

Laboratory Experiments to Evaluate Matrix Diffusion of Dissolved Organic Carbon Carbon-14 in Southern Nevada Fractured-rock Aquifers

Prepared by

Ronald L. Hershey and Wyatt Fereday

Submitted to

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ABSTRACT

Dissolved inorganic carbon (DIC) carbon-14 (^{14}C) is used to estimate groundwater ages by comparing the DIC ^{14}C content in groundwater in the recharge area to the DIC ^{14}C content in the downgradient sampling point. However, because of chemical reactions and physical processes between groundwater and aquifer rocks, the amount of DIC ^{14}C in groundwater can change and result in ^{14}C loss that is not because of radioactive decay. This loss of DIC ^{14}C results in groundwater ages that are older than the actual groundwater ages. Alternatively, dissolved organic carbon (DOC) ^{14}C in groundwater does not react chemically with aquifer rocks, so DOC ^{14}C ages are generally younger than DIC ^{14}C ages. In addition to chemical reactions, ^{14}C ages may also be altered by the physical process of matrix diffusion. The net effect of a continuous loss of ^{14}C to the aquifer matrix by matrix diffusion and then radioactive decay is that groundwater appears to be older than it actually is. Laboratory experiments were conducted to measure matrix diffusion coefficients for DOC ^{14}C in volcanic and carbonate aquifer rocks from southern Nevada.

Experiments were conducted using bromide (Br^-) as a conservative tracer and ^{14}C -labeled trimesic acid (TMA) as a surrogate for groundwater DOC. Outcrop samples from six volcanic aquifers and five carbonate aquifers in southern Nevada were used. The average DOC ^{14}C matrix diffusion coefficient for volcanic rocks was $2.9 \times 10^{-7} \text{ cm}^2/\text{s}$, whereas the average for carbonate rocks was approximately the same at $1.7 \times 10^{-7} \text{ cm}^2/\text{s}$. The average Br^- matrix diffusion coefficient for volcanic rocks was $10.4 \times 10^{-7} \text{ cm}^2/\text{s}$, whereas the average for carbonate rocks was less at $6.5 \times 10^{-7} \text{ cm}^2/\text{s}$. Carbonate rocks exhibited greater variability in DOC ^{14}C and Br^- matrix diffusion coefficients than volcanic rocks.

These results confirmed, at the laboratory scale, that the diffusion of DOC ^{14}C into southern Nevada volcanic and carbonate aquifers is slower than DIC ^{14}C . Because of the apparent sorption of ^{14}C -labeled TMA in the experiments, matrix diffusion coefficients are likely even lower. The reasons for the higher than expected $\text{Br}^-/^{14}\text{C}$ -labeled TMA are unknown. Because the molecular size of TMA is on the low end of the range in molecular size for typical humic substances, the matrix diffusion coefficients for the ^{14}C -labeled TMA likely represent close to the maximum diffusion rates for DOC ^{14}C in the volcanic and carbonate aquifers in southern Nevada.

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CONTENTS

ABSTRACT.....	iii
LIST OF FIGURES	vi
LIST OF TABLES	vi
LIST OF ACRONYMS	vi
LIST OF CHEMICAL SYMBOLS	vii
INTRODUCTION	1
EXPERIMENTAL MATERIALS AND METHODS	1
Rocks.....	1
Water Used in Experiments.....	3
Tracers.....	3
Batch Experiments to Verify Nonsorptions of ^{14}C Tracer.....	4
Matrix Diffusion Wafer Experiments	5
Wafer Preparation.....	5
Tracer Imbibition.....	5
Tracer Sampling	6
Experimental Results Interpretation	7
RESULTS AND DISCUSSION.....	8
CONCLUSIONS.....	16
REFERENCES	17
APPENDIX A: Matrix Diffusion Experimental Results and Model Fits for Volcanic and Carbonate Wafers.....	A-1
APPENDIX B. Mass Balance Calculations versus Actual Concentration for Tracer Uptake.....	B-1

LIST OF FIGURES

1. Aquifer outcrop rock sample locations.	2
2. Molecular structure of trimesic acid	4
3. (a) Prepared core wafer section; (b) matrix diffusion reactor on stir plate ready for sampling.	6
4. (a) Batch experiment results ¹⁴ C-labeled TMA in volcanic rocks; (b) batch experiment results ¹⁴ C-labeled TMA in carbonate rocks.....	8
5. Example results and model fit of matrix diffusion experiments for a volcanic wafer (a) and a carbonate wafer (b).	10
6. Br ⁻ and ¹⁴ C-labeled TMA matrix diffusion coefficients versus porosity.....	12

LIST OF TABLES

1. Aquifer outcrop rock sample locations with representative hydrostratigraphic units (HSU) from Figure 1.....	3
2. Batch experiment results ¹⁴ C-labeled TMA in volcanic and carbonate HSUs.	9
3. Volcanic and carbonate wafer porosities and diffusion coefficients (D _m in equations 1 and 3) for matrix diffusion experiments using Br ⁻ and ¹⁴ C-labeled TMA.	11
4. Free-water diffusion coefficients.	13
5. Matrix diffusion coefficients from other reports.	14

LIST OF ACRONYMS

DI	deionized
DIC	dissolved inorganic carbon
DOC	dissolved organic carbon
HSU	hydrostratigraphic unit
NNSS	Nevada National Security Site
NTTR	Nevada Test and Training Range

LIST OF CHEMICAL SYMBOLS

Br ⁻	bromide ion
¹⁴ C	carbon-14
CaCO ₃	calcite
cm	centimeter
cm ²	square centimeters
°C	degrees Celsius
DFBA	difluorobenzoate
dpm	disintegrations per minute
FBA	fluorinated benzoic acids
g	grams
g/mol	grams per mole
H ¹⁴ CO ₃ ²⁻	bicarbonate ion containing carbon-14
I ⁻	iodide
L	liter
mCi	millicuries
mL	milliliters
mg/L	milligrams per liter
mm	millimeters
μm	micrometers
NaBr	sodium bromide
NaN ₃	sodium azide
PFBA	pentafluorobenzoate
TFBA	trifluorobenzoate
TMA	trimesic acid

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INTRODUCTION

Dissolved inorganic carbon (DIC) carbon-14 (^{14}C) has long been used to estimate groundwater ages. However, because of chemical (e.g., carbonate mineral dissolution and precipitation) and physical processes (e.g., diffusion) between groundwater and aquifer rocks, the amount of DIC ^{14}C in groundwater can change and result in loss of ^{14}C that is not because of radioactive decay. This loss of ^{14}C by processes other than radioactive decay results in groundwater ages that are older than the actual groundwater age (Murphy *et al.*, 1989; Wassenaar *et al.*, 1991; Purdy *et al.*, 1992; Thomas *et al.*, 1996; Clark and Fritz, 1997; Burr *et al.*, 2001; Morse, 2002). Alternatively, dissolved organic carbon (DOC) ^{14}C in groundwater does not react chemically with aquifer rocks (Murphy *et al.*, 1989; Wassenaar *et al.*, 1991; Thomas, 1996). Because DOC ^{14}C in groundwater does not react with aquifer rocks, DOC ^{14}C ages are generally much younger than DIC ^{14}C ages (e.g., Thomas [1996] and Morse [2002]).

In addition to chemical reactions, ^{14}C ages may also be altered by the physical process of matrix diffusion. Matrix diffusion is the exchange of solute mass by molecular diffusion between fluid in fractures and fluid in the pores of a rock matrix (Liu *et al.*, 2007). This process is well-known in fractured rock/groundwater systems and can significantly retard the movement of solutes through the groundwater flow system (e.g., Neretnieks [1980], Grisak and Pickens [1980], Tang *et al.* [1981], and Maloszewski and Zuber [1984]). As ^{14}C diffuses into the rock matrix pores, it is removed from flowing groundwater in the fractures, which results in a loss of ^{14}C . Because ^{14}C decays, a continuous diffusional gradient exists between the flowing groundwater in the fractures and the stagnant water in the pores over long time periods. The net effect of ^{14}C loss to the aquifer matrix by matrix diffusion is that groundwater, again, appears to be older than it actually is. As described, the matrix diffusion process assumes that groundwater flow occurs in the fractures and that matrix groundwater flow is minimal. It is generally accepted that matrix diffusion of DIC ^{14}C occurs (Sudicky and Frind, 1981; Sudicky and Frind, 1982; Maloszewski and Zuber, 1991; Walker and Cook, 1991). However, because of the larger size of organic molecules (smaller free-water diffusion coefficients) relative to the inorganic bicarbonate molecule ($\text{H}^{14}\text{CO}_3^{2-}$), matrix diffusion of organic molecules containing ^{14}C may be an insignificant process when estimating groundwater ages using DOC ^{14}C . To test this hypothesis, laboratory experiments were conducted to measure matrix diffusion coefficients for DOC ^{14}C in volcanic and carbonate aquifer rocks. The results of this study can be used to evaluate the effect of matrix diffusion on DOC ^{14}C groundwater ages in southern Nevada aquifers.

EXPERIMENTAL MATERIALS AND METHODS

Rocks

Seven volcanic and five carbonate outcrop rock samples were collected from the Nevada National Security Site (NNSS), Sheep Range, and Spring Mountains (Figure 1). These rocks were selected from known aquifer hydrostratigraphic units (HSU) for the matrix diffusion experiments. Geologic units and HSUs for each sample are listed in Table 1. Outcrop samples were selected because archived rock core collected during well drilling from the same geologic units may have been contaminated with organic compounds found in drilling fluids.

