

QUANTITATIVE EXTRACTION OF DISSOLVED INORGANIC CARBON (AS CO₂) AND WATER BY VACUUM DISTILLATION FROM SEDIMENTS OF THE UNSATURATED ZONE FOR CARBON ISOTOPE ANALYSIS (¹³C AND ¹⁴C)

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ABSTRACT. Vacuum distillation is shown to be useful for the quantitative extraction of dissolved inorganic carbon (as CO₂) and water from sediments of the unsaturated zone in the Coastal Aquifer of Israel. Several tests of vacuum extractions from tap water and sediments are presented, including standard addition, which show that the distillation procedure is quantitative, with minimal or no carbon isotope fractionation. The optimal temperature of the sediment during the extraction was also defined. Examples of vacuum extractions of sediments are shown.

INTRODUCTION

Extraction of dissolved inorganic carbon (DIC) from sediment pore water is a difficult process. To study carbon isotopes in the unsaturated zone (USZ), the reliability of the extraction must be ascertained quantitatively with minimum fractionation. This is the subject of the present paper.

Three methods are generally available for the extraction of water and dissolved species, including DIC, from sediments: 1) centrifugation, 2) pressure squeezing, and 3) vacuum distillation of water and DIC (as CO₂). The most widely used and simplest method is centrifugation. Sediment is placed in centrifuge vials and centrifuged to squeeze pore water and dissolved chemicals out of it. Edmunds and Bath (1976), though, have observed changes in the chemical composition of progressive, partial fluid extraction from the sediment. A variation on this method uses an immiscible fluid to displace water from the sediment during centrifugation (Kinniburgh and Miles 1983). Here, too, changes in chemical composition are exhibited during progressive extractions. The second method is extraction of pore fluids by high-pressure squeezing (Böttcher et al. 1997). This method is cumbersome and, in addition, suitable equipment is not as widely available as centrifuges. Yet, likewise, an increase in the concentrations of practically all the chemical constituents with progressive pore water extraction is reported (Böttcher et al. 1997). In both the centrifugation and the pressure squeezing extraction techniques, the removal of the liquid phase is never complete because some of the liquid stays in the sediment. Also, these methods can work only with sediments that have high water content.

In the 3 investigations mentioned above, fractionation of carbon isotopes was not studied. However, it is reasonable to assume that fractionation of carbon isotopes does take place between the extracted fraction and the remaining sediment because, with progressive removal of liquid, the chemical constituents become more concentrated in the residue.

In the third method, sediment pore water along with CO₂ (from DIC) is distilled out of the sediment under vacuum (Davidson et al. 1995). As CO₂ leaves the solution, the equilibrium between the species of DIC shifts toward CO₂, which again leaves the solution. The information on the chemical composition of the sediment pore water is lost in this extraction method and fractionation of carbon isotopes may occur. Davidson et al. (1995) operated this method at 180 °C and reported a difference

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of -8% between vacuum distillation and high-pressure squeezing, ^{14}C fractionation of $<4\%$, and a loss of up to 60% of the carbon from the DIC by precipitation of carbonate according to the equation:



(Stumm and Morgan 1995). The findings of Davidson et al. (1995) are an *a priori* limitation on the use of this method for extraction of CO_2 from pore water in order to get reliable ^{14}C and DIC data. Thus, there is no “off the shelf” satisfactory extraction method; all 3 methods can be problematic in their application to DIC and its isotopic composition in pore water of the USZ. A method to successfully apply vacuum distillation to extract sediment water and DIC from sediments for quantitative analysis of DIC and isotopes is reported in this paper.

METHODS

In October 2003, a sediment profile was collected in a drilling to the water table at Nitzanim, in the Coastal Aquifer of Israel. The mineralogical composition of the sediment profile was clay (5–25%), quartz (50–80%), and carbonate (1–15%).

Attempts to extract sediment pore water from the Nitzanim sediments by centrifugation did not produce significant amounts of water for measuring DIC by available analytical methods. The use of pressure squeezing on the sediments was judged to be impractical (A Shvartzman, private communication, following visual inspection of the wet sediments). Therefore, it was decided to try improving the third option, of extracting DIC (as CO_2) and pore water by vacuum distillation (Davidson et al. 1995).

