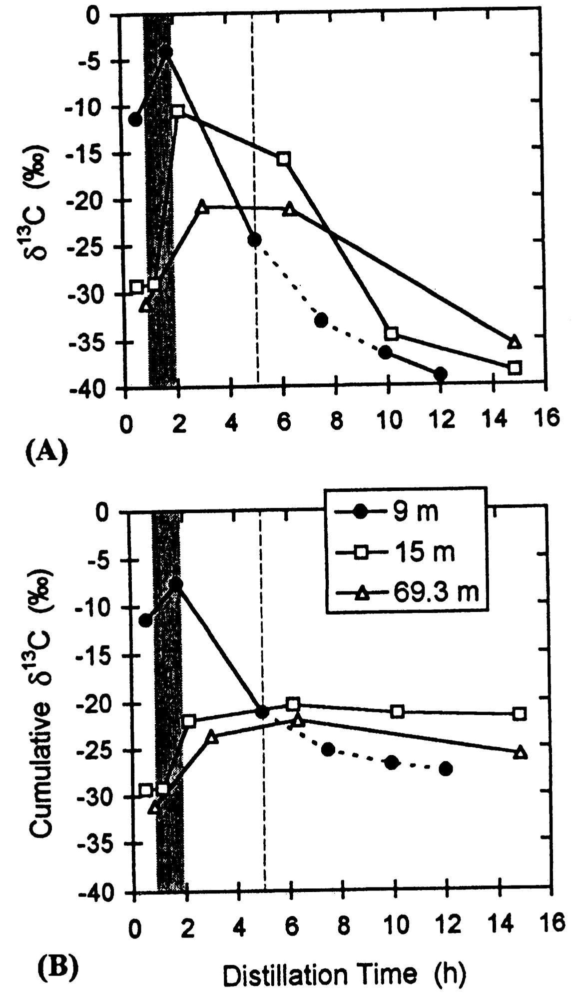

Fig. 6. A. $\delta^{13}C$ of carbon distilled from three DSB core samples *vs.* time. B. Cumulative $\delta^{13}C$ of carbon distilled from three DSB core samples *vs.* time. The fourth sample at 9 m was lost. The data point shown is extrapolated from the other points. ▓ identifies the period of increasing temperature. --- identifies the approximate time by which water recovery was essentially complete.

We attempted to reconstruct the original pore water $\delta^{13}C$ by acid leaching and analyzing the residual carbon from three distilled core samples. The $\delta^{13}C$ and mass of residual carbon was used to correct the $\delta^{13}C$ of the distilled carbon according to

$$\delta_{PW} = \delta_D f_D + \delta_L (1 - f_D) \tag{1}$$

where δ_{PW} is the reconstructed $\delta^{13}C$ of pore-water DIC, δ_D and δ_L are the measured $\delta^{13}C$ of distilled and leached carbon, respectively, and f_D is the fraction of distilled and leached carbon recovered by distillation alone. Table 4 compares the reconstructed $\delta^{13}C$ results with the measured values from pore waters obtained by compression (some data are repeated from Tables 1 and 3). The reconstructed $\delta^{13}C$ are similar to the measured values, but spatial heterogeneity in the isotopic composition of pore waters prevents firm conclusions from being drawn on the accuracy of this approach.

TABLE 3. Pore-water δ^{13}C in DSB core samples using distillation and compression methods. Distillation results are for cumulative carbon samples collected at the end of distillation. Analytical precision = 0.2‰ (2 σ)

Sample depth (m)	Distillation δ^{13}C (‰)	Compression δ^{13}C (‰)
9	−27.6	--
11	--	−13.7
12	--	−14.9
15	−21.7	--
20.5	−22	--
21	--	−18.5

The maximum error for uncorrected δ^{13}C measurements was with the order of 20‰, based on comparisons with the δ^{13}C of pore water collected by compression, and the δ^{13}C of formation CO_2 samples. Formation CO_2 was collected from seven 1-m intervals in the DSB at depths ranging from 4 to 130 m. The mean δ^{13}C was −21.7 ± 0.4‰ (1 σ). No trend was observed with depth. If isotopic equilibrium is established between mean formation CO_2 and pore water with a pH of 7 and a temperature of 20°C, the δ^{13}C of pore water DIC should be *ca.* −18‰ (Friedman and O'Neil 1977). The largest difference observed between this value and the distilled δ^{13}C results is *ca.* 18‰ (Fig. 5B). The largest difference observed between the δ^{13}C of samples obtained by distillation and by compression (Table 4) is *ca.* 22‰.

TABLE 4. Reconstructed pore-water δ^{13}C for DSB core samples are calculated using Eq. (1) and are compared with the measured values from pore water obtained by compression. Analytical precision for δ^{13}C = *ca.* 0.2‰. Summing possible errors for the reconstructed values gives a precision of *ca.* 1.0‰ (2 σ).

