SHALE KEROGEN – HYDRAULIC FRACTURING FLUID INTERACTIONS AND CONTAMINANT RELEASE

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Abstract

The recent increase in unconventional oil and gas exploration and production has prompted a large amount of research on hydraulic fracturing, but the majority of chemical reactions between shale minerals and organic matter with fracturing fluids are not well understood. Organic matter, primarily in the form of kerogen, dominates the transport pathways for oil and gas; thus any alteration of kerogen (both physical and chemical properties) upon exposure to fracturing fluid may impact hydrocarbon extraction. In addition, kerogen is enriched in metals, making it a potential source of heavy metal contaminants to produced waters. In this study, we reacted two different kerogen isolates of contrasting type and maturity (derived from Green River and Marcellus shales) with a synthetic hydraulic fracturing fluid for two weeks in order to determine the effect of fracturing fluids on both shale organic matter and closely associated minerals. ATR-FTIR results show that the functional group compositions of the kerogen isolates were in fact altered, although by apparently different mechanisms. In particular, hydrophobic functional groups decreased in the Marcellus kerogen, which suggests the wettability of shale organic matter may be susceptible to alteration during hydraulic fracturing operations. About 1% of organic carbon in the more immature and Type I Green River kerogen isolate was solubilized when it was exposed to fracturing fluid, and the released organic compounds significantly impacted Fe oxidation. Based on the alteration observed in both kerogen isolates, it should not be assumed that kerogenic pores are chemically inert over the timeframe of hydraulic fracturing operations. Shifts in functional group composition and loss of hydrophobicity have the potential to degrade transport and storage parameters such as wettability, which could alter hydrocarbon and fracturing fluid transport through shale. Additionally, reaction of Green River and Marcellus kerogen isolates with low pH solutions (full fracturing fluid, which contains hydrochloric acid, or pH 2 water) mobilized potential trace metal(loid) contaminants, primarily S, Fe, Co, Ni, Zn, and Pb. The source of trace metal(loid)s varied between the two kerogen isolates, with metals in the Marcellus shale largely sourced from pyrite impurities, whereas metals in the Green River shale were sourced from a combination of accessory minerals and kerogen.

1. Introduction

Over the past few decades, hydraulic fracturing of shales to produce oil and natural gas has expanded worldwide. The resulting increase in oil and gas production has been a major contributor to the energy security of the United States. However, this hydrocarbon extraction method remains relatively inefficient, with low estimated recoverable resources.[1] The reasons for such limited recovery remain poorly understood. Improving recovery efficiency and diminishing the environmental impacts of hydraulic fracturing require an improved understanding of the geochemical reactions that occur when fracturing fluids interact with the minerals and organic matter comprising oil and gas shales, driving changes in physical properties (*e.g.*, porosity and permeability), and composition of the shale matrix. Although recent studies have examined the response of the mineral matrix to simulated fracturing fluid exposure,[2,3,4] the response of shale organic matter has not been investigated. Minimizing formation damage due to chemical reactions, especially within the organic pores, could result in greater production of oil and gas from fewer wells, a lower environmental footprint, and reduced risk of contamination of surface water and groundwater.

As a result of depositional environment and diagenesis, shale reservoirs are typically poised at redox potentials much lower (more reducing) than the oxygenated fracturing fluids commonly injected to develop hydraulic fracture networks. Hydrochloric acid is routinely injected during fracture stimulation to help remove asperities near the well bore, dissolve fine-grained cement casing rubble, and help initiate opening of pre-existing carbonate-cemented fractures during the subsequent stages.[5] Thus, hydraulic fracturing of shales sets in motion a suite of redox- and acid-driven geochemical reactions.[2,3] Kerogen, which can comprise up to 40% of the shale volume of some major gas-producing shale plays,[6] is the precursor to economically important hydrocarbons and has complex associations with minerals in the shales such as pyrite and clays,[7] as well as heavy metals. Shale organic matter also contains abundant and relatively soluble bitumen. Organic pores are considered to be major conduits for oil and gas within shales.[8] Consequently, the wettability of kerogen is an important control on hydrocarbon migration and fluid flow in shales.[8] Because the wettability of kerogen is determined by the nature of its surface functional groups,[9] alteration of kerogen functional groups and particularly any loss of hydrophobic character (such as could occur if it were to become oxidized or hydrolyzed following reaction with fracturing fluid) would reduce transport of hydrocarbons through the shale matrix. Recently, modeling studies have suggested that fracturing fluids may imbibe into organic pores due to capillary effects,[10] raising the possibility that fracturing fluids may directly contact and react with kerogen and/or bitumen. Bitumen and other solubilized organics contain components such as heteroatoms that are relatively reactive, and understanding the extent of both kerogen and bitumen release is therefore important in predicting redox reactions during hydraulic fracturing.[2,11] Although functional group evolution during thermal maturation has been the subject of extensive research,[12,13] chemical interactions between hydraulic fracturing fluids and kerogen over timescales typical of hydraulic fracturing operations have not been examined systematically.