The extraction procedure comprised of the following: ~ 200 g of sediment were divided into subsamples of about 1 cm^3 , which were then introduced into a 1-L glass vessel that could be sealed by a valve. Before commencing to extract DIC and water, the vessel was connected to the vacuum system (Figure 1) and evacuated in 2 steps. The first step was pumping the vacuum system up to the valve of the glass vessel. In the second step, the valve was opened and the vessel evacuated for a few seconds down to ~ 100 torr. If the vessel had not been previously evacuated, atmospheric CO_2 contamination, estimated at ~ 0.2 mg C, would be present. After the rough pumping, this initial quantity of atmospherically derived CO_2 is reduced to ~ 0.03 mg C. This is quite negligible compared to the amount of carbon collected in the extractions. The target vacuum of the rough pumping is higher than the vapor pressure of water at room temperature. Following this pumping, the vessel is put in a heating mantle with temperature control.

The extraction was tested at 3 temperatures: 30, 70, and 100 °C. Water vapors and CO_2 were pumped out of the heated glass vessel and collected in the respective traps: 2 water traps cooled by a dry-ice/ethanol mixture and 3 traps for the CO_2 (derived from the DIC) cooled by liquid nitrogen (Figure 1). The process was interrupted periodically to measure the masses of water and of carbon (as CO_2) in order to evaluate the progress of the extraction. In several cases, partial fractions of CO_2 were harvested for ^{13}C measurement (Figure 8). Stable carbon isotopes ($\delta^{13}\text{C}$) were measured at the Weizmann Institute of Science using an Atlas Mat 250 mass spectrometer with a precision of $\pm 0.1\%$. ^{14}C was measured at the NSF AMS facility in Tucson. To gain confidence in the extraction procedure, several tests were performed:

1. Leaks in the extraction system. The empty vessel used for the extractions of water and DIC from the sediments was connected to the vacuum system (Figure 1). It was then evacuated to high vacuum to avoid collecting any initial atmospheric CO_2 . Following this, gases were collected by pumping for 6 hr through the cryogenic traps of dry ice/ethanol and of liquid nitrogen,

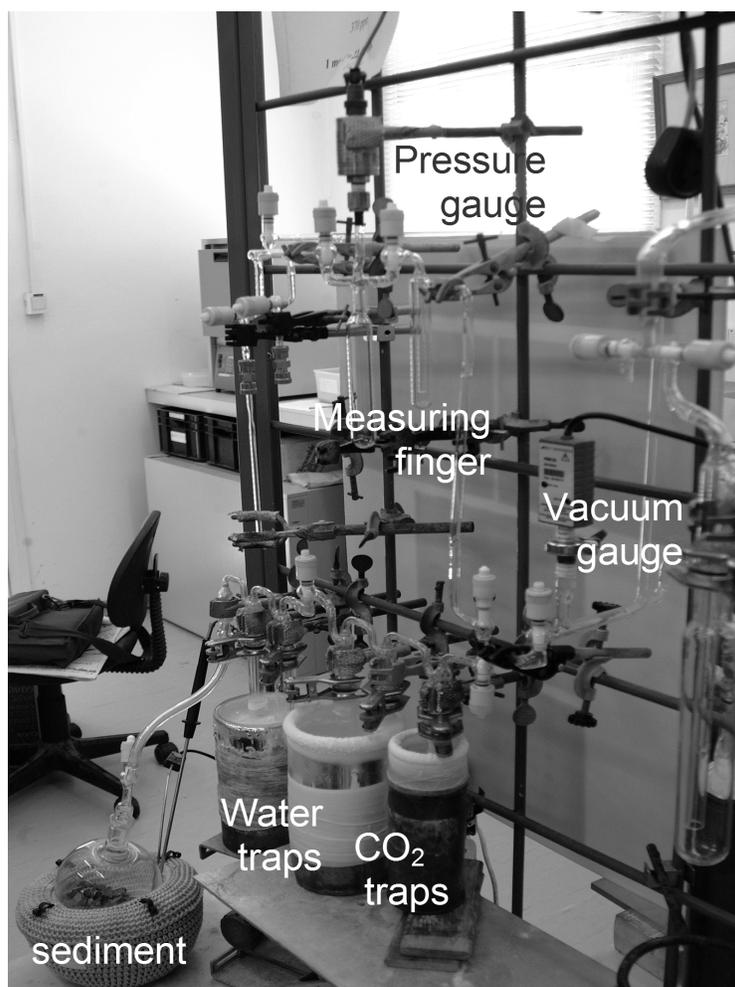


Figure 1 Sample preparation system, shown during the process of extraction of DIC and soil water from sediments in the vessel to the left inside the heating mantle. Note that in the large Dewar on the left there are 2 water traps and in the large Dewar next to it there are 2 CO₂ traps; in the small Dewar on the right is the third CO₂ trap.

keeping the vessel at room temperature. The volume of the collected gas was then measured in the measuring finger (Figure 1).