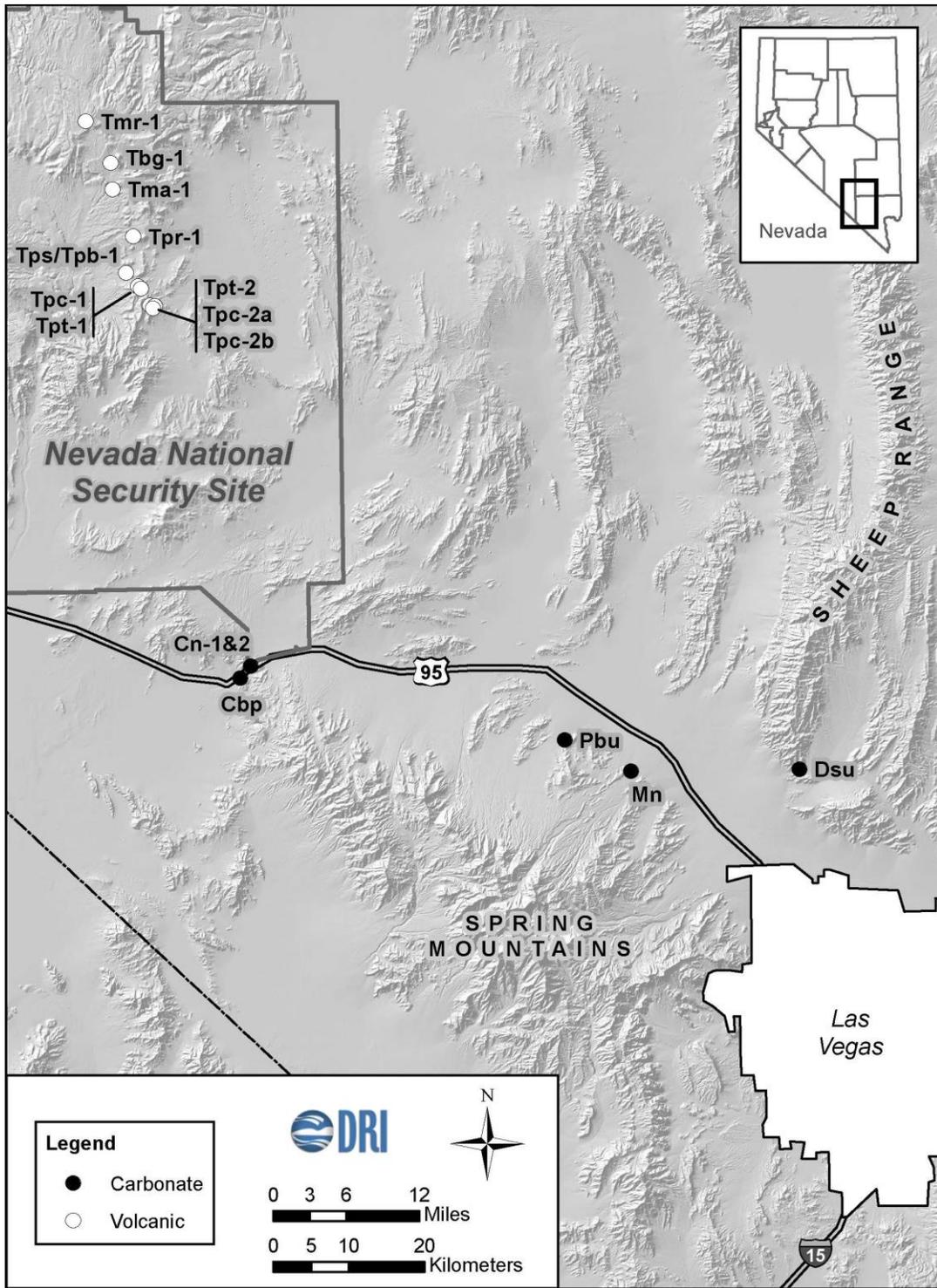


Figure 1. Aquifer outcrop rock sample locations. NNSS = Nevada National Security Site; NTTR = Nevada Test and Training Range.

Table 1. Aquifer outcrop rock sample locations with representative hydrostratigraphic units (HSU) from Figure 1.

Volcanic			
Name	HSU(s)	latitude	longitude
Tma-1	Timber Mountain	37°09'01.9"	116°15'53.7"
Tmr-1	Timber Mountain	37°13'53.8"	116°18'15.2"
Tps/Tpb-1	Benham	37°03'02.9"	116°14'45.0"
Tpc-1	Tiva Canyon, Paintbrush	37°01'53.6"	116°13'27.7"
Tpc-2a	Tiva Canyon, Paintbrush	37°00'38.6"	116°12'14.0"
Tpc-2b	Tiva Canyon, Paintbrush	37°00'28.7"	116°12'24.4"
Tpr-1	Paintbrush	37°05'38.2"	116°14'04.2"
Tpt-1	Topopah Spring, Paintbrush	37°02'04.4"	116°13'42.6"
Tpt-2	Topopah Spring, Paintbrush	37°00'40.7"	116°12'38.1"
Tbg-1	Belted Range	37°10'53.9"	116°16'03.4"
Carbonate			
Pbu	Lower Carbonate Aquifer	36°29'16.7"	115°36'16.8"
Mm	Lower Carbonate Aquifer	36°26'59.1"	115°30'25.6"
Dsu	Lower Carbonate Aquifer	36°26'56.4"	115°15'32.5"
Cn-1&2	Lower Carbonate Aquifer	36°34'51.3"	116°03'58.3"
Cbp	Lower Carbonate Aquifer	36°34'00.2"	116°04'55.0"

Water Used in Experiments

All experiments were conducted with calcite-saturated water prepared as described in Reimus *et al.* (2009). The calcite-saturated water was prepared by bubbling pure CO₂ gas through a suspension of 3 grams (g) CaCO₃ in 6 liters (L) distilled water for 10 minutes. The solution was constantly stirred in an unsealed container and allowed to equilibrate with atmospheric CO₂ until the pH stabilized at approximately 8.3, usually after several days of equilibration time. Once pH stabilized, more CaCO₃ (5-10 g) was added to provide sufficient excess solid calcite to maintain saturated conditions with respect to calcite while exposed to the atmosphere. The solution was stored in loosely sealed containers at ambient laboratory temperatures. The calcite-saturated water was stirred, and then filtered through a 0.45 micrometer (µm) cartridge filter, before being used in the experiments.

Tracers

The tracers used in the laboratory experiments included the halide bromide (sodium bromide [NaBr]) used as a nonsorbing tracer and trimesic acid (TMA) labeled with ¹⁴C (carboxyl-¹⁴C, C₉H₆O₆) used as a surrogate for DOC ¹⁴C in groundwater. The TMA is a hydrophilic fulvic acid complex, a benzoic acid that has three carboxyl groups (Figure 2), and a solubility of 2.63 x 10⁴ milligrams per liter (mg/L) at 23 degrees Celsius (°C) (molecular weight = 210 grams per mole (g/mol)). The size range of humic substances, including fulvic and humic acids, is not well-defined. However, Thurman *et al.* (1982) measured aquatic fulvic acid sizes from approximately 500 to 2,000 g/mol. Trimesic acid has been used in other laboratory studies as a surrogate for humic substances (e.g., Borah and

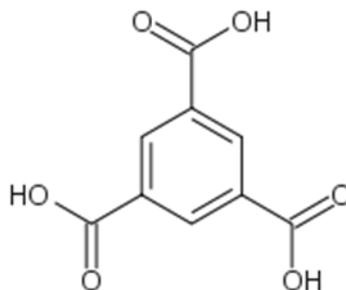


Figure 2. Molecular structure of trimesic acid (https://en.wikipedia.org/wiki/Trimesic_acid, accessed February 24, 2016).

Mahiuddin [2008], Angove *et al.* [2002], and Angove *et al.* [1999]). Because of its low molecular weight, the TMA may diffuse more readily into the matrix of the rocks selected for the experiments than larger fulvic acids, and therefore, provides a conservative estimate of DOC matrix diffusion in the experiments. More detailed discussions of the composition of DOC ^{14}C in groundwater can be found in Aravena *et al.* (2004), Artinger *et al.* (1996), Schiff *et al.* (1990), Murphy *et al.* (1989a), Murphy *et al.* (1989b), and Wassenaar *et al.* (1989). The pKa of TMA is 3.12 (<http://www.chemicaland21.com/specialtychem/perchem/TRIMESIC%20ACID.htm>, accessed February 19, 2016). The chemical form of TMA used was TMA in ethanol.

The tracer solution for the experiments was prepared by first dissolving 0.5 mL of ^{14}C -labeled TMA (0.1 millicurie per milliliter [mCi/mL]) in 1 L of DOC-free distilled water to create a stock solution of ^{14}C -labeled TMA. This stock solution was not neutralized or pH adjusted. Then, 32 mL of the ^{14}C -labeled TMA stock solution was added to 4 L of calcite-saturated water along with 15.45 g of NaBr and 15.7 milligrams (mg) of sodium azide (NaN_3) as a bactericide. This produced a tracer solution with 1,000 disintegrations per minute per milliliter (dpm/mL) of ^{14}C -labeled TMA and 3,600 mg/L Br $^-$. Over the time period of the experiments (one to two months), there was no change in ^{14}C activity by radioactive decay because of the long half-life of ^{14}C (5,730 years).

Batch Experiments to Verify Nonsorbtion of ^{14}C Tracer

Batch sorption experiments were conducted to verify that the ^{14}C -labeled TMA tracer did not sorb onto the volcanic and carbonate rock surfaces. In these experiments, the tracer solution with ^{14}C -labeled TMA was added to calcite-saturated water (370 dpm/mL), and then placed in contact with the various volcanic and carbonate HSU samples at a solid mass-to-solution volume ratio of 200 g/L. Rock samples were crushed and sieved to less than 100 μm diameter. The specific surface area of the crushed material was not measured directly, but was probably in the range of 0.1-0.5 square meter per gram (m^2/g) based on the expected range of particles and the low internal porosity of the rock (Reimus *et al.*, 2006). The relatively high solid-mass-to-solution-volume ratio and the small particle sizes used in the sorption experiments were intended to maximize the sensitivity of the experiments to potential small amounts of sorption. Aliquots of the solutions were removed for tracer analysis at 24, 48, 96, and 336 hours of contact time with the crushed rock. Control experiments (tracer with no rock) were conducted in parallel with the volcanic and carbonate experiments. All batch sorption experiments were conducted at room temperature.

Matrix Diffusion Wafer Experiments

Matrix diffusion estimates of the tracers were obtained by conducting diffusion wafer experiments based on those of Reimus *et al.* (2006). In these experiments, cylindrical wafers were cut from the outcrop samples, the circumference of the wafers were sealed to form a no-flux boundary along the circumference so that diffusion only occurred in the axial direction perpendicular to the cylindrical cross section of the wafer. The wafers were then saturated with tracer solution and placed in containers of tracer-free, calcite-saturated water and the change in concentration over time in the containers was measured as the tracers diffused out of the wafers.

Wafer Preparation

Five of the seven volcanic outcrop samples (Tma, Tpb/Tps, Tpc, Tpr, Tpt, and Tbg) and the five carbonate samples (Pbu, Mm, Dsu, Cn, and Cbp) were cored, sliced, and polished to make diffusion wafers (Tmr yielded no usable cores; Tpb/Tps wafers contained voids that produced unusually high diffusion coefficients [Reimus *et al.*, 2006]). Cores were cut from the outcrop rocks using a drill press with a 9-centimeter (cm) coring bit and DOC-free, deionized (DI) water for lubrication and cooling. The drill press and coring bit were precleaned with soap and water; a DOC-free DI water rinse; an ethanol rinse; and a final DOC-free, DI water rinse prior to use and between individual cores. Cores were then cut into circular wafers roughly 1-cm thick using a precleaned (same cleaning procedure as the drill press) tile saw with DOC-free, DI water. Two carbonate units (Dsu and Cbp) did not yield fully round cores. For these units, rectangular and triangular wafers were cut using the tile saw.

Circular and geometric wafers were then ground to uniform thickness (within approximately 250 μm) using a precleaned, diamond, lapping plate with DOC-free, DI water. Three geometric Dsu wafers were ground to a single thickness. Eight Cbp wafers were ground to two different thicknesses (for the sake of convenience) and placed in groups of three and five; one wafer was thicker than these eight. Wafer surface dimensions and thicknesses were measured within approximately 250 μm using a caliper. Geometric wafer edge lengths were measured from the midpoint of each edge to obtain the best average edge length. Measured surface areas were estimated within approximately 6.5×10^{-4} square centimeters (cm^2).