Additionally, kerogen has been shown to contain elevated concentrations of redox-sensitive metal(loids) and to be closely associated with a variety of secondary sulfide minerals.[14]

It is hypothesized that many of the metals present in shale were initially accumulated through sorption to organic matter, which was then preserved through the sedimentation process. Depositional environment, especially sulfate availability, is a strong control on the formation of sulfide metals and therefore the partitioning of metals throughout diagenesis.[15] Divergent results for the concentration of metal(loid)s in oil and gas shales demonstrate how substantial compositional heterogeneity translates into highly variable metal content. A sequential chemical extraction for the New Albany Shale of Indiana revealed Zn and Cu in sulfide minerals, Pb as a selenide, V within clays, and only Ni and Mo associated with organic matter.[16] Uranium has been shown to associate with silicates, organic matter, and phosphatic minerals, or can be present as crystalline or amorphous uraninite.[17,18,19] Glikson *et al.*[18] demonstrated that Ti and Cr are associated with humic acid fractions of Green River oil shale by transmission electron microscopy (TEM) and electron microprobe analysis. It is thought that carboxyl, hydroxyl, and amine groups are responsible for sorption of metal ions, and oil shale has been tested as an absorbent for Cu and Zn remediation due to its affinity for divalent cations.[20] Other than humic acids, it has been hypothesized that Mo is closely associated with kerogen by covalent bridges between Mo and sulfidized organic macromolecules.[21]

Metal(loid) contaminants in produced water are a primary environmental concern in hydraulic fracturing operations, but the sources and mobilities of various contaminants are not entirely understood.[4,19] For example, a previous study evaluated trace metals released from four different shales after exposure to fracturing fluid, but the multiple inorganic and organic phases and the complexity of the solution chemistry did not allow for a complete mass balance of contaminant sources.[3] Due to the variability in metal partitioning in shales, a greater understanding of the distribution of metals within organic and inorganic shale fractions, along with their potential mobility, will benefit the prediction of contaminant release in hydraulic fracturing operations. Although numerous studies have documented metal(loid)s associated with the organic fraction of shales, this source has not been evaluated in the context of contaminant loads in hydraulic fracturing operations.

In summary, quantifying the response of kerogen (*e.g.*, hydrophobicity, redox control, and metal(loid) release) to hydraulic fracturing fluids is an important component in building an overall conceptual framework that supports optimization of oil and gas recovery from hydraulic fracturing. In order to address this issue, two isolated kerogen fractions containing minor impurities were reacted for two weeks with a synthetic hydraulic fracturing fluid at a formation temperature representative of typical Marcellus gas wells (80°C). Green River and Marcellus shales were chosen to highlight differences in reactivity to fracturing fluids between kerogen isolates of contrasting compositions and maturities. Here we show that kerogen functional group composition was altered after reaction with fracturing fluid, although with different trends for the two shale kerogens. Alteration appears to be sensitive to the composition of the kerogen as well as to the presence of organic additives in the fracturing fluid. Additionally, minor amounts of organic compounds were released from the less mature, Type I Green River kerogen isolate. Metal(loid)s were released from both kerogen isolates during reaction, although only the metal(loid)s within the Green River shale appeared to be sourced from organic matter rather than the closely associated accessory minerals such as pyrite that could not be removed during isolation.