2. Efficiency of extraction of DIC from tap water. A measured quantity of tap water was vacuum distilled to check the efficiency of the extraction. The DIC and $\delta^{13}\text{C}$ of the water were independently determined by acid extraction with phosphoric acid under vacuum on aliquots of the tap water.
3. Decomposition of carbonate from the sediment in the extraction procedure. To check whether carbonate in the sediment may decompose during the process of vacuum extraction of DIC, 10 g of analytical-grade CaCO₃ (1200 mg of carbon) were put into a vessel connected to the vacuum system (Figure 1) and evacuated to high vacuum. The vessel was then heated to 100 °C and pumped. The pumped gases were collected in the cryogenic traps (Figure 1) over a period of 6 hr. Their volume was determined using the measuring finger (Figure 1).

4. Standard addition. Unprocessed sediment was wetted with a quantity of tap water. The amount added was equal to the water content of the sediment of the specific sample. Water and DIC, as CO₂, were then extracted at 100 °C for 8 hr.

RESULTS AND DISCUSSION

Leaks in the Extraction System

The collected gas from the CO₂ traps in this experiment was transferred to the calibrated finger in the vacuum system (Figure 1). The pressure gauge indicated 0 torr and the gas was measured with a vacuum gauge, which indicated 4.6×10^{-2} torr. It is quite possible that the vacuum gauge reading indicates the static vacuum of the system as opposed to the dynamic vacuum while pumping, which is $<1 \times 10^{-3}$ torr. At 25 °C and 60% relative humidity, there is ~2% water vapor in the atmosphere as well as ~0.04% CO₂. If there had been a leak, an accumulation of water from the atmosphere would have been very noticeable compared to the accumulated amount of CO₂. None was observed and, therefore, it seems that the extraction line was secure against leakage.

Extraction of DIC from Tap Water

Table 1 shows the measurements of DIC and $\delta^{13}\text{C}$ from several samples of tap water liberated by *acid extraction*. Aliquots of the same tap water samples were then used for vacuum extractions of tap water and for a standard addition experiment. The measured $\delta^{13}\text{C}$ (–10.0 to –12.3‰, Table 1) of the acid extractions are similar to that of the Coastal Aquifer of Israel (an average $\delta^{13}\text{C}$ [‰] of -11.4 ± 1.7 , calculated from Bruce et al. [2001]), which is the source of the tap water. The reproducibility of the first batch of 4 samples was good. Thus, subsequent measurements of DIC and its associated $\delta^{13}\text{C}$ liberated from the tap water by acidification employed only single aliquots.

Table 1 DIC and $\delta^{13}\text{C}$ from acid extraction of tap water.

Date of extraction	Tap water sample	Water used (g)	C recovered (mg)	DIC (mmole C /L)	$\delta^{13}\text{C}$ (‰)
12 Feb 2005	1a	80.4	3.9	4.0	–11.5
12 Feb 2005	1b	85.2	4.1	4.0	n.m.
12 Feb 2005	1c	43.0	2.0	3.9	n.m.
25 May 2005	1d	44.5	2.3	4.3	–12.0
25 May 2006	2	12.0	0.6	3.9	–12.3
17 Oct 2006	3	22.2	1.1	4.3	–10.0

The *vacuum extraction* of tap water was carried out by pumping it in the vacuum system at room temperature, in order to avoid extreme boiling of the water, during pumping. After the vacuum extraction of the tap water on 19 May 2005 (Table 2), a white precipitate formed at the bottom of the water vessel.

Table 2 DIC and $\delta^{13}\text{C}$ following vacuum extraction of tap water.

Date of extraction	Tap water sample	Water used (g)	C recovered (mg)	C (mmole/L)	$\delta^{13}\text{C}$ (‰)
19 May 2005	1c	51.3	2.6	4.2	–10.7
27 May 2006	2	13.4	0.6	3.7	–9.1

The precipitate dissolved in phosphoric acid, but it did not produce additional CO₂. It was concluded that the precipitate was devoid of carbonate and represented tap water mineral salts. The extraction of 27 May 2006 also produced a precipitate, which was redissolved in water and submitted for chemical analysis. The chemical analysis yielded concentrations of the major ions similar to those of tap water, though the bicarbonate was not measured because the sample was too small. The DIC of the vacuum extraction (Table 2) is quite similar to the same tap water measured by acid extraction (Table 1).