Sample depth (m)	Distilled fraction δ^{13}C (‰)	Leached fraction δ^{13}C (%)	Mean distilled recovery (%)	Reconstructed pore-water δ^{13}C (‰)	Measured pore-water δ^{13}C (‰)
9	−27.6	−15.2	30.0	−18.9	--
11	--	--	--	--	−13.7
12	--	--	--	--	−14.9
15	−21.7	−2.6	47.2	−11.6	--
20.5	−22	−5.3	61.3	−15.5	--
21	--	--	--	--	−18.5

A δ^{13}C error of 20‰ is large considering current analytical precisions of ±0.2‰ (2 σ) or less, and the interpretational importance of isotopic shifts of 1 or 2‰ (Davidson 1995). Isotopic fractionation of ^{14}C relative to ^{12}C will be about twice as large as ^{13}C/^{12}C fractionation (Fritz and Mozeto 1980; Mook 1980), but the error is less significant for ^{14}C than for δ^{13}C applications because analytical precision and interpretation of ^{14}C measurements are much less precise. Typical analytical precision using accelerator mass spectrometry (AMS) is *ca.* 1% (10‰) (2 σ), and shifts of 1 or 2% are negligible when interpreting results. A possible ^{14}C error of 4% is not trivial, but is relatively minor for most applications.

It is important to note that a possible 4% error does not mean that the measured ^{14}C activity will be 4 pMC lower than the true value. The error is a fraction of the true value, which means that the error in terms of pMC will decrease with older samples. For example, if the true activity of a sample is 75 pMC, a 4% error will give a result of 72 pMC (an error of 3 pMC). Likewise, if the true activity is 50 pMC, a 4% error will give a result of 48 pMC (an error of 2 pMC).

Figure 7 shows the results of a direct comparison of the ^{14}C activity of distilled samples with the activity of pore-water samples obtained by compression, and with the activity of formation air drawn from 1-m intervals in the DSB. The relative agreement between the different methods at equivalent depths demonstrates that distillation can be used to obtain representative ^{14}C activities of pore-water DIC. At each depth, the difference between the various methods is <4%.

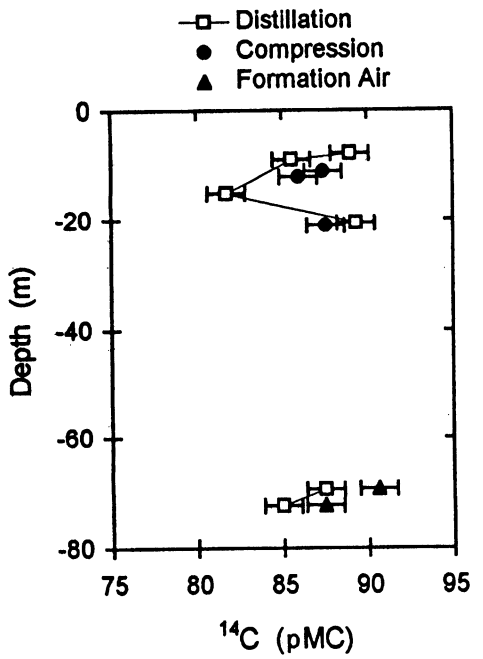

Fig. 7. ^{14}C activity of formation CO_2 drawn from 1-m intervals in the DSB, and of pore-water DIC obtained by distillation and by compression methods. Error bars represent the analytical precision (2 σ).

In-situ exchange between adsorbed and dissolved carbon appears to be fairly rapid. If exchange is very slow, distillation should produce samples with reduced ^{14}C activities as a result of incorporating older adsorbed carbon into the sample. Similarity between the activity of compressed and distilled samples indicates that the absorbed carbon extracted during distillation is not significantly older than the dissolved phase. Relatively rapid exchange is also indicated by the presence of post-bomb activity in two samples even though most of the mass was derived from the adsorbed phase (Fig. 5A).

CONCLUSION

About 15–60% of the inorganic carbon in the rock pores was recovered by distillation, with the remainder precipitating in the pores as solid carbonate or left behind as unretrieved adsorbed carbon. Incomplete recovery resulted in isotopic fractionation favoring the lighter isotopes in the recovered phase. Isotopic fractionation was too variable to allow corrections to be made for calculating the stable isotopic composition of the pore waters. Variability was especially high during the first 2 h of each distillation, but diminished after *ca.* 5 h. Attempts to reconstruct the original isotopic composition of pore water by comparing the mass and isotopic composition of recovered gas and residual carbon were inconclusive.

The impact of fractionation on ^{14}C measurements is much less significant. The maximum fractionation in this study, based on calculations using observed stable isotope fractionation, was *ca.* 4%. We found close agreement between the ^{14}C activity of distilled samples and the activity of formation CO_2 and pore-water DIC obtained by other methods. The maximum difference between samples from equivalent depths was <4%.

The carbon mass recovered from each sample was several times greater than that anticipated based on measured DIC concentrations in pore waters obtained by compression. Comparisons of $\delta^{13}C$ and ^{14}C measurements with distillation time eliminated the possibility of a leak in the distillation system. We speculate that the high yield is a result of recovering a sizable reservoir of adsorbed carbon. This reservoir appears to be readily exchangeable with the dissolved phase since incorporation of adsorbed carbon in distilled samples did not measurably alter the ^{14}C activity relative to compression pore water samples or formation CO_2 samples.

ACKNOWLEDGMENTS

This study was funded by the Nuclear Regulatory Commission (contract no. NRC-04-90-051). We express our appreciation to the staff at the NSF-Arizona AMS Facility for allowing us to use laboratory space and for their assistance in the use and repair of several high-vacuum lines.

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