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Isotopic fractionation during reductive dechlorination of trichloroethene by zero-valent iron: influence of surface treatment

G.F. Slater [a,b,*], B. Sherwood Lollar [b], R. Allen King [c], S. O'Hannesin [d]

[a] *Department of Marine Chemistry and Geochemistry, MS#4, Woods Hole Oceanographic Institution, 520 Woods Hole Road, Woods Hole, MA 02543-1543, USA*

[b] *Stable Isotope Laboratory, Department of Geology, University of Toronto, 22 Russell St., Toronto, Canada M5S 3B1*

[c] *Department of Geology, Washington State University, P.O. Box 642812, Pullman, WA, USA*

[d] *Envirometal Technologies, Inc., 745 Bridge St., Suite 7, Waterloo, Ontario, Canada N2V 2G6*

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Abstract

During reductive dechlorination of trichloroethene (TCE) by zero-valent iron, stable carbon isotopic values of residual TCE fractionate significantly and can be described by a Rayleigh model. This study investigated the effect of observed reaction rate, surface oxidation and iron type on isotopic fractionation of TCE during reductive dechlorination. Variation of observed reaction rate did not produce significant differences in isotopic fractionation in degradation experiments. However, a small influence on isotopic fractionation was observed for experiments using acid-cleaned electrolytic iron versus experiments using autoclaved electrolytic iron, acid-cleaned Peerless cast iron or autoclaved Peerless cast iron. A consistent isotopic enrichment factor of $\varepsilon = -16.7‰$ was determined for all experiments using cast iron, and for the experiments with autoclaved electrolytic iron. Column experiments using 100% cast iron and a 28% cast iron/72% aquifer matrix mixture also resulted in an enrichment factor of $-16.9‰$. The consistency in enrichment factors between batch and column systems suggests that isotopic trends observed in batch systems may be extrapolated to flowing systems such as field sites.

The fact that significant isotopic fractionation was observed in all experiments implies that isotopic analysis can provide a direct qualitative indication of whether or not reductive dechlorination of TCE by Fe^0 is occurring. This evidence may be useful in answering questions which arise at field sites, such as determining whether TCE observed down-gradient of an iron wall remediation scheme is the result of incomplete degradation within the wall, or of the dissolved TCE plume bypassing the wall.

Keywords: Dechlorination; Carbon isotopes; Iron; Acid-washed

1. Introduction

Reductive dechlorination of dissolved chlorinated ethenes by in situ passive iron wall remediation schemes has been of great interest in contaminant hydrogeology since its initial suggestion by Gillham and O'Hannesin (1994). Research on this process has focused on determining the mechanisms and controls on reductive

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[*] Corresponding author. Address: Department of Marine Chemistry and Geochemistry, MS#4, Woods Hole Oceanographic Institution, 520 Woods Hole Road, Woods Hole, MA 02543-1543, USA. Fax: +1-508-457-2164.

E-mail address: gslater@whoi.edu (G.F. Slater).

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dechlorination by iron metal, including research on pathways (Matheson and Tratnyek, 1994; Orth and Gillham, 1996; Roberts et al., 1996; Weber, 1996; Charlet et al., 1998; Fennelly and Roberts, 1998; Arnold and Roberts, 2000), kinetics (Johnson et al., 1996; Charlet et al., 1998; Scherer et al., 1998), sorption effects (Burris et al., 1998), hydrocarbon formation (Hardy and Gillham, 1995; Deng et al., 1997), the role of surface oxides (Sherer et al., 1997; Johnson et al., 1998; Su and Puls, 1999), long term wall performance (O'Hannesin and Gillham, 1998), and barrier design (Tratnyek et al., 1997). Much progress has been made in understanding the processes involved in reductive dechlorination by iron metal which is presently thought to occur via complexation of the chlorinated ethene to the metal surface. Subsequent electron transfer from the metal to the chlorinated ethene results in the loss of chlorine by either β-elimination or hydrogenolysis (Arnold and Roberts, 2000). However, questions remain concerning the mechanisms of electron transfer and complexation, and the role of oxides as barrier, semi-conductor or coordinating surface (e.g. Sherer et al., 1997). While there have been a number of successful field applications of permeable reactive barriers (PRBs), several challenges in monitoring the effectiveness of PRBs have arisen. Monitoring iron wall performance can be complicated by temporal variations in contaminant concentrations (e.g. O'Hannesin and Gillham, 1998). Further, confirming the effectiveness of dechlorination in a PRB can be complicated by the observation of trichloroethene (TCE) down-gradient from the wall. It is often impossible to determine whether this TCE is present due to bypass of the PRB through fracture flow or due to incomplete reaction due to insufficient reactor thickness.