Wafer edges were coated with silicon sealant (Figure 3a) to ensure that only the top and bottom of each wafer (i.e., the known surface area) were exposed to the water. Several wafers contained “nicks” on their edges. When a nick was deemed large enough to significantly increase the overall surface area, it was sealed with silicone and was subtracted from the total surface area calculation. Wafers were baked in an oven at 105 °C for 72 hours to ensure complete dryness. Each wafer was then weighed to establish a final dry weight.

Tracer Imbibition

After drying and weighing, the wafers were placed in glass bowls with the Br^- and ^{14}C -labeled TMA tracer solution. The wafers and glass bowls with tracer solution were kept under vacuum to assist in removing air from the pores and to expedite saturation of the wafers during tracer imbibition. Wafers and tracer solutions were held at approximately 5 °C. The wafers were periodically removed from the solution, blotted dry with a clean laboratory



Figure 3. (a) Prepared core wafer section; (b) matrix diffusion reactor on stir plate ready for sampling.

towel, weighed, and returned to the tracer solution. After roughly eight weeks, the wafers stopped gaining mass and were assumed to be saturated with the tracer solution. The porosity of the wafers was estimated by dividing the volume of the tracer solution uptake by the total wafer volume (measured surface area multiplied by thickness).

Tracer Sampling

To initiate the diffusion experiments, each wafer was placed in a sealed reactor vessel and immersed in tracer-free, calcite-saturated water. The wafers were suspended above the bottom of the reactor vessel by a short, perforated, copper ring so that both the top and bottom surfaces were in direct contact with the tracer-free, calcite-saturated water (Figure 3b). A magnetic stir bar was placed in each reactor vessel inside the copper ring. Between sampling events, the reactor vessels were kept in a refrigerator at 5 °C in the dark to minimize any biological activity. Before sampling, each reactor vessel was placed on a magnetic stir plate and the reactor water was stirred for ten minutes to ensure the water was well mixed. The water in the reactor vessels was sampled periodically so that the increase in tracer concentration in the reactor water as a function of time could be quantified.

Four sets of experiments were conducted. In Set 1 Carbonate, wafers were placed in 800 mL of calcite-saturated water. In Set 2 Carbonate and Sets 3 and 4 Volcanic, wafers were placed in 600 mL of calcite-saturated water. Four blank reactors were also prepared as experimental controls: two containing a circumference silicon-sealed rock wafer (one volcanic, one carbonate) and copper ring in calcite-saturated water with no tracers, and two containing copper rings with silicon sealant added to the rings in calcite-saturated water with ^{14}C and Br^- tracers, but without any rock wafers. A carbonate rock blank (no tracers) and a tracer blank (no rock) were run with the Set 2 Carbonate reactors. A volcanic rock blank and a tracer blank were run with the Set 3 Volcanic reactors.

For each sample, 3 mL were withdrawn from each reactor with a syringe and filtered through a 0.45 μm syringe filter (precleaned with DOC-free, DI water). The first 0.5 mL of sample was used to flush the filter with sample and discarded, leaving 2.5 mL that were placed into a clean plastic weighing dish. Then, 1 mL was pipetted from the dish into a scintillation vial for ^{14}C analysis by liquid scintillation counting. The remaining 1.5 mL of the sample was pipetted into a glass vial with a PolysealTM cone lid for Br^- analysis by the Desert Research Institute Water Analysis Laboratory in Reno, Nevada.

The reactors were sampled on a log time scale over several months. The increase in tracer concentration was equated to a one-dimensional flux through the upper and lower cylindrical cross-sectional area of the wafer, which in turn could be used to estimate a diffusion coefficient within the matrix of the wafer (assuming that all the pore space in the wafer was originally saturated with the tracer solution).

Experimental Results Interpretation

The diffusion experimental results were interpreted using a FORTRAN program that implemented an explicit-in-time, finite-difference algorithm to simulate one-dimensional diffusion in the axial direction through a wafer (no radial diffusion because of the no-flux boundary along the sealed circumference of the wafers). The wafers were assumed to be initially saturated with the tracer solution and a no-flux boundary was assumed to exist at the midpoint thickness of the wafer such that only half of the wafer is actually simulated (with the other half being equivalent by symmetry). The following equation and boundary condition expressions were solved using an explicit-in-time numerical algorithm:

$$\frac{\partial C}{\partial t} = -D_m \frac{\partial^2 C}{\partial x^2} \quad (\text{within wafer}) \quad (1)$$

$$\frac{dC}{dx} = 0 \quad \text{at } x = 0 \quad (\text{midpoint thickness of wafer}) \quad (2)$$

$$V_{\text{res}} \frac{dC_{\text{res}}}{dt} = -\phi(2A_w)D_m \frac{\partial C}{\partial x} \quad \text{at } x = 0.5T_w \quad (\text{outer surface of wafer}) \quad (3)$$

where:

- C = concentration of tracer in wafer, arb/ml
- C_{res} = concentration of tracer in reservoir (or beaker), arb/ml
- D_m = tracer diffusion coefficient in matrix, cm²/s
- V_{res} = volume of water in reservoir (or beaker), ml
- A_w = surface area of wafer exposed to solution (one side), cm²
- T_w = wafer thickness, cm
- ϕ = porosity of wafer
- x = distance in the axial direction inside the wafer, cm
- t = time, hr

The matrix diffusion coefficient, D_m, was adjusted to obtain a fit to the concentration versus time data acquired by sampling the reservoir over the course of the diffusion experiment. The initial tracer concentrations in the wafer and the reservoir are required inputs. In some cases, it was necessary to adjust the initial tracer concentration in the reservoir to a higher-than-expected value to account for the tracer that was washed off the surface of the wafer when it was first immersed in the reservoir. However, this initial wash-off generally had little effect on the best-fitting values of D_m obtained from a given data set.

RESULTS AND DISCUSSION

The results of the batch sorption experiments for the ^{14}C -labeled TMA for volcanic and carbonate HSUs are shown in Figure 4 and Table 2. The TMA did not sorb significantly onto the volcanic rocks compared with the volcanic blank (tracer solution, no rock). The TMA sorbed slightly onto most of the different carbonate HSUs because the average change in experimental ^{14}C activity in the batch reactors compared with the average carbonate blank activity ranged from -6.9 to 1.3 to percent (Table 2) with an average loss of approximately 5 percent. Any sorption of TMA tracer to the carbonate rocks occurred mostly in the first 24 to 48 hours of the batch experiments. Bromide was not measured in the batch experiments because previous studies have shown that Br^- does not sorb onto volcanic and carbonate rocks from southern Nevada in laboratory batch experiments (e.g., Reimus *et al.* [2006]).

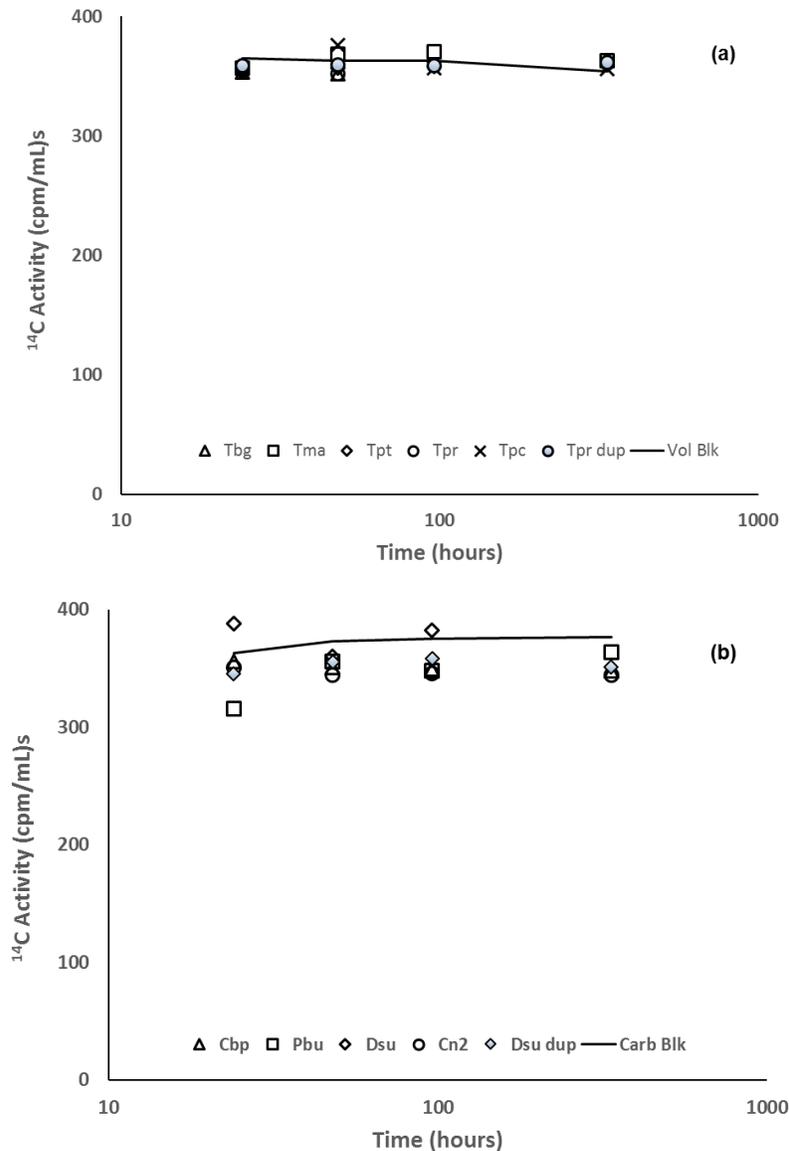


Figure 4. (a) Batch experiment results ^{14}C -labeled TMA in volcanic rocks; (b) batch experiment results ^{14}C -labeled TMA in carbonate rocks.

Table 2. Batch experiment results ^{14}C -labeled TMA in volcanic and carbonate HSUs. Results are in dpm/mL.