The last experiment with tap water was carried out in 3 steps. The first step was a vacuum extraction, to dryness at room temperature. The second step was pumping of the precipitate at 100 °C for 2 hr and collecting the gas. The third and final step was acidifying the residual precipitate and pumping off the CO₂. The results are shown in Table 3. C_{extracted} and (C_{pumped} + C_{acidified}) have similar values, indicating that in this extraction ~50% of the DIC was released as CO₂ and ~50% precipitated as carbonate in the vessel. More important, there is clear evidence that 40% of the precipitated carbonate (C_{pumped} + C_{acidified}) decomposed by continued pumping of the hot, dry vessel (step 2).

Table 3 Extraction of DIC from tap water sample 3, in 3 steps.

Date of extraction	Water used (g)	C _{total} recovered (mg)	C (mmole/L)	C _{extracted} (mg)	C _{pumped} (mg)	C _{acidified} (mg)
11 Jul 2006	14.1	0.9	5.0	0.4	0.2	0.3

Thus, 2 tentative scenarios of extraction have been observed in the tap water extraction. In the first scenario, no carbonate is left as precipitate, so that all had decomposed during the first stage of the extraction (Table 2). In the second scenario, carbonate did precipitate but then decomposed (assumed completely)¹, so that the total carbon is collected in 2 stages (Table 3). It is not clear which conditions define the prevalence of 1 of the 2 scenarios in the extraction process. Examples for the operation of the 2 scenarios on sediments are shown below.

Decomposition of Carbonate

The experiment to extract solid carbonate mimics possible decomposition of sedimentary carbonate during vacuum extraction of the sediment. At the end of the carbon decomposition experiment, the gases from the CO₂ traps measured a static vacuum of 5×10^{-1} torr on the vacuum gauge. This pressure is 1 order of magnitude higher than in the leak test described above. A rough estimate of the amount of the gas released via decomposition of carbonate can be made. If it is assumed that the reading is solely related to pressure of CO₂, then, in the specific vacuum system that was used, 0.5-torr pressure corresponds to 0.025 mg C. Thus, at most 0.002% of the carbonate could conceivably have been decomposed. This small quantity is insignificant compared to the extracted DIC (several mg of carbon for a typical sample) and has a negligible effect on the extracted DIC and its carbon isotopes.

Standard Addition Experiment

Sediment, weighing 100.2 g, from a depth of 13.5 m in the USZ was used. Tap water (14.6 g), with 4.3 mmole C/L (sample 3 in Table 1), was added to it. The extraction was carried out for 8 hr at

¹Qualitative observation by the first author was that during the distillation of groundwater for electrolytic enrichment prior to tritium analysis, when the water vessel was dry and the precipitate heated for some time, in several cases the precipitate evaporated almost completely and the vessel became almost clear, with some nonvolatile salts remaining.

100 °C. During a previous extraction of this sediment, in which DIC and isotopes were measured, the water content of 100.2 g of sediment was 15.0 g and the yield of carbon was 15.3 mmole C/L. In the standard addition experiment, 29.3 g of water were extracted. Of this, 14.6 g represent the added tap water, while 14.7 g were derived from the sediment (i.e. 98% efficiency). The measured DIC of the standard addition was 10.1 mmole C/L. This can be compared to a calculation of the DIC of the standard addition from the DIC of the tap water (sample 3 in Table 1) and from that of the isotope extraction (15.3 mmole C/L). From the quantities of the tap water and the sediment water that were used, it is possible to calculate:

$$\frac{4.3 \times 14.6 + 15.3 \times 15.0}{29.3} = 9.9 \text{ mmol C/L.}$$

Thus, the measured DIC is 102%, which is practically the same as the calculated value. The $\delta^{13}\text{C}$ of the standard addition experiment was -10.6‰ , very close to the values of tap water, -10.0‰ (Table 1), and for DIC extracted from the 13.5 m sediment, -10.4‰ . The ^{13}C data cannot unequivocally contribute to the evaluation of the standard addition experiment because all the $\delta^{13}\text{C}$ values are so similar. Yet, it can support the contention that a complete extraction was obtained in this experiment. The experiment is summarized in Table 4.

Table 4 Summary of the standard addition experiment (SA).