Stable carbon isotopic analysis is a potential technique for investigation and monitoring of reductive dechlorination of chlorinated ethenes by in situ granular iron treatment systems. Stable carbon isotopic analysis involves measurement of the ratio of the two stable isotopes of carbon present in a sample. This ratio is expressed as a δ^{13}C value where:

$$\delta^{13}\mathrm{C} = (R_{\mathrm{sample}}/R_{\mathrm{standard}} - 1) \times 1000 \tag{1}$$

R_{sample} is the ^{13}C/^{12}C ratio in a given sample, R_{standard} is the ^{13}C/^{12}C ratio in a standard reference material, in this case V-PDB. Non-degradative processes such as volatilization from groundwater and sorption do not result in significant changes, or fractionation, of δ^{13}C, within the 0.5‰ accuracy and reproducibility of online gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS) (Poulson and Drever, 1999; Slater et al., 1999). In contrast, reductive dechlorination by zero-valent iron results in a large stable carbon isotope fractionation of chlorinated ethenes (Slater et al., 1998; Dayan et al., 1999). The isotopic composition, δ^{13}C, of the residual chlorinated ethene pool can be enriched by up to 40‰ during reductive dechlorination by zero-valent iron. These shifts are highly reproducible and can be modeled using a simple isotopic model known as the Rayleigh model (Slater et al., 1998; Dayan et al., 1999). The Rayleigh model assumes that there is a consistent preferential reaction of one isotopomer over the other during a process. This preference is expressed as a fractionation factor, α, which relates the isotopic composition of the reactant to the extent of degradation as in Eq. (2):

$$R/R_0 = f^{(\alpha-1)} \tag{2}$$

R is the ratio of ^{13}C to ^{12}C in the sample at a given fraction remaining, f. R_0 is the initial ratio of ^{13}C to ^{12}C. This fractionation factor can be converted into a permil enrichment factor, ε, where $\varepsilon = 1000(\alpha - 1)$.

This study characterized the isotopic effects associated with reductive dechlorination of TCE by both electrolytic and cast iron, in order to assess whether differences in iron type, surface pre-treatment or observed reaction rate result in differences in isotopic fractionation. Further, this study compared isotopic fractionation in batch microcosm systems to column systems containing 100% cast iron, and a mixture of cast iron and aquifer material, in order to assess whether the results observed in batch systems can be extrapolated to open systems under dynamic flow conditions more analogous to field systems. The long-term goal of the research is to explore the utility of using stable carbon isotopic analysis as a tool to investigate the mechanisms and effectiveness of abiotic dechlorination in the laboratory and the field.

2. Material and methods

This study consisted of three experiments using different types of iron and surface pre-treatments. The two types of iron used were electrolytic iron and cast iron. Electrolytic iron is essentially free from impurities and is commonly used in laboratory studies of this reaction. In contrast, cast iron contains impurities, in particular graphite, and is used in field applications of this remediation technology. These two iron types were compared in order to determine whether the purity of the iron has a significant effect on isotopic fractionation during reductive dechlorination. The cast irons used in this study were from two different suppliers, Peerless and Connelly. These companies supply cast iron filings which are used in field applications of this remediation technology. Some differences in behavior have been observed during the use of iron from these suppliers so the isotopic fractionation by case iron from these two sources was compared. Two different surface pre-treatments were also compared in this study. Acid washing is commonly used in laboratory studies to remove/reduce the oxidized coating on the iron filings and thus increase the reactivity of the iron. In the field no surface pre-treatment is used and thus the surface is oxidized. Autoclaving was used in these studies to provide sterile iron with an oxidized surface which would be more analogous to that used in the field.

Three experiments were carried out in this study. Experiment 1 compared the isotopic fractionation during reductive dechlorination of TCE by Peerless cast iron at three different observed reaction rates by varying the iron/water ratio. Experiment 2 compared isotopic fractionation by two different types of iron, electrolytic iron powder and Peerless cast iron, which had each undergone two different types of pre-treatment, acid washing and autoclaving. This experiment assessed differences in isotopic fractionation between the two types of iron, as well as the impact of pre-treatment on isotopic fractionation during reductive dechlorination. Experiment 3 assessed the utility of isotopic analysis as an indicator of reaction efficiency in dynamic flow-through column studies. Field conditions were simulated as closely as possible by using aquifer material and groundwater from a contaminated site. Two column studies were carried out, the first with a column containing 100% cast iron, and the second with a column containing 28% cast iron and 72% aquifer material.

2.1. Experimental set up

2.1.1. Chemicals

All solvents used were high purity and were obtained from the following suppliers. TCE: ACP Chemical Inc., grade 99.5%. Pentane: EMS Scientific, spectrophotometric grade. Methanol: ACP Chemicals Inc., ACS reagent grade. HCL: BDH, ACS reagent grade. All water was deionized water (conductivity > 17 MΩ). Two different lots of Iron Electrolytic Powder, certified were obtained from Fisher Scientific. Peerless and Connelly cast iron filings were supplied by Envirometal Technologies Inc.

2.2. Batch systems

Batch experiments were carried out in 60 ml serum vials capped with Teflon faced septa and an iron to water ratio of 0.25 g/ml for electrolytic iron and 0.10 g/ml for Peerless cast iron. Different iron water ratios were used for the two iron types in order to match observed degradation rates as closely as possible. Batch vials contained degassed, deionized water, 20 ml headspace, iron, 80 μM pentane as an internal standard and TCE added as a high concentration ($\sim$500 000 mg/l) TCE/methanol stock solution. Vials were placed on a rotator at 6 rpm and 22 ± 1 °C. Controls consisted of serum vials containing water, pentane, TCE and acid washed glass beads to make up the volume occupied by the iron. Initial TCE concentrations were 20 mg/l.