2. Methods

2.1 Shale samples

Shales from the Marcellus and Green River formations were collected for these experiments in order to compare and contrast two end member compositions. Marcellus shale was collected in July 2016 from an outcrop of the Oatka Creek Member of New York, USA (GPS: Lat. 42.98, Long. -77.99), and Green River shale (GPS: Lat. 39.58, Long. -107.89) was collected in August 2015 from an outcrop of the Mahogany Ledge Member of Colorado, USA. Previous research on these samples investigating Fe-redox states showed that oxidative alteration of the rock due to weathering at depths greater than 3 cm from the rock surface was minimal to non-existent.[2] Therefore, samples for extraction were taken > 5 cm below the rock surface for all samples. The selected Marcellus kerogen samples are representative of a thermally mature, Type II kerogen,[22] whereas the selected Green River kerogen samples are more thermally immature and Type I.[23] Although only the Marcellus shale is currently of economic importance, the Green River shale was chosen as a useful contrast based on its contrasting composition and its abundance of kerogen.

2.2 Kerogen isolation

Kerogen samples were isolated from both Green River and Marcellus shales using the modified procedure of Goklen *et al.*[24] Specific steps of the isolation varied for the two shales based on mineralogy and organic content. Shale samples were ground and sieved to <100 μm and reacted with 3 N hydrochloric acid in a stirred beaker at 70° C to remove carbonates (two rounds of 24 hours for the Green River, one round of 24 hours and one round of 12 hours for the Marcellus). The samples were then rinsed with doubly de-ionized (DDI) water. Following drying, the shale was reacted with 3:1 toluene:methanol in a Soxhlet extractor for 12 hours (Marcellus) or 24 hours (Green River) to remove soluble organic matter (bitumen). After drying, silicates were removed with 1:1:1 hydrofluoric acid:hydrochloric acid:DDI water in a stirred beaker (two 1-hour periods for the Green River and three 1-hour periods for the Marcellus, with fresh solution used each period) and rinsed with DDI water. Samples were rinsed with 500 mL 3:1 DDI water:hydrochloric acid and 12 g boric acid in a stirred beaker at 70° C and reground. Due to the possibility of precipitation of fluoride-bearing minerals, boric acid was added to prevent the formation of ralstonite [$Na_xMg_xAl_{2-x}(F,OH)_6*(H_2O)$]. Finally, most of the sulfide minerals were removed from the Marcellus kerogen by density separation with water and reground after drying. However, as presented in the results and the **Supporting Information**, the kerogen isolates contain both quartz and sulfide mineral fractions that persisted through the isolation procedure and are likely closely associated with the organic matter. Each step of the extraction was monitored with X-ray diffraction (XRD), X-ray fluorescence (XRF), attenuated total reflectance Fourier transform infrared spectrometry (ATR-FTIR), and C/N elemental analysis (EA), described below. Of note, the two batches of kerogen were isolated for the Marcellus because the first batch did not yield enough material for all experiments. These kerogens had slightly different residual mineral contents.

2.3 Fracturing fluid composition

The fracturing fluid composition (**Table 1**) for the following experiments was based on the composition of the fluid used in the National Energy Technology Laboratory's (NETL) Marcellus Well E in Greene County, PA.[25] Differences include the absence of a silica proppant and two of the biocides (2,2-Dibromo-3-nitrilopropionamide and dibromoacetonitrile), which are present in extremely low quantities in the NETL fluid. Although fracturing fluid chemicals are often introduced to the subsurface by sequential injections, all chemicals were mixed simultaneously for the purpose of these experiments. After addition of hydrochloric acid, the pH of the fracturing fluid was approximately 2.

2.4 Reaction of kerogen isolates with fracturing fluid

Experiments were performed in 125 mL borosilicate glass serum bottles sealed with butyl-rubber stoppers and aluminum crimp seals. Trace organics and contaminants were removed from the glassware and stoppers: glassware was acid washed, rinsed with DDI water, and heated at 700° C in a furnace, while stoppers were boiled in 0.1 M KOH for one hour and rinsed with DDI water. The reactors were filled with 0.5 g of isolated kerogen and 100 mL of solution, leaving 25 mL headspace. The fluid:kerogen ratio was chosen to minimize the amount of fluid while allowing for the necessary sampling of sufficient fluid at each time point and not to reproduce realistic reservoir ratios.