HSU							
Carbonate							
Hours	Cbp	Cn2	Dsu	Dsu Duplicate	Mn	Pbu	Carbonate Blank
24	356	351	388	345	366	315	363
48	351	344	360	355	365	355	373
96	349	346	382	358	362	348	375
336	348	344	-	351	359	363	376
Average	351	346	377	352	363	346	372
% Change	-5.7%	-6.9%	1.3%	-5.2%	-2.4%	-7.1%	
Volcanic							
Hours	Tbg	Tma	Tpc	Tpr	Tpr dup Duplicate	Tpt	Volcanic Blank
24	353	357	357	355	359	357	365
48	352	368	376	352	359	357	363
96	-	371	356	-	359	358	-
336	-	363	356	361	362	360	354
Average	353	365	361	356	360	358	361
% Change	-2.2%	1.1%	0.2%	-1.3%	-0.3%	-0.8%	

An example of matrix diffusion experimental results and model fits for a volcanic and a carbonate wafer is shown in Figure 5. Plots for all experiments are shown in Appendix A. These examples (as well as all the plots in Appendix A) show that the experiments in the volcanic wafers were well behaved, but there was a lot of scatter in the data in the carbonate wafer experiments. Because of the lower porosity of the carbonate wafers, less tracer was taken up by the wafers and correspondingly, less tracer diffused out into the experiment reservoirs. This resulted in low tracer concentrations that were close to the analytical detection limits, which produces greater variability in analytical results along with normal sampling errors. The results for blanks run during the experiments are also presented at the end of Appendix A. Over the course of the volcanic experiments, there were no changes in tracer concentrations (tracer, no rock, Br^- and ^{14}C -labeled TMA). In the carbonate blanks, as in the carbonate experiments, there was a lot of scatter in the data. There was an approximate loss of 4 mg/L of Br^- and gain of 5 dpm/mL over the course of the experiments. Because of the low tracer concentrations in the blanks, which were close to the detection limits of the analytical methods, and because of normal sampling errors, the experimental data were not corrected for the small observed changes in the tracer blanks.

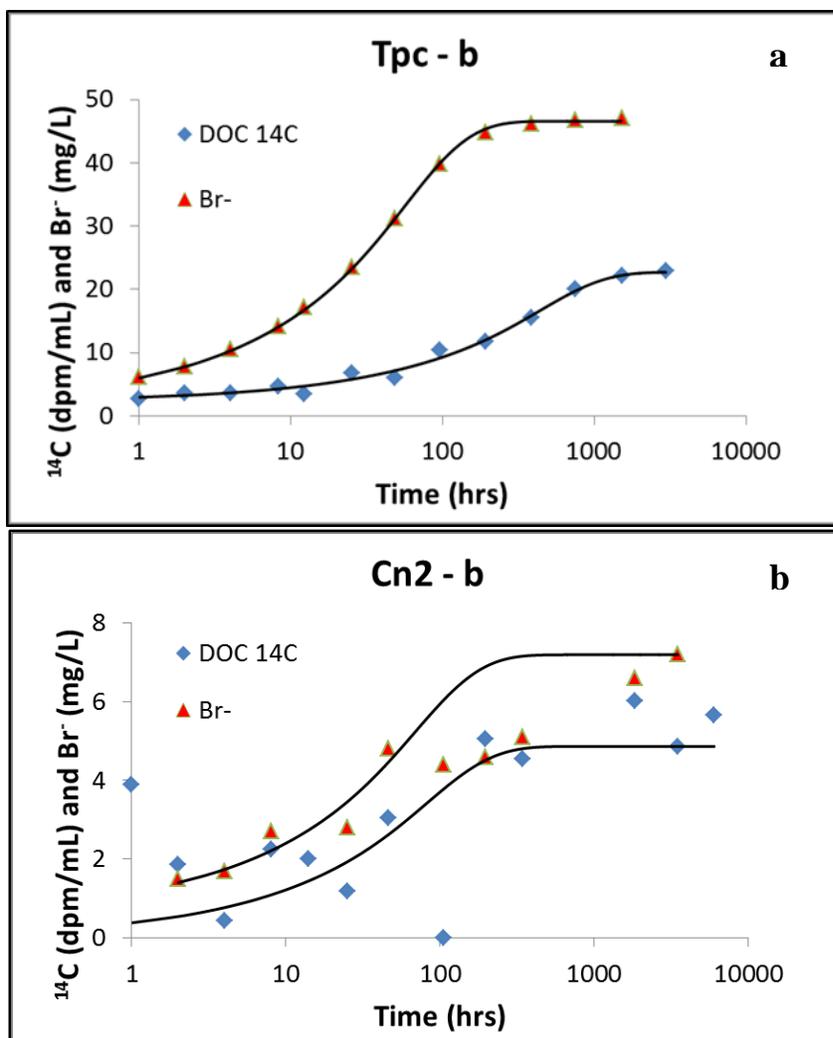


Figure 5. Example results and model fit of matrix diffusion experiments for a volcanic wafer (a) and a carbonate wafer (b).

Matrix diffusion coefficients (D_m in equations 1 and 3) versus rock porosity are shown in Table 3 and Figure 6 for five volcanic units (Tma, Tpc, Tpr, Tpt, and Tbg) and five carbonate units (Pbu, Mm, Dsu, Cn2, and Cbp). The results for the Tpb/Tps wafer are not shown because the matrix diffusion coefficients were much higher than expected based on the porosity. After reexamining the wafer, it was determined that the wafer had relatively large voids that acted as short-circuit pathways that gave artificially high matrix diffusion coefficients and invalidated the method. Carbonate wafers exhibited greater variability in Br^- matrix diffusion coefficients relative to porosity than the volcanic wafers (lower R^2 values, Figure 6), but the slopes of the trend lines are the same. The ^{14}C -labeled TMA matrix diffusion coefficients in the carbonate wafers were all similar in value and unrelated to porosity. Reimus *et al.* (2007) suggested that permeability is a better indicator of matrix diffusion coefficients than porosity, but permeability of the volcanic and carbonate wafers was not measured in this study.

Table 3. Volcanic and carbonate wafer porosities and matrix diffusion coefficients (D_m in equations 1 and 3) for matrix diffusion experiments using Br^- and ^{14}C -labeled TMA.

Wafer	Porosity	TMA* $^{14}\text{C} \times 10^{-7}$ (cm^2/s)	$\text{Br}^- \times 10^{-7}$ (cm^2/s)	$\text{Br}^- / ^{14}\text{C}$
<u>Volcanic</u>				
Tma - a	0.15	2.29	7.14	3.1
Tma - b	0.16	2.29	7.14	3.1
Tpc - a	0.12	1.57	4.86	3.1
Tpc - b	0.12	1.51	5.76	3.8
Tpr - a	0.37	6.14	21.4	3.5
Tpr - b	0.38	5.43	22.0	4.1
Tpt - a	0.27	4.43	17.9	4.0
Tbg - a	0.10	1.51	4.00	2.6
Tbg - b	0.10	1.23	3.00	2.4
Average	0.20	2.93	10.4	3.3
<u>Carbonate</u>				
Pbu - a	0.05	1.14	9.29	8.2
Pbu - b	0.06	1.34	6.46	4.8
Mm - a	0.02	3.57	8.00	2.2
Mm - b	0.02	1.51	7.23	4.8
Dsu - a	0.01	1.60	2.93	1.8
Cn2 -a	0.01	1.37	2.29	1.7
Cn2 -b	0.02	1.51	8.71	5.8
Cbp - a	0.04	1.60	7.43	4.6
Average	0.03	1.71	6.54	4.2

*TMA = Trimesic acid

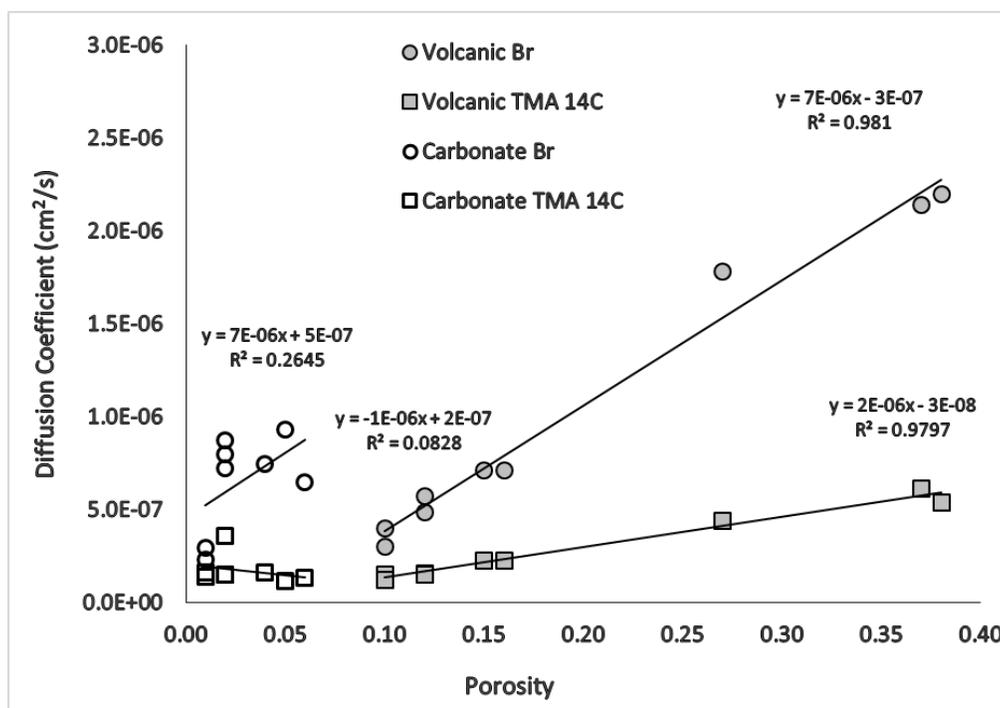


Figure 6. Br⁻ and ¹⁴C-labeled TMA matrix diffusion coefficients versus porosity.

Porosities for the volcanic wafers ranged from 0.10 to 0.38. The matrix diffusion coefficients for Br⁻ in the volcanic wafers ranged from 3.0×10^{-7} to 22×10^{-7} cm²/s with an average of 10.4×10^{-7} cm²/s, about an order of magnitude lower than the free-water diffusion coefficient for Br⁻ (210×10^{-7} cm²/s, Table 3). Matrix diffusion coefficients for ¹⁴C-labeled TMA in the volcanic wafers ranged from 1.2×10^{-7} to 6.1×10^{-7} cm²/s with an average of 2.9×10^{-7} cm²/s (Table 3), more than an order of magnitude lower than the free-water diffusion coefficient for ¹⁴C-labeled TMA (76.3×10^{-7} cm²/s, Table 4). The ratio of the free-water diffusion coefficient for Br⁻ to the free-water diffusion coefficient for TMA is 2.7. The average ratio of the matrix diffusion coefficients for Br⁻ in the volcanic wafers to the ¹⁴C-labeled TMA is 3.3, a little higher than the ratio of the free-water diffusion coefficients as would normally be expected (e.g., Bechtel SAIC [2004]). There was very good repeatability between experiments conducted within the same geologic units (e.g., Tpr-a and Tpr-b, Table 3).

Diffusion cell experiments conducted by Reimus *et al.* (2007) in volcanic core from well ER-20-6 #1 on Pahute Mesa and in volcanic core from wells UE-25c #1 and UE-25c #2 near Yucca Mountain had porosities ranging from 0.09 to 0.37, which is essentially the same range as the volcanic wafers in this study (Table 5). In those experiments, iodide (I⁻) was used as the halide tracer at ER-20-6 #1, which produced matrix diffusion coefficients from 0.9×10^{-7} to 43×10^{-7} cm²/s, consistent with the Br⁻ matrix diffusion coefficients from volcanic wafers in this study. Bromide was used by Reimus *et al.* (2007) as the halide tracer at UE-25c #1 and UE-25c #2, which produced matrix diffusion coefficients ranging from 3.8×10^{-7} to 62×10^{-7} cm²/s that are also consistent with Br⁻ in the volcanic wafers in this study. These matrix diffusion coefficients are all well below the Br⁻ and I⁻ free-water diffusion coefficients 208×10^{-7} and 204×10^{-7} cm²/s, respectively (Table 4).