2.2.1. Experiment 1

In order to compare isotopic fractionation at different observed reaction rates, the iron/water ratio was varied in batch systems using the same autoclaved Peerless cast iron. The objective was to test the effect of variation in observed reaction rate, rather than surface normalized reaction rate, as this parameter may vary in the field. The goal of the experiment was to determine whether such a variation in the field would affect isotopic fractionation. Autoclaved iron was used in order to ensure sterility in the experiments. Isotopic behavior during these experiments could therefore be assumed to be due to abiotic reductive dechlorination alone and not to concurrent biological reductive dechlorination which also has isotopic effects associated with it (Hunkeler et al., 1999; Sherwood Lollar et al., 1999; Bloom et al., 2000; Slater et al., 2001) and has been shown to occur in some abiotic degradation systems (Novak et al., 1998; Gu et al., 1999). Experiments were run using three iron/water ratios, 0.1, 0.05 and 0.025 g/ml. Based on previous experiments it was determined that these ratios would degrade the TCE over a period of one week, two weeks, and four weeks respectively. For each of the three iron/water ratios, 12 reaction vials were set up. At each sampling point, two vials from each of the three series were analyzed.

2.2.2. Experiment 2

Experiment 2 compared isotopic fractionation between two lots of electrolytic iron (Fisher Scientific) and one batch of cast iron (Peerless cast iron, obtained from Envirometal Technologies Inc.). The two lots of electrolytic iron were compared to ensure there was no variation between lots from the manufacturer. All experiments were carried out in duplicate reaction vials that were sampled repeatedly over the course of degradation. For both types of iron, experiments were run using (i) iron that had been acid-cleaned and dried anaerobically, and (ii) iron which had been autoclaved and dried aerobically. Autoclaving or acid cleaning the iron ensured that no microbial activity occurred during degradation and therefore that isotopic fractionation was solely due to abiotic reductive dechlorination. During acid cleaning, the iron was soaked in degassed 1 N HCl for 30 min, then rinsed five times with degassed deionized water, rinsed once with acetone and then dried under UHP Ar and stored under N_2 until use (Roberts, pers. comm.). Experiments using acid-cleaned iron were assembled under nitrogen atmosphere using degassed, deionized water to minimize oxidation of the iron during initial stages of the experiment. The autoclaved iron was dried under high purity air and experiments using autoclaved iron were assembled under aerobic conditions, resulting in oxidation of the iron surface.

2.3. Column systems

2.3.1. Experiment 3

Experiment 3 investigated the effect of dynamic flow conditions on isotopic fractionation during reductive dechlorination by untreated Connelly cast iron. Column experiments were carried out using Envirometal Technologies Incorporated (ETI) test columns constructed to test the application of iron wall remediation at an industrial facility in California. The column construction and analytical methods are described in detail in Gillham and O'Hannesin (1994).

Briefly, two columns were constructed of Plexiglas tubes with a length of 100 cm and an internal diameter of 3.8 cm. Seven sampling ports were positioned along the length at distances of 5, 10, 20, 30, 40, 60 and 80 cm from the inlet end the samples could be collected from the influent and effluent solutions of the column as well.

One column was packed with 100% Connelly cast iron with a surface area of 1.8 m^2/g. To assure a homogeneous mixture, aliquots of iron material were dry-packed vertically in lift sections within the column. The second column was packed with 28% by weight of the same Connelly cast iron, with the balance consisting of aquifer material from the industrial facility in CA. The column tests were performed at room temperature and the iron was not pre-treated, as would be the case in field applications.

An Ismatec IPN pump was used to feed the site water spiked with 40 mg/l TCE from a collapsible Teflon bag to the influent end of the columns. The column was sampled daily over time until steady state concentration profiles were achieved. In the bench-scale tests, steady state was defined as the time when volatile organic compound concentrations versus distance profiles do not change significantly between sampling events.

2.4. Concentration analysis

For the column experiments, samples were withdrawn from the column ports via syringe. Analysis of TCE, and its breakdown products, *cis*- and *trans*-dichloroethene (*c*DCE and *t*DCE), and vinyl chloride (VC), involved pentane extraction of the water sample followed by analysis on a Hewlett Packard 5890 Series II gas chromatograph equipped with a Hewlett Packard 7673 autosampler. The chromatograph was equipped with a ^{63}Ni electron capture detector and DB-624 megabore capillary column (30 m × 0.538 mm ID, film thickness 3 μm). The gas chromatograph had an initial temperature of 50 °C, with a temperature time program of 15 °C/min to a final temperature of 150 °C. The detector temperature was 300 °C. The carrier gas was helium and makeup gas was 5% methane and 95% argon, with a flow rate of 30 ml/min.