Total incubation time for all experiments was two weeks. For both the Marcellus and Green River kerogens, experiments were conducted with either fracturing fluid or water and hydrochloric acid only (pH = 2), each setup with a separate control reactor containing either fracturing fluid or pH 2 water but no kerogen isolate. Solutions and headspaces were initially in equilibrium with the atmosphere. All reactors were incubated in a convection oven at 80° C and sampled periodically (described below).

The experiments were sampled at time intervals of 6, 24, 48, 96, 192, and 324 hours. At each sampling point, 4-5 mL of solution was taken by needle and syringe and filtered through a 0.2 μm PES syringe filter into a 15 mL polypropylene centrifuge tube. All solutions were immediately analyzed for pH, total Fe concentration, and Fe(II) concentration. Iron was measured by a Hewlett-Packard model 8452 photo diode array UV/Vis spectrophotometer at a 562 nm wavelength, using samples treated with the ferrozine method (and hydroxylamine hydrochloride for total Fe). At the conclusion of the experiments, reactors were unsealed and fluid was filtered through 30 mm filter paper in order to retain the reacted kerogen for further analysis. Kerogen isolates were rinsed and dried in a vacuum desiccator.

2.5 Pyrolysis

Kerogen samples were shipped to GeoMark Research in Houston, TX to be analyzed by a Rock-Eval II pyrolysis unit in duplicate. The unit was held at 300° C for 3 minutes (S1), ramped from 300° C to 550° C at 25° C/min and held at 550° C for 1 minute (S2), and finally trapped between 300° to 390° C (S3). The S1 peak corresponds to measured hydrocarbons, the S2 peak to pyrolyzed kerogen, and S3 to generated CO_2. From this, parameters such as the Hydrogen Index (HI) and Oxygen Index (OI) could be calculated.

Total organic carbon (TOC) values for the HI and OI calculations were obtained from a Carlo-Erba NA 1500 analyzer in the Stanford Environmental Measurements Laboratory. Because all carbonate was removed by the isolation procedure (confirmed by XRD, **Supporting Information**), the C values obtained were used as TOC. Ground samples were weighed in tin containers and transferred by auto sampler to the combustion reactor, which was maintained at 1020° C. Atropine obtained from Elemental Microanalysis Limited was used to create a standard curve for the analyses and the Brush Creek Shale SBC-1 reference material (obtained from the U.S. Geological Survey) was used as a standard reference material. The shale standard measured in triplicate for C was accurate to within 0.1% total C and resulted in a standard deviation of 1%. Standard deviations for the kerogen samples are higher due to physical heterogeneity of the material. Data are shown in the **Supporting Information**.

2.6 Ion chromatography

A Dionex DX-500 Ion Chromatograph with a Dionex AERS 500 suppressor in the Stanford Environmental Measurements Laboratory was used to measure sulfate for time points 1, 4, and 6 of all reactors on the Dionex IonPac AS11-HC Hydroxide-Selective Anion-Exchange column, to verify S concentrations by ICP-OES. Standards used to construct a standard curve were created from an inorganic reference solution purchased from Inorganic Ventures. Chromatograms were analyzed using the Chromeleon software package.

2.7 Total organic carbon/total nitrogen (TOC/TN)

Solution samples from each time point were analyzed for total carbon (TC, maximum error 1.5%), total inorganic carbon (TIC, maximum error 1.5%), and total nitrogen (TN, maximum error 3%) using the Shimadzu TOC-L Autoanalyzer in the Stanford Environmental Measurements Laboratory. Total organic carbon (TOC) was then calculated by subtracting TIC from TC. Standard curves were created by analyzing samples made from the ICCA organic C standard (50 ppm C stock) and the ICCA nitrate nitrogen standard (10 ppm N stock). A dilution factor of 0.05 was used.