Table 4. Free-water diffusion coefficients.

Tracer	Free-water Diffusion Coefficient (cm ² /s)	Reference
Br ⁻	2.08 x 10 ⁻⁵	Newman (1973), Reimus <i>et al.</i> (2007)
I ⁻	2.04 x 10 ⁻⁵	Newman (1973), Reimus <i>et al.</i> (2007)
Trimesic acid	7.63 x 10 ⁻⁶	Hayduk and Laudie method (Tucker and Nelken, 1982)
2,5 DFBA *	7.3 x 10 ⁻⁶	Farnham <i>et al.</i> (1997), Reimus <i>et al.</i> (2006)
2,6 DFBA *	7.3 x 10 ⁻⁶	Farnham <i>et al.</i> (1997), Reimus <i>et al.</i> (2006)
2,4,5 TFBA *	8.0 x 10 ⁻⁶	Farnham <i>et al.</i> (1997), Reimus <i>et al.</i> (2006)
PFBA *	~7.6 x 10 ⁻⁶	Bowman (1984), Farnham <i>et al.</i> (1997), Reimus <i>et al.</i> (2007)
H ¹⁴ CO ₃ ⁻	1.1 x 10 ⁻⁵	Newman (1993)

*DFBA = Difluorobenzoate; TFBA = Trifluorobenzoate; PFBA = Pentafluorobenzoate

Using pentafluorobenzoate (PFBA), a nonreactive organic-acid tracer (Stetzenbach *et al.*, 1982; Bowman, 1984), Reimus *et al.* (2007) matrix diffusion coefficients ranged from 0.2×10^{-7} to 20×10^{-7} cm²/s (Table 5). The ¹⁴C-labeled TMA in volcanic wafers in this study fall within that range. Pentafluorobenzoate has approximately the same free-water diffusion coefficient (76×10^{-7} cm²/s; Table 4) and a similar atomic mass to TMA, which suggests that PFBA and TMA should have similar matrix diffusion coefficients in similar volcanic rocks with similar porosities.

There is good agreement between halide (Br⁻) matrix diffusion coefficients in this study in similar volcanic rocks with similar porosities and halide (Br⁻, I⁻) matrix diffusion coefficients from Reimus *et al.* (2007). There is also reasonably good agreement between matrix diffusion coefficients for ¹⁴C-labeled TMA and PFBA matrix diffusion coefficients. The ratio of the average ¹⁴C-labeled TMA to the average of the Br⁻ matrix diffusion coefficients in this study in volcanic rocks was slightly higher (3.3 versus 2.7) than the corresponding free-water diffusion coefficients.

Porosities for the carbonate wafers ranged from 0.01 to 0.06 (Table 3). The matrix diffusion coefficients for Br⁻ in carbonate wafers ranged from 2.3×10^{-7} to 9.3×10^{-7} cm²/s with an average of 6.5×10^{-7} cm²/s, which was more than an order of magnitude lower than the free-water diffusion coefficient for Br⁻. Matrix diffusion coefficients for ¹⁴C-labeled TMA in carbonate wafers ranged from 1.1×10^{-7} to 3.6×10^{-7} cm²/s with an average of 1.7×10^{-7} cm²/s, which was more than an order of magnitude lower than the free-water diffusion coefficient for the TMA tracer (Table 4). The average ratio of the matrix diffusion coefficients for Br⁻ in carbonate wafers to the ¹⁴C-labeled TMA is 4.2, which is roughly one and one-half times the ratio of the free-water diffusion coefficients. Again, it is expected that the ratio of the free-water diffusion coefficients and the ratio of the matrix diffusion coefficients would be similar (e.g., Bechtel SAIC [2004]). Overall, there is good agreement between experiments conducted within the same geologic units (e.g., Pbu-a and Pbu-b, Table 3).

Table 5. Matrix diffusion coefficients from other reports.

Well Name	Minimum Porosity	Maximum Porosity	Minimum Halide*	Maximum Halide*	Average Halide*	Minimum FBA**	Maximum FBA**	Average FBA**
			(x10 ⁻⁷) (cm ² /s)					
Reimus <i>et al.</i> (2007)								
ER-20-6#1	0.11	0.37	0.9	43	19	0.2	16	7
UE-25C	0.09	0.30	3.8	62	23	1.1	20	6
Reimus <i>et al.</i> (2006)								
ER-6-1	0.01	0.06	17	230	104	8.5	110	54

*Br⁻ or I⁻

**DFBA, PFBA, or TFBA

Similar wafer matrix diffusion experiments conducted by Reimus *et al.* (2006) using both Br⁻ and I⁻ in core from well ER-6-1 completed in the Lower Carbonate Aquifer (LCA) produced a range of matrix diffusion coefficients from 17 x 10⁻⁷ to 230 x 10⁻⁷ cm²/s with an average matrix diffusion coefficient of 104 x 10⁻⁷ cm²/s (Table 5), which is approximately one-and-one-half orders of magnitude greater than the average matrix diffusion coefficient for Br⁻ in the carbonate wafers of this study. However, the halide matrix diffusion coefficients for carbonate rocks in Reimus *et al.* (2006) are also approximately five times higher than those reported for volcanic rocks, which have much higher porosities in Reimus *et al.* (2007). Reimus *et al.* (2006, 2007) suggest that matrix diffusion coefficients from both diffusion cell and wafer experiments are positively but weakly correlated with porosity, which was also demonstrated in this study (Figure 6).

Reimus *et al.* (2006) also used several different fluorinated benzoic acids (FBAs) in core from well ER-6-1 completed in the LCA to produce matrix diffusion coefficients. These matrix diffusion coefficients ranged from 8.5 x 10⁻⁷ to 110 x 10⁻⁷ cm²/s with an average of 54 x 10⁻⁷ cm²/s (Table 5), which is also approximately one-and-one-half orders of magnitude greater than the average ¹⁴C-labeled TMA matrix diffusion coefficients in these experiments (average 1.7 x 10⁻⁷ cm²/s), even though the range in porosities was similar (0.01 to 0.06). Fluorinated benzoic acids have similar free-water diffusion coefficients (72 x 10⁻⁷ to 80 x 10⁻⁷ cm²/s; Table 4) and atomic masses to TMA, which suggests that the FBAs and TMA should have similar matrix diffusion coefficients in carbonate rocks with similar porosities.

The matrix diffusion coefficients for Br⁻ in carbonate rocks in this study are approximately one-and-one-half orders of magnitude lower than halide (Br⁻, I⁻) matrix diffusion coefficients for similar carbonate rocks from Reimus *et al.* (2006). The matrix diffusion coefficients for ¹⁴C-labeled TMA in carbonate rocks in this study are also one-and-one-half orders of magnitude lower than diffusion coefficients for FBAs in similar carbonate rocks from Reimus *et al.* (2006), even though TMA and the FBAs have similar organic molecule structures and similar atomic masses. The matrix diffusion coefficients in Reimus *et al.* (2006) for carbonate rocks using both halides and FBAs are five-to-seven times higher than for volcanic rocks with much higher porosities from Reimus *et al.* (2007). The reason for the high matrix diffusion coefficients in low porosity carbonate rocks in Reimus *et al.* (2006) is unknown, so they are not considered further in this report.

As seen in Figure 6, matrix diffusion coefficients using both Br^- and ^{14}C -labeled TMA in volcanic rocks are correlated with porosity, are consistent with matrix diffusion coefficients in similar volcanic rocks in Reimus *et al.* (2007), and have $\text{Br}^-/^{14}\text{C}$ -labeled TMA similar to, but slightly higher than, the ratio for the free-water diffusion coefficients (3.3 versus 2.7) and matrix diffusion coefficients in Reimus *et al.* (2007; 2.9). Mass-balance calculation results using the porosity of the volcanic wafers and the initial tracer concentrations in the imbibition solutions compared with the actual final tracer concentrations in the experimental reservoirs (Appendix B) are in good agreement with Br^- . Mass balance results for ^{14}C -labeled TMA are on average approximately 30 percent lower than observed. The reason for the higher final ^{14}C -labeled TMA activities in the experimental reservoirs is not readily apparent. Sorption of ^{14}C -labeled TMA on the volcanic-rock surfaces during imbibition could provide the extra ^{14}C -labeled TMA observed, but the initial batch sorption experiments did not show any significant sorption (Figure 4a). Higher porosity rocks take up more tracer solution during imbibition (and therefore, more total tracer mass), which allows more tracer to diffuse from the pores during the experiments and results in higher final tracer concentrations in the experimental reservoirs and larger matrix diffusion coefficients. Sorption of additional tracer would result in higher reservoir tracer concentrations and larger matrix diffusion coefficients.

Although the batch sorption experiments indicate that sorption of the ^{14}C -labeled TMA on the volcanic rocks is minimal, small amounts of ^{14}C -labeled TMA could sorb onto certain mineral surfaces in the pores of the volcanic rocks. The pH of the experimental solution (i.e., the calcite-saturated water) is approximately 8.3 and the pKa of trimesic acid is 3.1. At this pH, trimesic acid will deprotonate to trimesate with a -3 charge. With this strong negative charge, the TMA/trimesate will behave nonconservatively and sorb onto positively charged mineral surfaces. At pH 8.3, phases such as amorphous iron hydroxides ($\text{Fe}(\text{OH})_3$) and Goethite ($\alpha\text{-FeOOH}$), both with a point of zero charge (pH_{PZC}) of 8.5 (Appelo and Postma, 1993), would have slightly positive surface charges where the deprotonated TMA would sorb onto these surfaces. Benedict *et al.* (2000) showed the presence of Fe oxides in fracture linings of Pahute Mesa volcanic rocks.

Matrix diffusion coefficients using Br^- in carbonate rocks are weakly correlated with porosity (Figure 6), but they are consistent with matrix diffusion coefficients for Br^- in volcanic rocks in this study and in similar volcanic rocks using Br^- and I^- (Reimus *et al.*, 2007) in that matrix diffusion coefficients decrease with decreasing porosity (Figure 4, Reimus *et al.*, 2007). Matrix diffusion coefficients using ^{14}C -labeled TMA in carbonate rocks are all similar and uncorrelated with porosity. The ratios of Br^- to ^{14}C -labeled TMA in carbonate rocks are higher than the ratio for the free-water diffusion coefficients (4.2 versus 2.7). Mass-balance calculations (Appendix B) are in good agreement with Br^- (same as volcanic rock mass balance). Mass balance results for ^{14}C -labeled TMA are on average approximately six times lower than observed. The reason for the higher final ^{14}C -labeled TMA activities in the experimental reservoirs is likely caused by sorption of additional ^{14}C -labeled TMA. Initial batch sorption experiments showed some sorption (Figure 4b) of ^{14}C -labeled TMA.