For analysis of concentrations of TCE and its breakdown products (*c*DCE, *t*DCE, VC, ethene and acetylene) in the batch experiments, 300 μl of headspace were removed from the microcosm with a gas-tight syringe and injected into a Varian 3300 Gas Chromatograph equipped with a 30 m × 0.53 mm GS-Q megabore column and an FID detector. The temperature program used was 70 °C hold 1 min, increase to 200 °C at 26 °C/min then increase to 225 °C at 5 °C/min and hold 2 min. External standards were prepared having the same volume of headspace and liquid as the experimental vials and covering the range of concentrations observed in the experiments. Reproducibility on standard analyses was ±5%. Reproducibility on replicate injections was ±5%.

2.5. Isotopic analysis

For isotopic analysis in the column experiments, a 10 ml water sample was collected from a sample port into a 15 ml serum bottle capped with a Teflon coated silicon septa. The samples were returned to the University of Toronto and analyzed within two days. For isotopic analysis, 300–1000 μl of headspace were removed from the experimental vial (Experiments 1 and 2) or the 15 ml sampling vial (Experiment 3) using a gas-tight syringe and injected on a gas chromatograph-combustion-isotope ratio mass spectrometer (GC-C-IRMS) consisting of a Varian 3400 GC equipped with a 30 m × 0.25 mm DB-624 (J&W Scientific) capillary column connected via a combustion interface to a Finnigan Mat 252 isotope ratio mass spectrometer. While internal reproducibility based on triplicate sample injections is <0.3‰ for this system, datapoints are assigned an accuracy and reproducibility (error bars) of 0.5‰ to incorporate not only variation due to reproducibility but variation due to different split settings as per Dempster et al. (1997).

2.6. Iron characterization

In order to assess the impact of acid-washing and autoclaving on the surface of the iron, the irons used in Experiment 2 were examined under SEM and by XRF. XRF analysis was carried out on a Phillips PW 2404 XRF. Iron fillings were attached to an oxygen free graphite cup using two sided tape. The oxygen blank was less than the 0.1% detection limit for oxygen. Surface areas of the iron were determined by Micrometerics (Norcross, GA) using BET N_2 adsorption.

3. Results

3.1. Experiment 1

TCE was degraded with autoclaved Peerless iron at three different iron/water ratios. Degradation for the one week, two week and four week degradations could be described with observed first order rate constants of 0.0038, 0.0028, and 0.0021 (h^{-1}) (Table 1). Surface normalized rate constants (K_{SA}) were not determined as the iron used was from the same lot and thus the surface normalized rate constants should be identical. Degradation products were consistent with those reported in the literature, including *c*DCE, *t*DCE, VC, ethene, and acetylene, but were not quantified. No change in TCE concentration was observed in the control vials within ±5%.

3.1.1. Isotopic results

For all three rates of degradation, the residual TCE became progressively more enriched in the heavier isotope (^{13}C) as dechlorination proceeded (Fig. 1). The final isotopic composition of the residual TCE was up to 40‰ more positive than the initial isotopic composition of −30.5‰. Such isotopic enrichment of the residual TCE is consistent with a process that degrades ^{12}C–^{12}C bonds at a faster rate than ^{13}C–^{12}C bonds. No significant change in isotopic composition was observed for the control vials within 0.5‰.

Table 1
First order rate constants and enrichment factors for reductive dechlorination of TCE by Peerless cast iron at three iron/water ratios, Experiment 1

Iron/water ratio	Rate (h^{-1})	r^2	ε	r^2	95% CI
0.1	0.0038	0.94	−15.8	0.84	±2.9
0.05	0.0028	0.86	−15.2	0.88	±3.0
0.025	0.0021	0.98	−16.8	0.95	±2.5

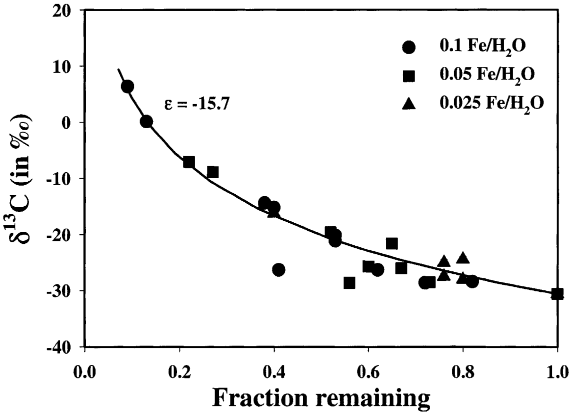

Fig. 1. Carbon isotopic composition of TCE versus fraction of TCE remaining during reductive dechlorination by Peerless zero-valent cast iron at three different iron/water ratios in Experiment 1. Error bars represent 0.5‰ accuracy and reproducibility and are smaller than plot symbols. The line represents a Rayleigh model curve based on an enrichment factor of −15.7‰ determined from all data using Eq. (3) (see text).