2.8 Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy

The infrared spectra of kerogen isolate samples were measured in duplicate using a Nicolet iS50 FT/IR Spectrometer with a diamond/ZnSe single bounce attenuated total reflection (ATR) crystal in the Stanford Soft and Hybrid Materials Facility. A wavelength range of 4000-450 cm^{-1} was used, with 16 scans taken for each sample. Spectra were analyzed using the multi-peak analysis feature of the Igor Pro software package. Peak assignments were based on several literature sources.[26,27,28] Fits to spectra were restricted to two separate regions of interest; 1500-1200 cm^{-1} and 1800-1500 cm^{-1}. These two regions capture the most important peaks: a region of aliphatic C-H bend which includes a peak representing CH_2 and CH_3 (~1450 cm^{-1}) and a peak representing only CH_3 (~1375 cm^{-1}), and the aromatic C=C stretch (1650-1600 cm^{-1}) and C=O stretch indicative of carbonyl (1700 cm^{-1}). Fits were most precise when different backgrounds were applied to the different regions (**Figure 1**). Duplicate splits of the same samples were measured and the standard deviation between duplicate spectra was 0.9-18.3%, which we attribute to physical heterogeneity in the kerogen isolate samples (*i.e.* particle scale spatial variability of organic matter and remaining mineral matrix within the samples). Sources of error included uncertainties in manual fitting and variation in the influence of mineral matter on spectra backgrounds.

2.9 X-ray fluorescence (XRF)

Total concentrations of Na and heavier elements were measured using the Spectro Analytical XRF model XEPOS HE in the Stanford Environmental Measurements Laboratory. The Brush Creek Shale SBC-1 reference material, obtained from the U.S. Geological Survey, was used as a standard reference material. 1.5 g of the Brush Creek shale standard was run (approximately the same volume of the measured kerogen isolate). Measurement errors were within 20%.

2.10 Inductively coupled plasma mass spectrometry and optical emission spectrometry (ICP-MS and ICP-OES)

The concentrations of major elements and trace elements were determined using a Thermo Scientific ICAP 6300 Duo View ICP-OES and a Thermo Scientific XSERIES 2 Quadropole ICP-MS, respectively. Both are housed in the Stanford Environmental Measurements Laboratory. Samples from each time point of each reactor were run in triplicate, using a dilution factor of 0.085 in a 2% hydrochloric acid matrix. ICP-OES and ICP-MS standards were made using nitric acid-based TraceCERT certified reference materials purchased from Sigma-Aldrich. Quality control standards were run at regular intervals to measure for instrumental drift.

Calcium, Fe, K, Mg, Na, S, and Si were measured by ICP-OES. Li, Be, Al, Ti, Cr, Mn, Co, Ni, Cu, Zn, Se, Rb, Sr, Mo, Ag, Cd, Ba, Pb, and U were measured by ICP-MS. Concentrations of Be, Cr, Se, Cd, and U were below the detection limit. Ba concentrations were not used in this analysis because of anomalously high background levels in the water supply.

3. Results

3.1 Investigation of functional group composition

Aliphatic chain length, an important parameter in estimating the extent of kerogen maturation or reaction, was investigated before and after reaction by comparing the relative intensities of peaks due to CH_3 vs. CH_2 bending modes.[29,30,31] Similarly, alteration of kerogen was also monitored by observing the carbonyl stretching:aromatic stretching peak ratios, which monitor two important classes of shale organic matter functional groups.[31] Thus, ATR-FTIR analysis of unreacted and reacted kerogen can indicate relative changes in different organic functional group types in kerogen after reaction (detailed results presented in the **Supporting Information**).[26]

The ATR-FTIR results for CH_3 bending:(CH_3+CH_2) bending ratios show different trends in chain length after reaction for the two kerogen isolates (**Figure 2 A).** Both the fracturing fluid and water and hydrochloric acid-only Green River reactors were not significantly different from the unreacted kerogen isolate. The CH_3:(CH_3+CH_2) ratio for the Marcellus kerogen decreased when exposed to fracturing fluid, indicating an increase in average chain length. In contrast to this behavior, when organic additives were absent (*i.e.* in the "M W" sample, which contained only water and hydrochloric acid), then the CH_3:(CH_3+CH_2) ratio increased, suggesting that the type of alteration that occurred is dependent on the presence of organic fracturing fluid additives.