At the pH of the calcite-saturated water, approximately 8.3, calcite surfaces with a pH_{PZC} of 9.5 (Appelo and Postma, 1993) would have a net positive charge that the ^{14}C -labeled TMA would sorb to. Some of the additional ^{14}C -labeled TMA that sorbed to the calcite surfaces during imbibition would then desorb and diffuse into the experimental reservoir resulting in higher ^{14}C activities and higher matrix diffusion coefficients for the carbonate wafers.

Based on the experimental results from this study, diffusion of $\text{DOC } ^{14}\text{C}$ into the low porosity matrices of carbonate rocks and the higher porosity matrices of the volcanic aquifers in southern Nevada is slow. Therefore, diffusion of $\text{DOC } ^{14}\text{C}$ from groundwater in fractures into dead-end pores in the aquifer matrix should have little impact on $\text{DOC } ^{14}\text{C}$ groundwater ages and travel times, at least at the scale of the laboratory experiments.

The free-water diffusion coefficient of $\text{DIC } ^{14}\text{C}$ ($\text{H}^{14}\text{CO}_3^-$) is 1.4 times that of the TMA (surrogate for $\text{DOC } ^{14}\text{C}$) used in the matrix diffusion experiments in this study (Table 4). Note that the free-water diffusion coefficient of $\text{H}^{14}\text{CO}_3^-$ is only approximately 0.5 that of the average for the conservative halide tracers. Because the free-water diffusion coefficient of $\text{H}^{14}\text{CO}_3^-$ is greater than the free-water diffusion coefficient of the ^{14}C -labeled TMA (but less than the free-water diffusion coefficient of Br^-), it is expected that $\text{H}^{14}\text{CO}_3^-$ would diffuse more rapidly into the volcanic and carbonate wafers than the ^{14}C -labeled TMA. The greater diffusion of $\text{DIC } ^{14}\text{C}$ relative to $\text{DOC } ^{14}\text{C}$ would result in greater changes in groundwater ages estimated with $\text{DIC } ^{14}\text{C}$. Additionally, the molecular size of the TMA used in the experiments is on the very low end of the size range for humic substances. Considering the small molecular size of the TMA relative to general humic substances, the matrix diffusion coefficients measured using TMA in these experiments likely represent close to the maximum diffusion rates (at the laboratory scale) for $\text{DOC } ^{14}\text{C}$ in groundwater (excluding any effects from TMA sorption in these experiments).

CONCLUSIONS

The results of the wafer matrix diffusion experiments in this study confirmed that the diffusion of $\text{DOC } ^{14}\text{C}$ (^{14}C -labeled TMA was used as a surrogate for DOC) into southern Nevada volcanic and carbonate aquifers is slower than $\text{DIC } ^{14}\text{C}$ (at the laboratory scale). Matrix diffusion coefficients for ^{14}C -labeled TMA ranged from 1.1×10^{-7} to $6.1 \times 10^{-7} \text{ cm}^2/\text{s}$ and were much more than an order of magnitude lower than Br^- matrix diffusion coefficients in both volcanic and carbonate rocks. Because of apparent sorption of ^{14}C -labeled TMA in the experiments, matrix diffusion coefficients are likely even lower. The reasons for the higher than expected $\text{Br}^-/^{14}\text{C}$ -labeled TMA are unknown. Because the molecular size of TMA is on the low end of the range in molecular size for typical humic substances, the matrix diffusion coefficients for the ^{14}C -labeled TMA likely represent close to the maximum diffusion rates for $\text{DOC } ^{14}\text{C}$ in the volcanic and carbonate aquifers in southern Nevada.