Fig. 1 shows that the relationship of $\delta^{13}C_{TCE}$ to fraction of TCE remaining follows an exponential pattern. This type of exponential relationship is characteristic of processes that can be described by a Rayleigh isotopic evolution model. The Rayleigh model can be applied to an irreversible one step process if the fractionation factor, α, is constant throughout the reaction (Mariotti et al., 1981). Because α are characteristic of the reaction, and do not depend on the extent to which the reaction proceeds, fractionation factors are an effective means of describing and comparing the isotopic fractionation occurring during different experiments. Fractionation factors for the Rayleigh model curves in Fig. 1 were determined by plotting the data from Experiment 1 using the approach of Mariotti et al. (1981) shown in Eq. (3):

$$(\alpha - 1)\ln f = \ln(((\delta^{13}C_{TCE}/1000) + 1) \\ /((\delta^{13}C_{TCE_0}/1000) + 1)) \qquad (3)$$

where $\delta^{13}C_{TCE}$ and $\delta^{13}C_{TCE_0}$ are the isotopic compositions of the TCE at a given time and the initial time respectively. A least squares regression of a plot of $\ln f$ vs $\ln(((\delta^{13}C_{TCE}/1000) + 1)/((\delta^{13}C_{TCE_0}/1000) + 1))$ yields a slope of $\alpha - 1$. Fractionation factors were converted to permil enrichment factors, $\varepsilon = 1000(\alpha - 1)$ for comparison.

Enrichment factors (ε) determined for the three iron/water ratios used in this experiment are shown in Table 1 along with their r^2 correlation factors and 95% confidence intervals for the Mariotti type least squares regression used to determine the enrichment factors. The high r^2 factors obtained for the Mariotti type least square regressions demonstrate that the isotopic behavior in these systems is consistent with a Rayleigh model. The fact that the enrichment factors are the same for all three rates of degradation shows that isotopic fractionation is independent of rate over this range of rates. When all the data for these three iron/water ratios is combined the overall enrichment factor is −15.7‰, with an r^2 of 0.87 and a 95% confidence interval of ±1.6. This overall enrichment factor is the same as the individual enrichment factors for each experiment within 95% confidence and hence in Fig. 1 a single Rayleigh curve based on the overall value is used for all the data.

Early in the experiment ($f > 0.4$) there were some datapoints which did not fall on the $\varepsilon = -15.7$ Rayleigh curve. While this deviation could be the result of non-equilibrium partitioning of TCE between the solid, liquid and gaseous phases in early stages of the experiment, equilibration should have occurred by the time these samples were taken. It is more likely that some variation in the individual reaction vials sampled at these points, such as a slight leak, resulted in deviation observed by these samples. By repeatedly sampling the same reaction vial in subsequent experiments this problem was avoided. This trend does not appear in results from Experiment 2. It is important to note that removing this early data results in an enrichment factor of −16.4‰ ($r^2 = 0.92$, 95% CI ±1.4), which is not significantly different from the value obtained using all the data.

3.2. Experiment 2

Degradation of TCE to less chlorinated ethenes and ethene and acetylene was observed consistent with reports in the literature, but these breakdown product concentrations were not quantified. No change in TCE concentration was observed in the control vials within ±5%. First order degradation rate constants also describe the data obtained in Experiment 2 (Table 2). Observed reaction rates varied by over two orders of magnitude between experiments. The highest observed rate was for autoclaved electrolytic iron from batch 1 which had the highest surface area (0.2410 m^2/g). The surface area analysis of batch 1 acid-cleaned electrolytic iron was approximately a factor of four lower (0.0569 m^2/g). Surface normalized rate constants (K_{SA} $h^{-1}\ m^{-2}\ l$) for these two surface treatments were very similar (0.0081, 0.0071). This suggests that observed rate of reaction for these two experiments is controlled by the surface area of the iron, consistent with the literature (Johnson et al., 1996). The surface areas of batch 2 electrolytic iron were not determined so no comparison between the surface areas of these batches could be made.

There was less difference between surface areas of the acid-cleaned and autoclaved Peerless irons (0.3757 and 0.3525 m^2/g respectively). The highest observed rate did correspond to the higher surface area however, consistent with the electrolytic results. The surface normalized rate constant for the autoclaved Peerless iron was nearly an order of magnitude lower than that observed for the acid cleaned Peerless iron. This difference is the same as that found for the observed rate. However, accurate surface normalized rate constants, which take into account the presence of non-reactive graphite in the cast iron, could not be calculated as the carbon content of this Peerless iron was not known.

3.2.1. Isotopic results

Fig. 2 shows the isotopic composition of TCE versus fraction remaining for acid-cleaned batch 1 electrolytic iron (A), autoclaved batch 1 electrolytic iron (B), acid-cleaned Peerless iron (C), and autoclaved Peerless iron (D). The results of the batch 2 electrolytic iron are similar to batch 1 and are therefore not shown in this figure. Enrichment factors for batch 1 and batch 2 electrolytic iron, and for Peerless cast iron are given in Table 2. The r^2 correlation co-efficients and 95% confidence intervals for the Mariotti type least squares regression are also given in Table 2. The high r^2 values (0.92–0.99) demonstrate that the isotopic behavior of these systems is consistent with a Rayleigh model.