Results for carbonyl stretching:aromatic stretching ratios also differed for the kerogen isolates sourced from the different shale types. The Green River kerogen isolate showed a clear and consistent loss of carbonyl, whereas Marcellus kerogen isolates either lost aromatic character or gained carbonyl. In fact, the Marcellus carbonyl stretching:aromatic stretching ratios increased by up to 35%, which is over double the maximum measured variation between duplicate samples. Overall, the two types of kerogen isolates exhibited contrasting behaviors. Carbonyl functional groups are considered to be moderately hydrophilic, whereas aromatic groups are hydrophobic and oil-wet. The different trends for the changes in the CH_3:(CH_3+CH_2) and carbonyl:aromatic ratios between Green River and Marcellus samples suggest that the observed changes are indeed compositional changes in the kerogen rather than a factor such as sorption of fracturing fluid additives.

RockEval pyrolysis was completed on kerogen isolates as an additional probe for possible changes in organic matter composition after reaction (**Figure 3**). Plotting the hydrogen index (HI) and oxygen index (OI) and observing the loss or addition of either of these two indicative elements provides information on possible cleavage, hydrolysis, or oxidation reactions, among others. For the Marcellus kerogen isolates, fluids containing only water and hydrochloric acid ("M water" in **Figure 3**) showed a slight increase in the HI from *ca* 180 to *ca* 265 with no significant change in the OI, indicating addition of reduced hydrogen. In contrast, when organic additives were present in the fluid, the OI values doubled, from *ca* 12 to *ca* 28, indicating that it had acquired oxygen, which in turn implies that the kerogen had become partially oxidized, more charged, and hence less hydrophobic. This conclusion is consistent with the ATR-FTIR results (**Figure 2B**).

RockEval analysis of Green River kerogen shows a different alteration pattern than the Marcellus isolates. Specifically, reaction with either the organic-free, pH 2 fluid ("GR W" reactor) or the full fracturing fluid caused a slight increase in OI (*ca* 17 to *ca* 25). The increase in OI again implies oxidation of the kerogen.

In addition to analyzing solids to determine changes in kerogen composition, solutions from each time point were analyzed for total carbon (TC) and total inorganic carbon (TIC). TIC was not detectable, and therefore all C measured in solution was assumed to be organic carbon. TOC in Marcellus reactors after exposure to fracturing fluid was comparable to levels observed in the no-kerogen control reactors (*i.e.* little to no carbon was released during the reaction period). In contrast, solutions from the Green River experiments yielded measurable TOC release compared to controls. The difference in carbon concentrations between the kerogen isolate and control reactors was significantly higher in the experiments containing fracturing fluid additives than in the water- and hydrochloric acid-only experiments (**Figure 4**), indicating that organic amendments in the full fracturing fluid promoted dissolution of organic C. This corresponds to a carbon loss of less than 1% in the Green River reactors containing fracturing fluid additives.

3.2 Metal(loid) content

XRF analyses of both kerogen isolates indicate that they are enriched in a variety of metal(loid)s. It is important to note, however, that the isolated kerogen materials contain sulfide minerals. Although the dominant iron sulfide in the Marcellus shale is pyrite,[32] there is often significant pyrrhotite and marcasite content in the Green River shale.[33] However, the iron sulfide peaks in the Green River XRD patterns best match pyrite (**Supporting Information**). Other sulfide or oxide minerals insoluble in hydrofluoric acid are presumably present in trace amounts, although not detectable by XRD.

The Marcellus shale, and therefore kerogen isolate, is much more enriched in pyrite due to its marine depositional environment.[34] The sulfate-limited, lacustrine depositional environment of the Green River shale did not allow for the same extent of sulfide mineral formation.[33] Subtracting the quantified weight percent of C and quartz, it can be assumed that 22 wt% of the Green River isolated kerogen and 60-66 wt% of the Marcellus isolated kerogens are accessory sulfide and oxide minerals (depending on the kerogen batch). However, given the low density of kerogen, organic matter comprises the majority by volume. Roughly half of the pyrite present in the Marcellus shale was removed through density separation, but the remaining Marcellus kerogen isolate still had a significantly higher mineral content when compared to the isolated Green River kerogen isolate. The residual pyrite is likely nanoparticulate and intimately associated with the kerogen.[15]

Enrichment factors were calculated based on the concentration of a particular element in the isolated kerogen product divided by its concentration in the corresponding bulk shale (**Figure 5**). Many elements are greatly enriched in the kerogen isolate relative to bulk shale. The most enriched elements are S and Se, most likely due to the presence of pyrite. For a majority of the measured elements, the Green River kerogen isolate has a greater enrichment factor than the Marcellus kerogen isolate, with the exception of V, Mn, Fe, Zn, and Pb. Green River enrichment factors are noticeably higher for Co, Cu, and As, which are all potential contaminants of concern. As with the sulfide mineral content, the difference in depositional environments and therefore redox conditions likely played a dominant role in the varying metal(loid) content and partitioning in the Green River and Marcellus shales.