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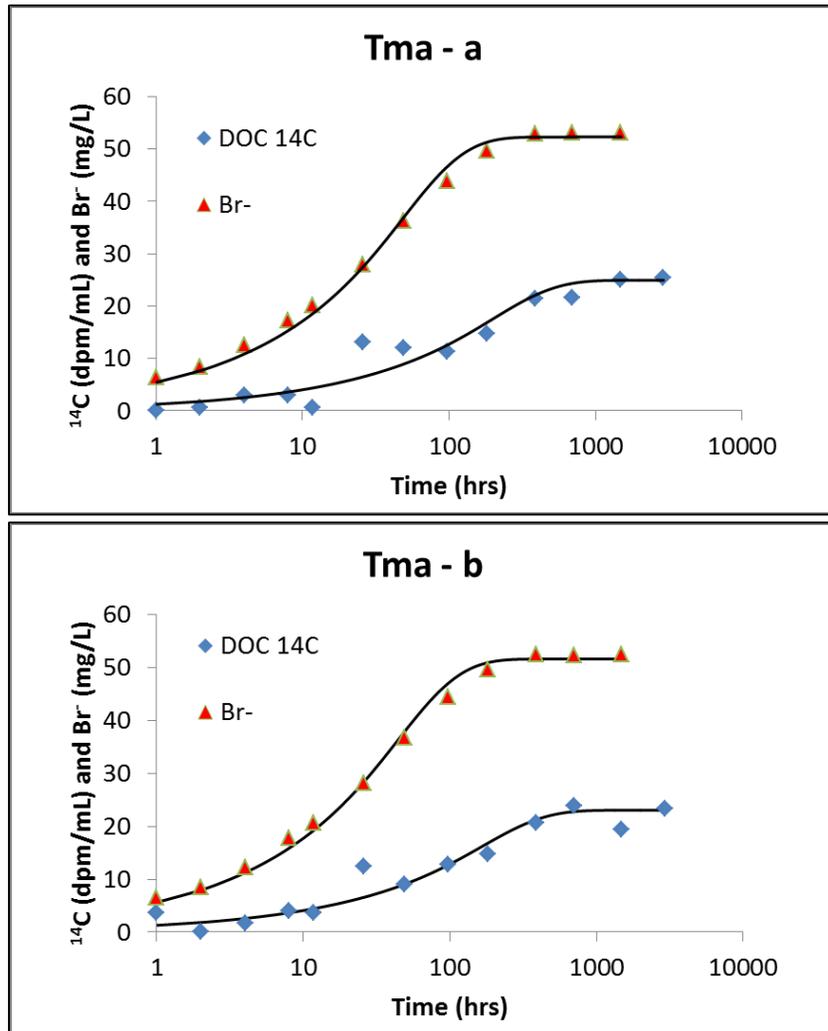
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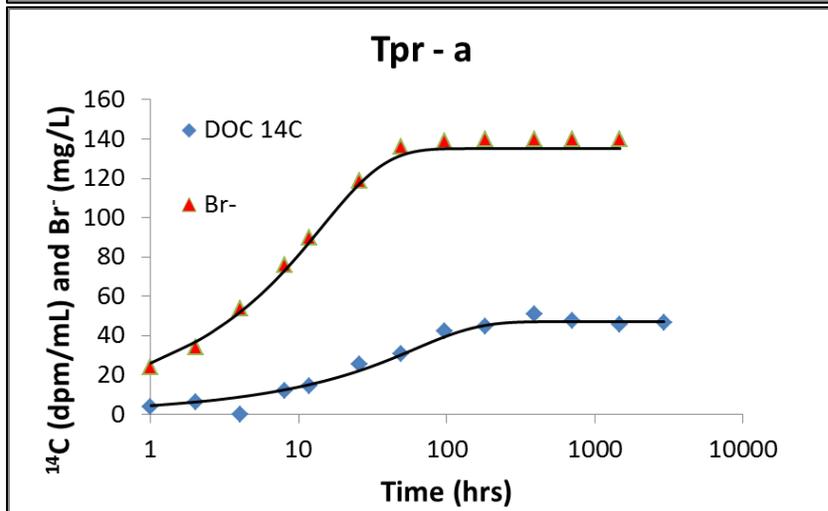
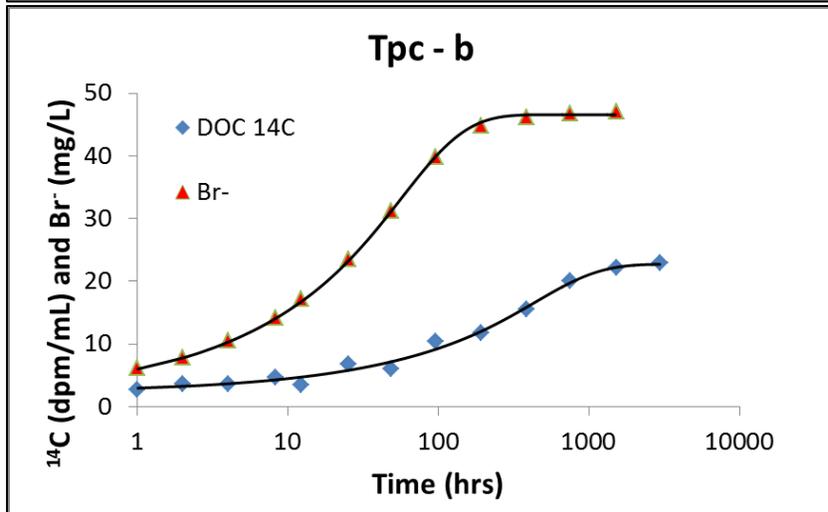
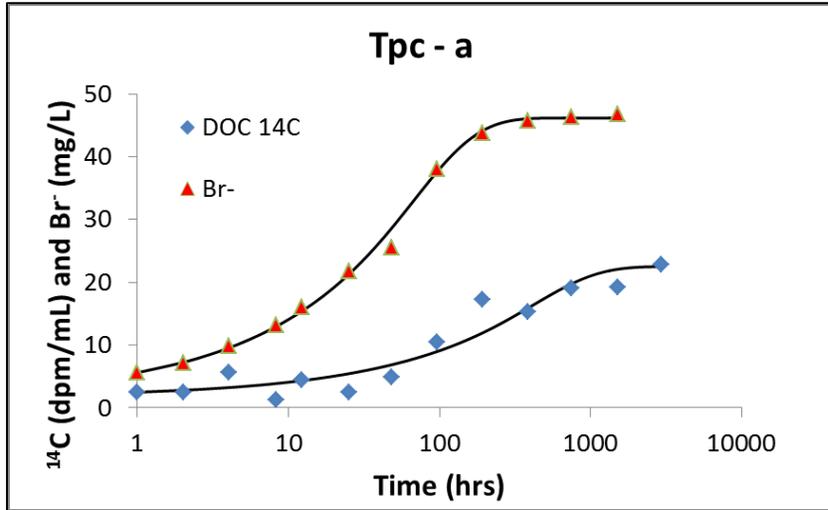
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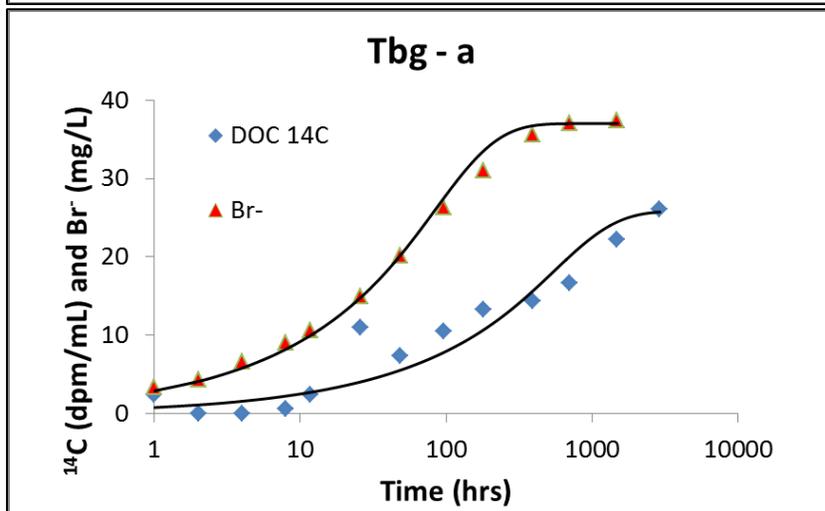
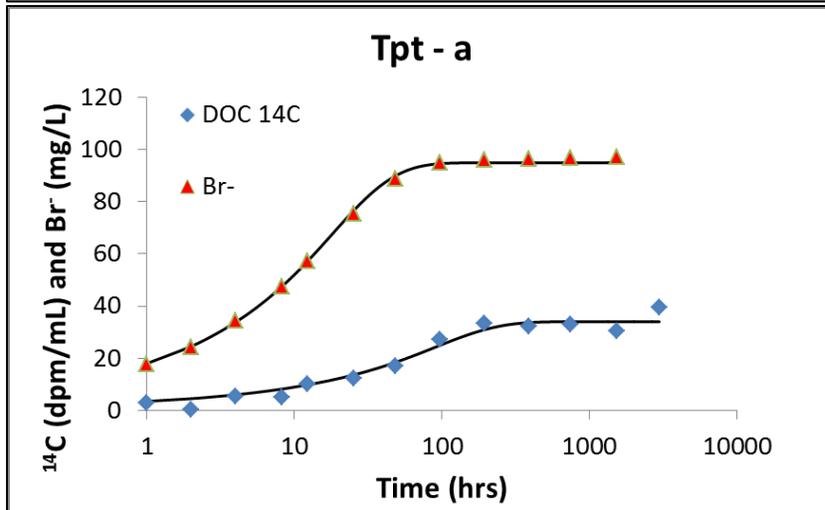
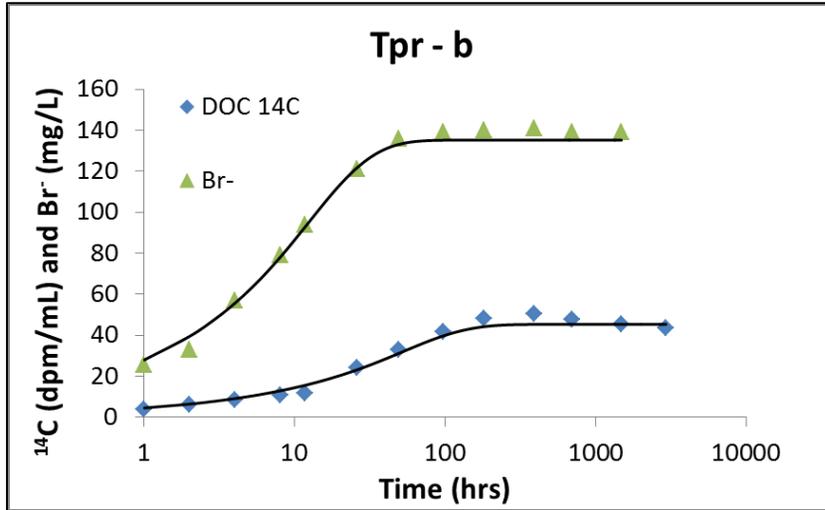
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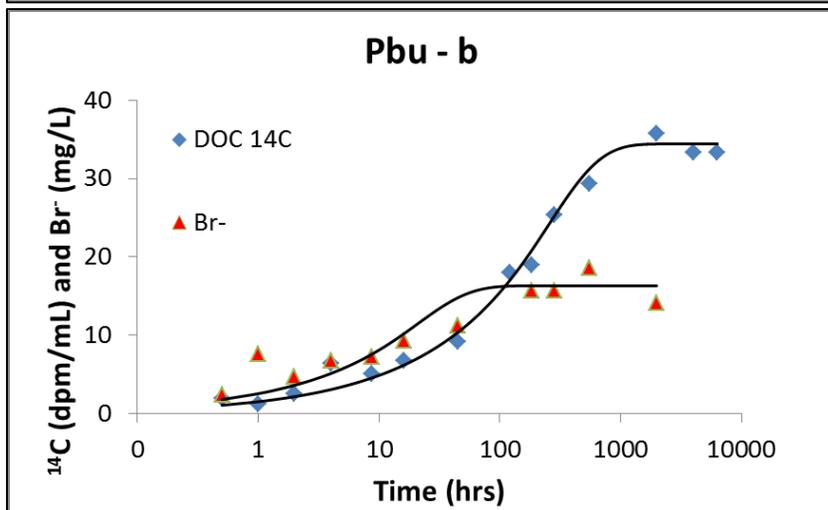
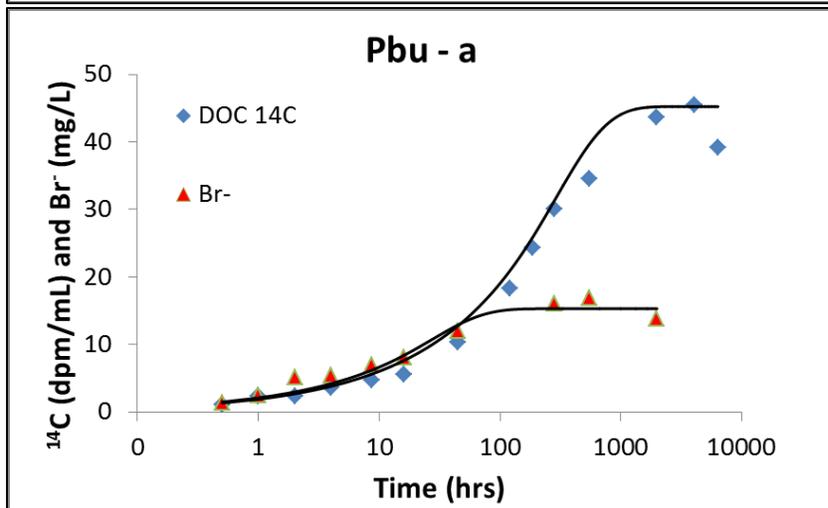
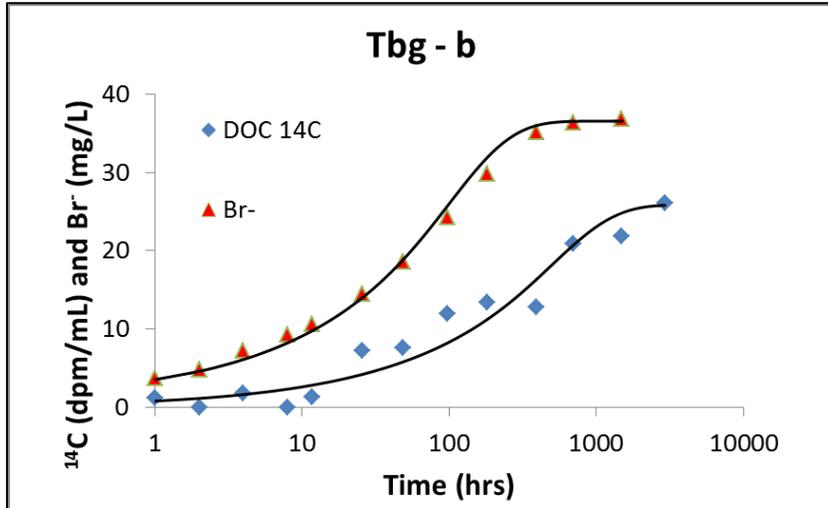
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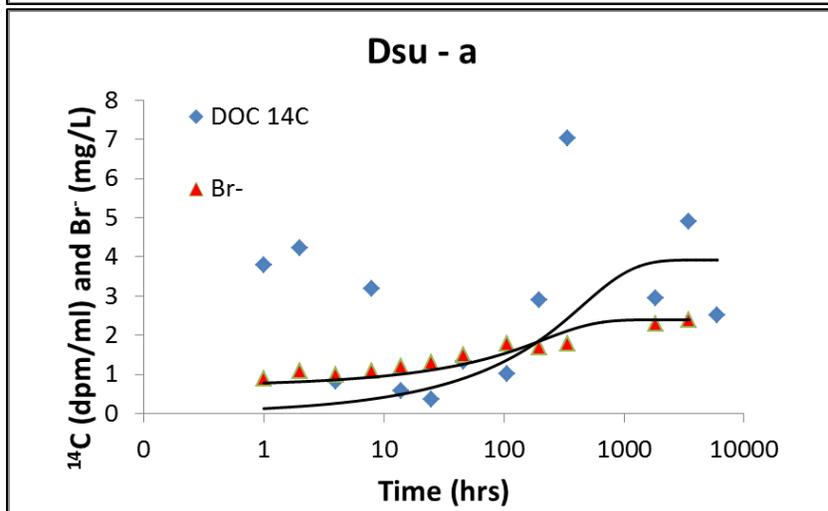
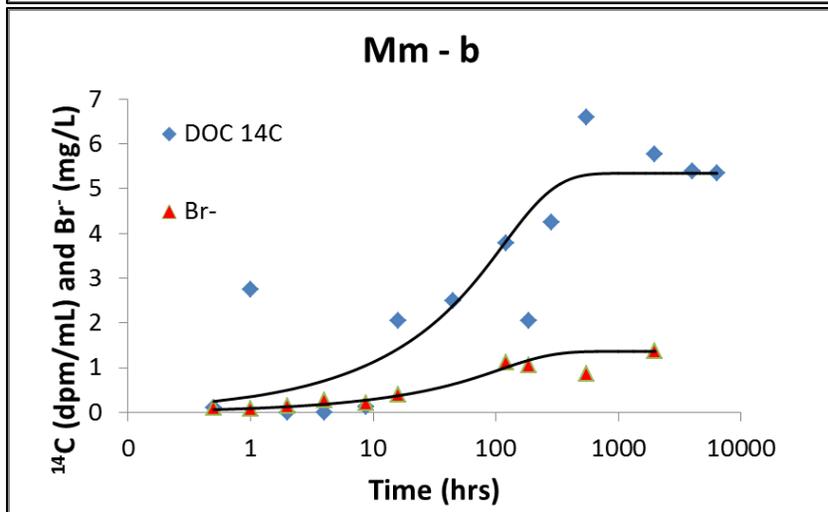
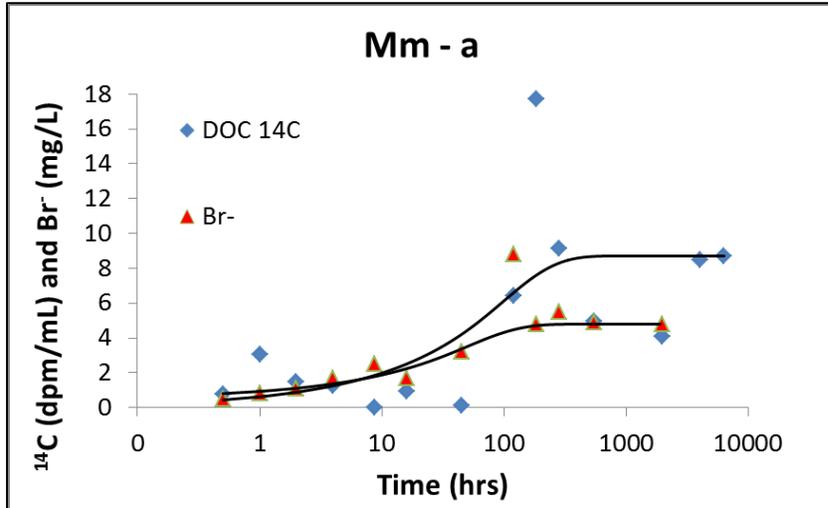
APPENDIX A: MATRIX DIFFUSION EXPERIMENTAL RESULTS AND MODEL FITS FOR VOLCANIC AND CARBONATE WAFERS.