Table 2 shows that enrichment factors for acid-cleaned and autoclaved Peerless iron are the same within 95% confidence intervals. In addition, enrichment factors for both batches of autoclaved electrolytic iron are the same within 95% confidence intervals as those observed for Peerless cast iron. Only acid-cleaned electrolytic iron has enrichment factors that are significantly different. The enrichment factors for the acid-cleaned electrolytic iron in batch 1 and batch 2 are −20.3‰ and −24.8‰, significantly more negative than enrichment factors for autoclaved electrolytic iron with respect to the error of the measurements.

3.3. Experiment 3

3.3.1. Isotopic results

Fig. 3 shows the results of the column studies. Both columns showed dechlorination of >95% of the initial

Table 2
First order rate constants and enrichment factors for dechlorination of TCE by different zero-valent iron types and surface treatments, Experiment 2

Iron type	Surface treatment	Rate (h^{-1})	r^2	K_{SA} ($h^{-1}\ m^{-2}\ l$)	ε	r^2	95% CI
Electrolytic batch 1	Acid cleaned	0.12	0.82	0.0081	−20.3	0.98	±1.7
	Autoclaved	0.45	0.99	0.0071	−17.2	0.99	±0.4
Electrolytic batch 2	Acid cleaned	0.11	0.95	Nd	−24.8	0.96	±1.9
	Autoclaved	0.0028	0.99	Nd	−18.7	0.96	±4.1*
Peerless	Acid cleaned	0.0091	0.96	0.0027	−17.1	0.98	±1.4
	Autoclaved	0.0012	0.96	0.00039	−16.4	0.92	±1.7

Nd: surface areas for batch 2 electrolytic iron were not determined.

* 95% confidence intervals were large due to the small number of datapoints obtained in this experiment.

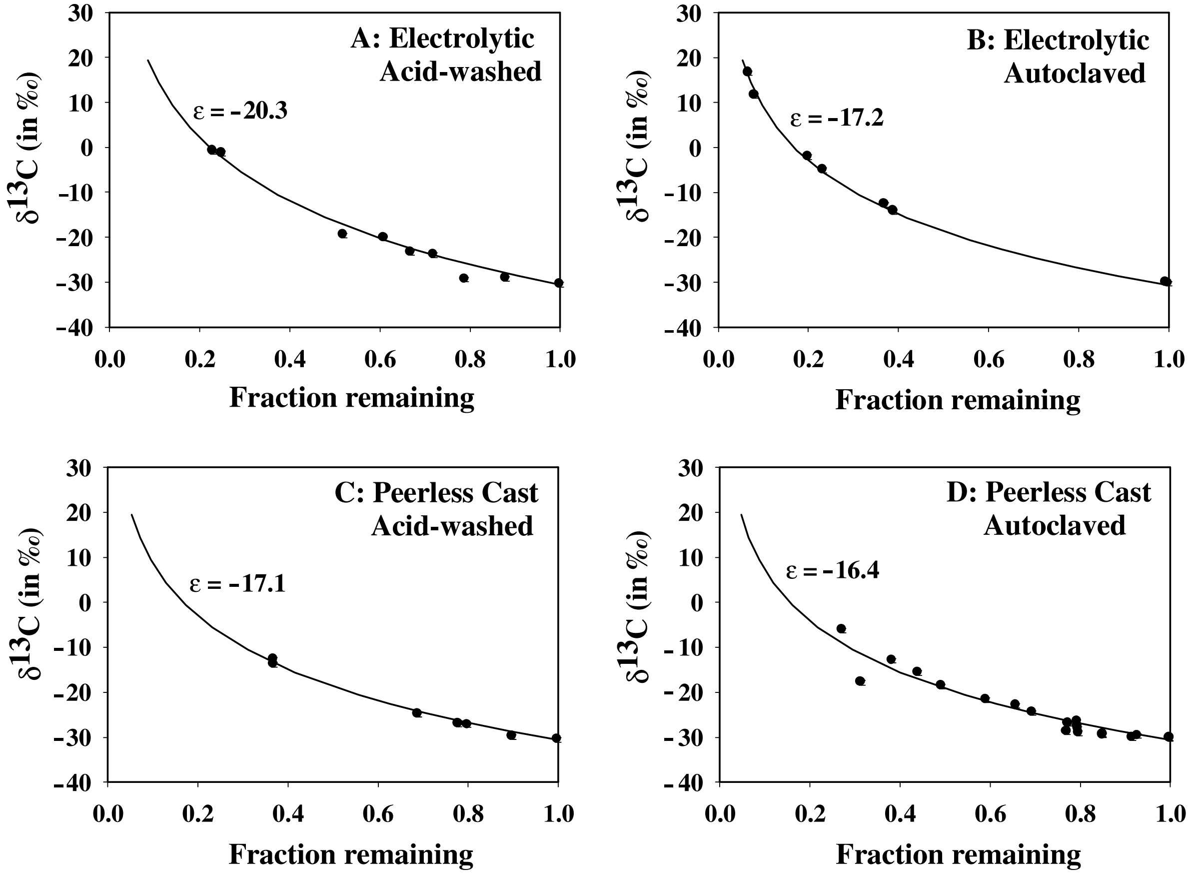

Fig. 2. A–D: Carbon isotopic composition of TCE versus fraction of TCE remaining during reductive dechlorination by zero-valent iron in Experiment 2. A: Batch 1 Electrolytic iron-acid washed. B: Batch 1 Electrolytic-iron autoclaved. C: Peerless iron-acid washed. D: Peerless iron-autoclaved. Error bars represent 0.5‰ accuracy and reproducibility and are smaller than plot symbols. Lines represent Rayleigh model curves based on enrichment factors determined from all data for each experiment using Eq. (3) (see text).