Sample	DIC (mmole C/L)	Water (g)	$\delta^{13}\text{C}$ (‰)
Sediment	15.3	15.0	-10.4
Added tap water	4.3	14.6	-10.0
Expected in SA run	9.9	29.6	
Measured in SA run	10.1	29.3	-10.6
Yield (%)	102	98	

Extractions

Extractions from Sediments Having Different Clay Content at the Same Temperature

Figures 2 and 3 compare the amounts of water and carbon liberated, over time, at an extraction temperature of 30 °C, from sediments having greater and lesser percentages of clay: 25% at 9 m depth and 15% at 15 m depth. The extraction was continued for a significant amount of time after the extraction curve “flattened.” It seems that the clay component of the sediment exerts a retarding influence on the rate of the extraction.

The Effect of Increasing the Temperature of the Extraction

The effect of increasing the temperature from 30 to 70 °C during a continuous extraction of sediment rich in clay (25%) is shown in Figure 4. An additional 4% of water and 14% of CO_2 were extracted. Figure 5 shows the effect of increasing the temperature from 70 to 100 °C during the continuous extraction of sediment containing only 15% clay. This increased the yield of water by 0.8% and gave off an additional 3% of CO_2 . The extractions were always continued to a stage in which no further CO_2 and water were released from the sediment.

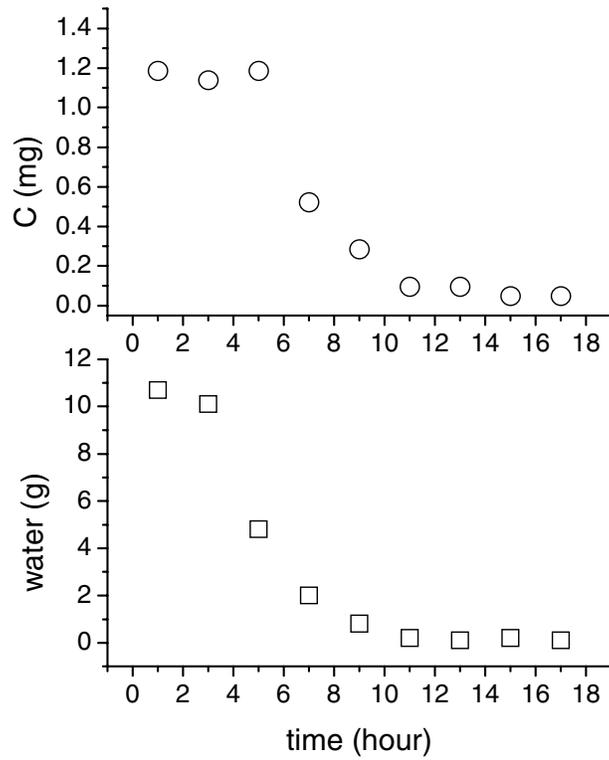


Figure 2 Extraction of water and DIC at 30 °C from sediment richer in clay from 9 m depth.

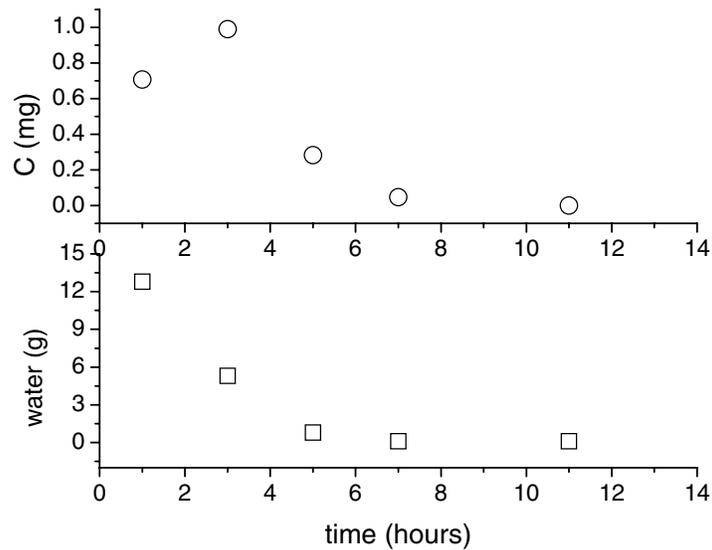


Figure 3 Extraction of water and DIC at 30 °C from sediment poorer in clay from 15 m depth.