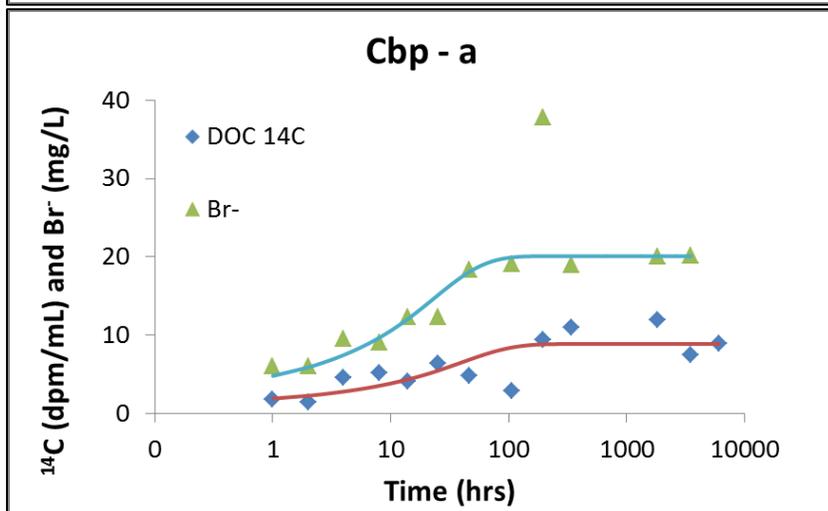
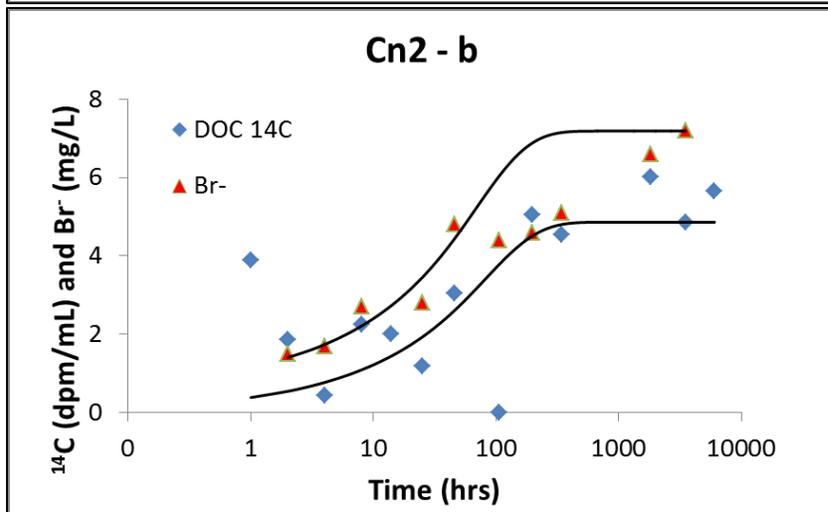
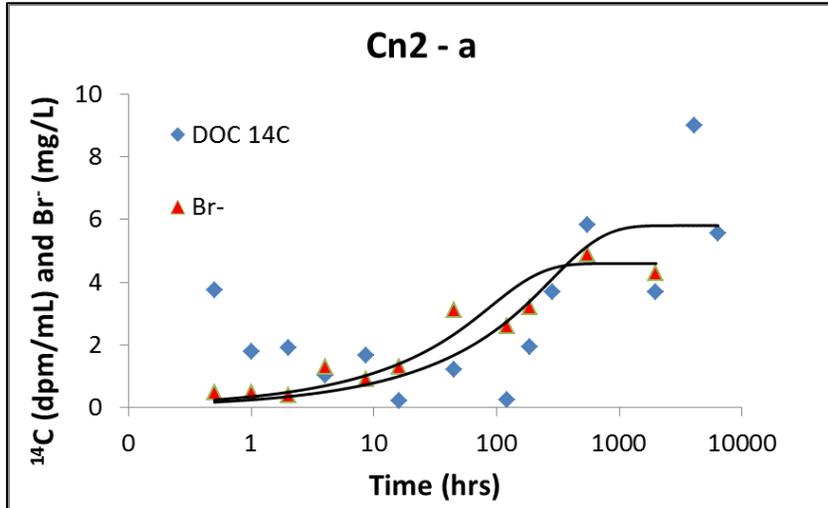


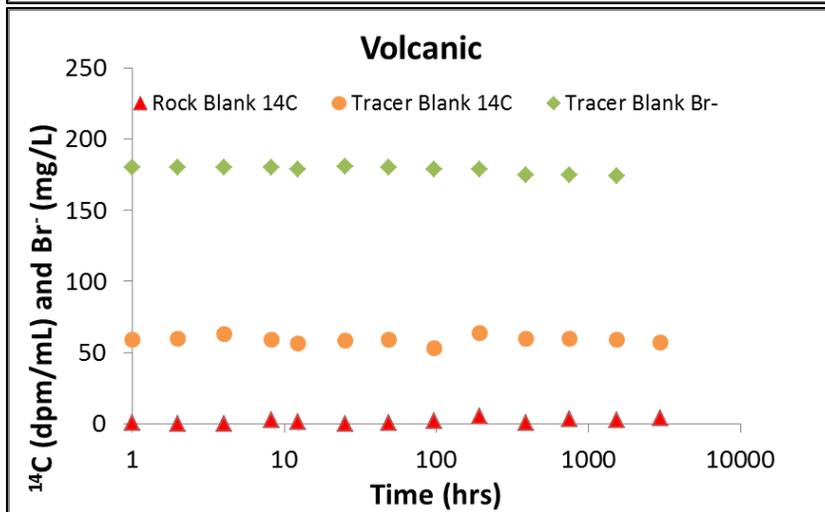
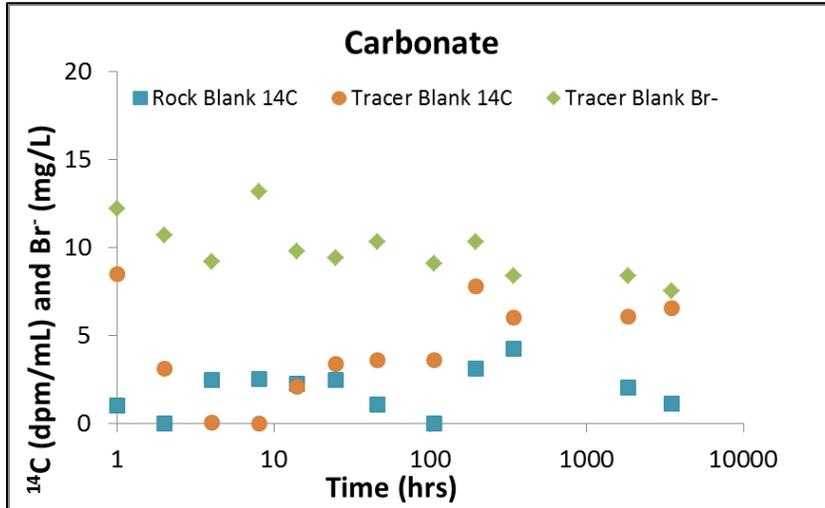












APPENDIX B. MASS BALANCE CALCULATIONS VERSUS ACTUAL CONCENTRATION FOR TRACER UPTAKE

Wafer	Wafer Volume (cm ³)	Wafer Porosity	Concentration Br Imbibed (mg/L)	Activity ¹⁴ C Imbibed (cpm/mL)	Experiment Volume (mL)	Concentration Br Calculated (mg/L)	Concentration Br Actual (mg/L)	Br Calculated /Actual	Activity ¹⁴ C Calculated (cpm/mL)	Activity ¹⁴ C Final (cpm/mL)	¹⁴ C Calculated /Actual
Tpc-a	59.43	0.12	3600	1000	600	42.3	45.7	0.93	12.1	19.2	0.63
Tpc-b	57	0.12	3600	1000	600	40.8	45.7	0.89	11.7	18.9	0.62
Tpt-a	57	0.27	3600	1000	600	89.6	93.3	0.96	25.6	30.7	0.83
Tbg-a	59	0.1	3600	1000	600	35.3	36.3	0.97	10.1	19.2	0.53
Tbg-b	58	0.1	3600	1000	600	34.4	36.0	0.95	9.8	20.1	0.49
Tma-a	61	0.15	3600	1000	600	54.4	53.0	1.03	15.5	22.0	0.71
Tma-b	57	0.16	3600	1000	600	53.6	52.0	1.03	15.3	20.1	0.76
Tpr-a	57	0.37	3600	1000	600	123	140	0.88	35.2	45.1	0.78
Tpr-b	55	0.38	3600	1000	600	122	139	0.88	34.9	47.0	0.74
Mm-a	41	0.02	3600	1000	800	3.7	4.8	0.76	1.0	7.7	0.14
Pbu-a	57	0.05	3600	1000	800	12.7	14.0	0.91	3.6	37.4	0.10
Pbu-b	51	0.06	3600	1000	800	13.7	15.0	0.92	3.9	30.7	0.13
Cn2-a	57	0.01	3600	1000	800	2.5	4.0	0.64	0.7	4.8	0.15
Cn2-b	56	0.02	3600	1000	600	6.7	6.6	1.02	1.9	4.6	0.42
Dsu-a	42	0.01	3600	1000	600	2.5	1.8	1.39	0.7	4.4	0.16
Cpb-a	74	0.04	3600	1000	600	17.7	20.0	0.88	5.0	9.6	0.53

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