TCE to less chlorinated products (*c*DCE, *t*DCE, VC) before the end of the column. Isotopic enrichment of TCE was observed in both the column experiments and could be described by a Rayleigh model. The enrichment factors for the two columns were −16.9‰ ($r^2 = 0.89$) and −17.4‰ ($r^2 = 0.99$) for the 100% and 22% iron columns respectively. The outlier point on Fig. 3 is likely due to an error in the measurement of the concentration at this point. The variation in this point from the rest of the data resulted in large 95% confidence intervals. The overall enrichment factor for the combined data from both column experiments was −16.9‰ with an r^2 of 0.90 and a 95% confidence interval of ±4.1‰.

4. Discussion

In all experiments, significant isotopic enrichment of the TCE was observed during reductive dechlorination by zero-valent iron. This enrichment is consistent with a reaction that degrades ^{12}C containing molecules at a slightly faster rate than ^{13}C containing molecules. Such a process can be modeled using the Rayleigh model (Mariotti et al., 1981).

The results of Experiment 1 illustrated that enrichment factors were independent of observed reaction rate over a range of a factor of 2. The results obtained from Experiment 2 confirm that there is no systematic effect of rate on enrichment factor. In fact, there is a variation of 2 orders of magnitude in observed reaction rate between autoclaved electrolytic experiments, yet there is only slight (1.5‰) variation in enrichment factor. This suggests that observed rate of reaction does not play a major role in determining the isotopic fractionation during reductive dechlorination by zero-valent iron over the range of rates investigated in this study. This observation is important for the application of isotopic analysis to monitoring iron wall reductive dechlorination at field sites.

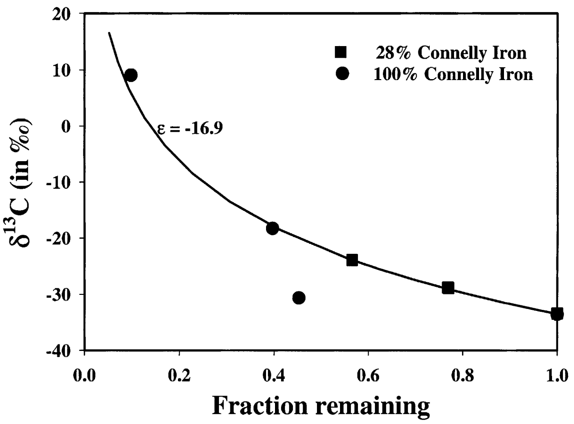

Fig. 3. Carbon isotopic composition of TCE versus fraction of TCE remaining during reductive dechlorination by Connelly zero-valent cast iron in column experiments in Experiment 3. Error bars represent 0.5‰ accuracy and reproducibility and are smaller than plot symbols. The line represents a Rayleigh model curve based on an enrichment factor of −16.9‰ determined from all data using Eq. (3) (see text).

4.1. *Effect of surface treatment*

Since the data from these experiments can be described by a Rayleigh model, the enrichment factor from each experiment can be used to compare isotopic fractionation between experiments. Surface pre-treatment had a significant effect on isotopic fractionation by electrolytic iron. The acid-cleaned electrolytic irons had enrichment factors of −20.3‰ and −24.8‰, while the autoclaved electrolytic irons had enrichment factors of −17.2‰ and −18.7‰ (Table 2). In contrast, there was no significant effect on enrichment factor due to surface pre-treatment of the Peerless cast iron. The enrichment factors for acid-cleaned and autoclaved Peerless iron were the same within 95% confidence intervals.

The change in fractionation factor observed for electrolytic iron is co-incident with oxidation of the iron surface. XRF analysis indicates that autoclaving the iron significantly increased the amount of oxygen present on the iron surface. XRF analysis of the electrolytic iron from Experiment 1 revealed that there were significant amounts of oxygen (1.5%) within the first 0.8 μm of the autoclaved electrolytic iron, while there were insignificant amounts of oxygen (<0.1%) within the first 0.8 μm of the acid-cleaned electrolytic iron. Because XRF response decays exponentially, if the oxygen on the autoclaved iron was evenly distributed, 50% of the oxygen would be within 0.2 μm of the surface. However, in this case it is likely that the oxygen was located on the iron surface, and that the actual percentage of oxygen on the surface was much higher than 1.5%. SEM examination did not show any observable effect on the surface morphology of the autoclaved versus acid-cleaned electrolytic iron. Nor is there any systematic relationship between enrichment factor and differences in surface area or K_{SA} between autoclaved and acid-cleaned electrolytic iron.