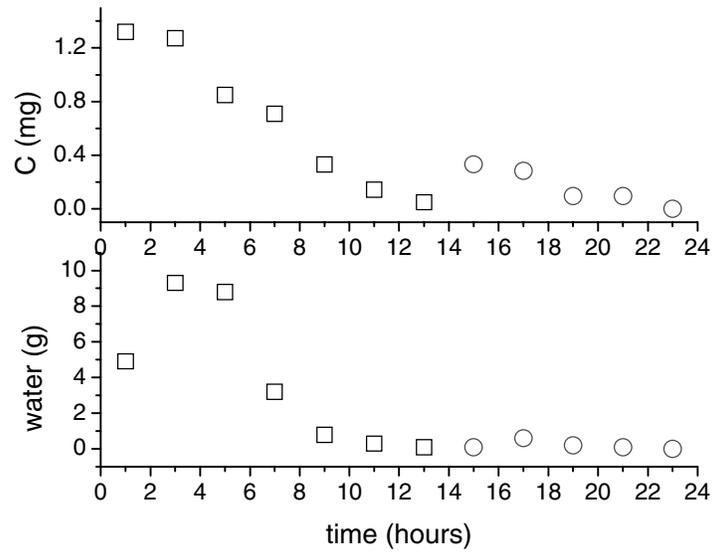


Figure 4 Continuous extraction of DIC and water at 13.5 m, at 30 °C (squares) and 70 °C (circles), from sediment rich in clay.

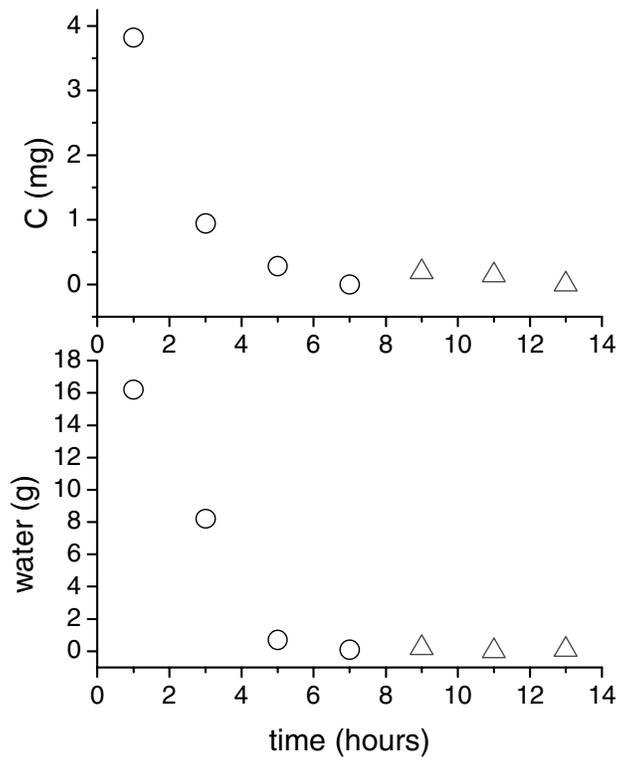


Figure 5 Continuous extraction of DIC and water at 70 °C (circles) and 100 °C (triangles) from sediment poor in clay from 10.5 m depth.

Twin Peaks Extractions

In the extraction from the sediment at 12 m at temperatures of 30 °C and 100 °C, a second phase of CO₂ production was noted, unaccompanied by additional water production (Figures 6 and 7, respectively). This effect was not observed in the 12 other extractions of Nitzanim sediments, although they were carried out for a comparable amount of time. Considering the test for carbonate decomposition discussed previously, it is clear that sedimentary carbonate decomposition cannot be the source of the second-phase CO₂.

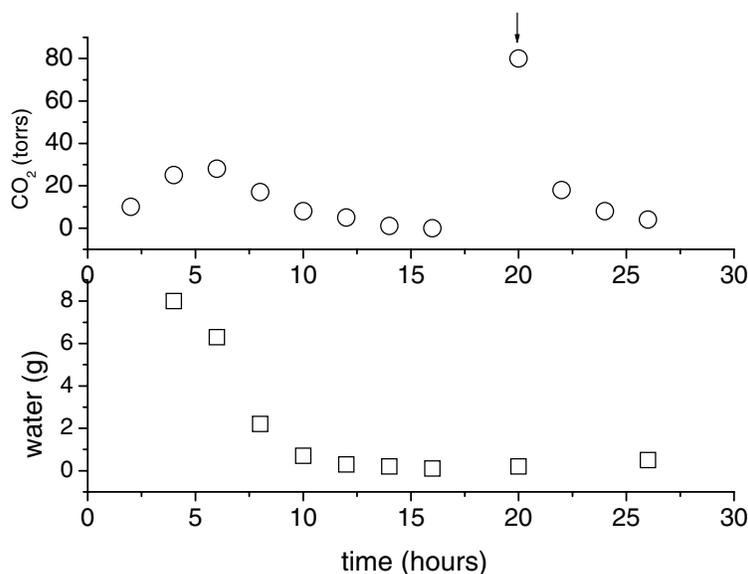


Figure 6 Secondary evolution of CO₂ in the 12 m sediment, 30 °C extraction (1 mg C = 21.5 torr).