3.3 Metal(loid) release

Solution data indicate substantial release of many metal(loid)s to solution during reaction with fracturing fluid. The elements mobilized from the Marcellus kerogen isolate in large concentrations (Fe, S, Co, Ni, Pb, **Figure 6**) are those that are generally associated with pyrite,[35] which presumably undergoes oxidative dissolution under these geochemical conditions. The batch of kerogen used for the fracturing fluid reactor contained roughly 60% pyrite whereas the batch used for the water and hydrochloric acid reactor contained roughly 66% pyrite. The variation in metal concentrations in solution is attributed to the minor difference in initial pyrite content, as well as heterogeneity in pyrite distribution in the solids.

The extent of pyrite dissolution over time during the reactions can be estimated by comparing the Fe:S ratios in the reactor solutions (**Figure 7**). The Fe:S ratios in both the Marcellus and Green River solutions (Fe:S = 1.0 to 2.5) are significantly higher than the values expected if Fe was released only from pyrite (Fe:S = 0.5). The Fe enrichment is much greater in the Green River reactors. Because iron is unlikely to be associated with the quartz fraction, the iron source in the Green River samples can be most likely assigned to kerogen. However, as discussed in the Supporting Information, there may be trace oxide or other non-sulfide phases. This is consistent with the finding that a significant portion of the iron is directly bound to carbon in the Green River shale, as detailed in a recent companion manuscript using the same Green River shale and isolated kerogen..[2] This companion study documented EXAFS shell-by-shell fitting that revealed Fe bound to organic carbon in multiple shales, including 13% of the Fe in the Marcellus shale. The spectra for the Green River samples were more complex than the other shales, but the Fe-organic C pathway was the dominant Fe scattering pathway.

Interestingly, all Fe:S ratios are highest in the early hours of the experiment but approach the ratio expected if only iron sulfide dissolution were occurring as the reaction progresses. This observation indicates that Fe was leached from kerogen faster than from pyrite. The same trend is seen for ratios of other metals with S, including Co:S, Ni:S, Zn:S, and Cu:S (**Figure 8**). Sulfur is incorporated in the kerogen structure as S-containing functional groups, largely as thiophenes.[36,37] These groups appear to maintain their stability, remaining in the kerogen fraction rather than mobilizing as the Fe does.

The Fe oxidation state in solution differed between the Green River and Marcellus experiments. Iron in solutions from the Green River-fracturing fluid experiment was almost exclusively Fe(III) at the earliest time points (**Figure 9**). In contrast, for the water and hydrochloric acid only reactors, Fe was predominantly Fe(II) throughout the duration of the experiments. Therefore, it is clear that some mechanism caused iron to oxidize in the Green River-fracturing fluid experiment. Iron in the Marcellus reactors was predominately Fe(II) for the entire experimental timeframe, and solution composition did not correlate with Fe oxidation.

Trace element data in solution reveal some additional insights. Cobalt, Ni, and Pb concentrations (common impurities within pyrite) were much greater in Marcellus solutions.

However, Zn concentrations were similar in Marcellus and Green River reactors and Cu concentrations were much higher in Green River reactors (**Figure 10**). There may have been some Cu re-precipitation or sorption in the Marcellus reactors, because Cu is the only element measured that dropped in concentration after obtaining maximum values earlier in the experiments (**Figure 10**).