This increased concentration of oxygen on the surface of the autoclaved electrolytic iron corresponded to a reduction in enrichment factor for the autoclaved electrolytic iron relative to the acid-cleaned electrolytic iron. The mechanism causing this relationship is not clear. However, it is possible that oxidation may be affecting the activation energy of the reaction. Iron with surface oxidation and/or impurities may require higher activation energy to transfer electrons to the TCE. Su and Puls (1999) calculated that untreated iron (more oxidized) had higher activation energies than acid-cleaned iron (less oxidized). In addition, they point out that impurities, different reactive sites on the metal surface, structure and morphology, could all be playing a role in affecting the activation energy of the reaction. Further research is planned to determine whether the effect of oxidation on the enrichment factor of this reaction is due to a change in activation energy, or to some other as yet unknown factor.

While enrichment factors for the autoclaved versus acid-cleaned Peerless cast iron are the same within 95% confidence intervals (−16.4‰ and −17.1‰ respectively), there is a slight absolute reduction in enrichment factor for the autoclaved cast iron. Possibly for cast iron, the isotopic effects due to oxidation during autoclaving are not as significant relative to other factors, such as the presence of carbon impurities.

4.2. *Implications for reaction mechanism studies*

The relatively large ε values reported in Table 1 ($\varepsilon = -15$ to -25) are consistent with a primary kinetic isotope effect. Arnold and Roberts (2000) hypothesized that formation of a di-σ-bonded intermediate is the rate determining step during abiotic reductive dechlorination of chlorinated ethenes. They noted that the primary kinetic isotope effect observed ($\varepsilon = -17$ to -22) for other reactions involving conversion of a π bond to a di-σ-bond are very similar to those reported in Table 1 ($\varepsilon = -15$ to -25). Thus, this isotopic evidence provides support for their model of the abiotic reductive dechlorination mechanism.

A comparison of this study with other fractionation values reported in the literature shows that in some cases there are variations in ε which are larger than those observed in this study. In some cases, ε reported are the same as this study, for instance, Bill et al. (2001), observed an enrichment factor of −16‰ for dechlorination of TCE by cast iron. In contrast, a study by Schüth et al. (submitted for publication) reports an enrichment factor of −10.1‰ for reductive dechlorination of TCE by cast iron removed from PRBs in Belfast, Ireland and Tuebingen, Germany. In addition, Dayan et al. (1999) reported a fractionation factor of −8.6‰ during reductive dechlorination by acid-cleaned electrolytic iron, a much lower value than observed in our study (−20.4‰, −24.8‰). The reason for the observation of these lower fractionation factors is not clear. The observed variations in isotopic fractionation do not appear to be related to observed rate of reaction, surface areas or surface treatments. Iron from different sources was used in each of these experiments. Dayan et al. (1999) used acid cleaned electrolytic iron, Schüth et al. used untreated cast iron and iron from a field installation. Bill et al. (2001) used a cast iron similar to that used by Schüth et al. Potentially the observed variations are due to some difference in surface condition of the iron which is not resolved by present descriptions of the surface pretreatment. Alternatively they may indicate that in some cases conversion to a di-σ-bonded intermediate is not the rate determining step, or that some other as yet unclear factor is involved in the expression of isotopic fractionation during this process. Further study of the causes of these variations in isotopic enrichment factors may yield insights into the mechanisms of this reaction. In addition, understanding of the controls on isotopic fractionation during reductive dechlorination by zero-valent iron is required before isotopic enrichment factors can be used as a quantitative tool to monitor the reaction progress and thus the performance in the complex environment of an iron reactive barrier as suggested by Schüth et al. (submitted for publication).

4.3. Field implications

Though isotopic enrichment factors cannot be applied quantitatively in the field at this time, the observation that reductive dechlorination by zero-valent iron consistently produces a large isotopic enrichment in the $\delta^{13}C$ value of the residual TCE indicates that isotopic analysis can provide a qualitative indicator of the effectiveness of this remediation approach in the field. Further, the consistency between the enrichment factors for the batch and column experiments in this study indicate that the large isotopic fractionations observed in the batch studies should be observed in the field and that the presence of other matricies, such as aquifer material, will not affect the patterns of isotopic fractionation. Potential applications of isotopic analysis to field situations include determining whether TCE observed down-gradient of an iron wall is the result of insufficient reaction time within the wall, or due to the groundwater plume bypassing the wall. Partially degraded TCE will have isotopically enriched $\delta^{13}C$ values relative to TCE up-gradient of the iron wall, while TCE which has bypassed the wall should have $\delta^{13}C$ values similar to TCE up-gradient of the wall. If TCE observed down-gradient from a PRB is determined to be due to insufficient reaction time within the wall, extensive action must be taken to increase the wall thickness or install a second wall. If the TCE is due to wall bypass, then localization of the bypass zone and repair may be carried out. While considerably more research must be undertaken to constrain the precise controls on isotopic fractionation during reductive dechlorination of TCE, the consistent large isotopic enrichment in residual TCE produced by abiotic degradation already has the potential to be an effective tool in evaluating and optimizing passive remediation barrier technology.

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