The second scenario of the vacuum extraction of tap water can explain the secondary CO₂ as decomposition of carbonate molecules precipitated from the DIC and, therefore, it originates from the DIC. Davidson et al. (1995) suggest that the secondary release of CO₂ mimics the decomposition of calcite.

Progressive Fractions

To study the evolution of $\delta^{13}\text{C}$ with progressive extraction of DIC (as CO₂), 2 extraction experiments were performed at 30 °C on the same sediment (from 9 m depth at Nitzanim). In these experiments, consecutive fractions of CO₂ were collected and the $\delta^{13}\text{C}$ of each CO₂ fraction was measured. In a single-stage extraction of DIC as CO₂ from sediment, the CO₂ and the $\delta^{13}\text{C}$ are integrated during the process. In the consecutive fraction experiments, it was possible to calculate the progressive weighted average of $\delta^{13}\text{C}$. The final weighted average of $\delta^{13}\text{C}$, obtained by extrapolation to the cumulative CO₂ fraction of 1, is equivalent to a single-stage extraction.

The results of the 2 experiments are presented in Table 5. In both experiments, the first fraction of CO₂ to be released exhibited extreme depletion having $\delta^{13}\text{C}$ values of -33‰ and -30‰ , respectively. As the extraction progressed, the CO₂ became progressively more enriched and the $\delta^{13}\text{C}$ in the last fractions collected for the first and second experiment were -0.6‰ and $+1.7\text{‰}$, respectively.

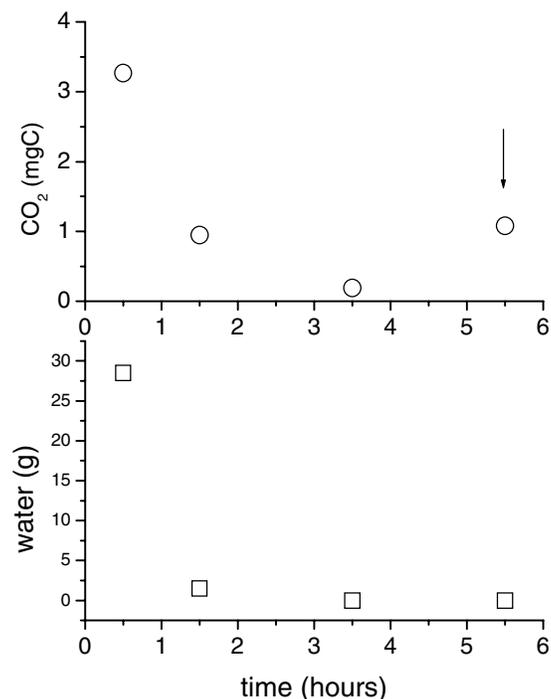


Figure 7 Secondary evolution of CO₂ in the 12-m sediment, 100 °C extraction.

Table 5 Cumulative extraction experiments.

Stage	Experiment 1				Experiment 2			
	CO ₂ torr	CO ₂ fraction	Cum. CO ₂ fraction	δ ¹³ C (‰) measured	CO ₂ torr	CO ₂ fraction	Cum. CO ₂ fraction	δ ¹³ C (‰) measured
1	9	0.0957	0.0957	-33.0	20	0.1961	0.1961	-30.0
2	21	0.2234	0.3191	-24.6	19	0.1863	0.3824	-23.3
3	21	0.2234	0.5426	-6.3	24	0.2353	0.6176	-17.0
4	20	0.2128	0.7553	0.5	22	0.2157	0.8333	-6.9
5	7	0.0745	0.8298	-0.6	7	0.0686	0.9020	4.7
6	9	0.0957	0.8255		4	0.0392	0.9412	1.8
7	3	0.0319	0.9574		2	0.0196	0.9608	
8	1	0.0106	0.9681		1	0.0098	0.9706	
9	2	0.0213	0.9894		2	0.0196	0.9902	
10	1	0.0106	1.0000		1	0.0098	1.0000	
	Σ = 94				Σ = 102			

Figure 8 shows the dependence of the progressive δ¹³C on the weighted CO₂ of both experiments. The results of the 2 experiments are quite similar. An extrapolation to the cumulative fraction of CO₂ = 1 yields a value of -14.3‰. This value is somewhat depleted compared to those obtained in single-stage extractions performed at higher temperatures. Isotopic comparisons of progressively liberated fractions could not be performed at higher temperatures because the extractions proceeded too rapidly to obtain a reasonable number of discrete fractions.

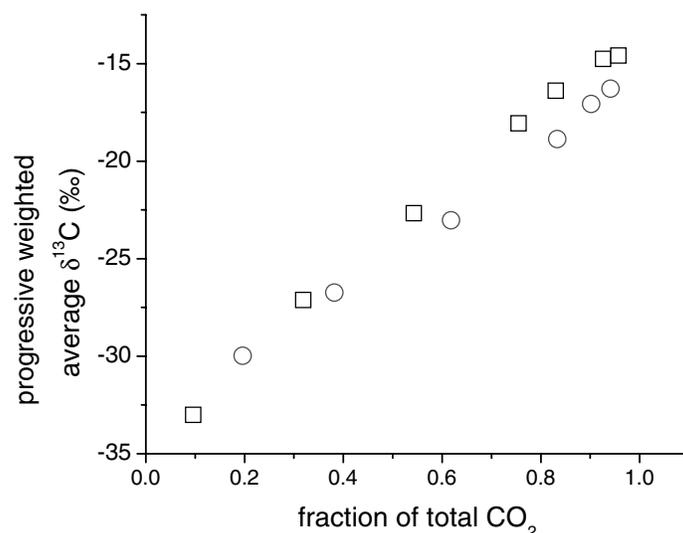


Figure 8 Correlation between the progressive weighted $\delta^{13}\text{C}$ (‰) and the cumulative fraction of the total CO_2 , F_i , of experiment 1 (squares) and experiment 2 (circles). The best-fit line is: weighted $\delta^{13}\text{C} = 19.88F_i - 34.6$ ($r^2 = 0.98$), where the progressive weighted $\delta^{13}\text{C}$ is $\sum \delta^{13}\text{C}_i \times f_i / F_i$ and $F_i = \sum f_i$ and $\delta^{13}\text{C}_i$ is the isotopic value of the CO_2 of the fraction f_i .

Comparison of the Effect of Increasing the Temperature

Table 6 compares the results of 2 pairs of extractions of sediments from 15 and 20.2 m, at different temperatures. The effect of increasing the extraction temperature is clearly seen in the liberation of more enriched $\delta^{13}\text{C}$. The ^{14}C results of the pair at 15 m depth are quite similar, and for the pair at 20.2 m they are quite different. The 2 ^{14}C results at 15 m depth can be fully explained by the difference of 5.5‰ in $\delta^{13}\text{C}$. The difference between the 2 results of the 20.2-m pair cannot be readily explained based on the $\delta^{13}\text{C}$ results. As at higher temperatures the yield of DIC and water are higher, the conclusion is that the extraction should be carried out at the higher temperatures.

Table 6 Comparison between extractions at temperatures of 30, 70, and 100 °C.

Code (RTT)	Depth (m)	Extraction temperature (°C)	DIC mmole C/L	$\delta^{13}\text{C}$ (‰)	^{14}C pMC
6040	15.0	30	8.6	-9.7	94.9 ± 0.4
6040.1	15.0	100	8.7	-4.2	93.8 ± 0.4
6068	20.2	30	4.3	-20.5	66.9 ± 0.6
5217	20.2	70	4.2	-13.6	71.5 ± 0.5

CONCLUSION

The average value of $\delta^{13}\text{C}$ of the 13 vacuum extractions of the Nitzanim sediments is $-9.5 \pm 2.9\text{‰}$ (Carmi et al., unpublished data), which is within range of the average of the Coastal Aquifer, $-11.4 \pm 1.7\text{‰}$. The cumulative information from the vacuum extraction procedures, from the tests performed and from the $\delta^{13}\text{C}$ data, lead to a conclusion that the vacuum extraction method of water and DIC works well for the Coastal Aquifer of Israel, for extraction temperatures of 70–100 °C. Though

the procedure is rather lengthy—up to or exceeding 10 hr for a single extraction—the fractionation in $\delta^{13}\text{C}$ is very minor, making the correction of ^{14}C data for fractionation very small or unnecessary. This makes the method suitable for ^{14}C measurement of sediment water in order to improve the dating of groundwater by radiocarbon. It may be of interest to test the method elsewhere.

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