4. Discussion

4.1 Response of kerogen to hydraulic fracturing fluid: Two different alteration mechanisms

The conclusions from TOC, RockEval, and ATR-FTIR analyses all suggest that kerogen is most strongly altered in the presence of organic additives. **Table 1** shows that two moderately strong organic solvents were present in the full fracturing fluid recipe, kerosene and 2-ethyl hexanol. Both have the ability to dissolve organic matter and possibly to influence the relative abundances of functional groups in the remaining kerogen isolates. We tentatively conclude that these organic solvents play an important role in kerogen alteration distinct from water and acid attack.

Organic matter was solubilized in both the Green River fracturing fluid and water and hydrochloric acid reactors, although much more was solubilized from the fracturing fluid reactor (about 1% of the total organic matter). At the same time, ATR-FTIR demonstrated a loss in carbonyl content for both reactors. These two observations suggest that oxygen-containing functional groups, such as carboxylates, were preferentially solubilized. One possible explanation for this behavior is that extraction of soluble organic matter from the Green River kerogen was not complete during isolation, and it was therefore mobilized when in the presence of organic additives for extended periods of time. The Green River material was reacted with toluene:methanol for over twelve hours in the Soxhlet reactor until solutions ran clear, but previously unexposed soluble components may have been made available after removal of the silicates. Additionally, Green River bitumen has been shown to be rich in carbonyl, perhaps explaining the decline in the Green River carbonyl stretching:aromatic stretching ATR-FTIR ratios.[38] RockEval pyrolysis results also showed an increase in the OI for both Green River samples, indicating the kerogen was partially oxidized during reaction. However, since carbonyl was lost during the reactions, the additional O was in the form of singly bonded C-O, such as OH or alcohols. Whether the organic compounds were sourced from kerogen or bitumen, it is clear that the addition of small amounts of shale-sourced organic compounds can strongly influence solution chemistry and reaction progress. For example, Fe oxidation by solubilized organic material in subsurface hydraulic fracturing operations could have a substantial impact on the precipitation of Fe(III)-oxyhydroxide leading to the occlusion of pores and pore necks.[2]

The Marcellus kerogen isolates clearly underwent a different type of alteration. Neither Marcellus reactor had measurable TOC in solution, but it may be that minor solubilization of organics played a role in the different ATR-FTIR signatures between the two experiments. The decreased CH_3 bending:(CH_3+CH_2) bending ratio in the fracturing fluid reactor indicates that the more soluble shorter chain compounds were preferentially mobilized by the solvents present in the fluid. The fracturing fluid experiment was also the only Marcellus sample to experience a significant increase in OI, indicating the additives within the fracturing fluid played a role in accelerating oxidation of the kerogen isolate. However, both fracturing fluid and water and hydrochloric acid experiments showed an increase in the carbonyl stretching:aromatic stretching ratio. One feasible mechanism for kerogen alteration is Fenton reactions. Iron cycling by Fenton reactions creates abundant reactive oxygen species (ROS) that are strong oxidants for organics.[39,40] Hydroxyl radicals, for example, have been shown to attack both aliphatic and aromatic C and to create hydroxylated organics and small fatty acids during dissolved organic matter attack.[41,42] The magnitude of Fenton reactions is generally dependent on the amount of Fe in solution. Because there was O_2 present along with a significant amount of dissolved Fe(II) in solution (roughly six times more than in Green River reactors), we conclude that Fenton cycling of Fe likely contributed to the alteration of the kerogen isolates. The observed shift in the carbonyl stretching:aromatic stretching ratio could be due to either an increase in carbonyl or a destruction of aromatic C. Although destruction of aromatic rings by ROS is a possibility, the addition of carbonyl is the most consistent with the increase in OI observed in the fracturing fluid experiment. It is likely that the organic additives complexed with the Fe(II) present in solution, accelerating reaction.

4.2 Implications for wettability and hydrocarbon transport in unconventionally stimulated shales

Wettability, defined as the contact angle between a gas or liquid phase and a solid, is strongly controlled in organic matter by the affinity of the predominant functional groups for water as well as the distribution of these groups.[9] Because hydrocarbons are predominantly transported through oil-wet kerogen conduits, the distribution of water-wet and oil- or gas-wet surfaces is expected to be a strong control on the distribution and transport of hydrocarbons and fracturing fluid within the shale.[8] If kerogen wettability by water were to be enhanced, then hydrocarbon production would likely be reduced (negative impact). The potential for such change is not generally considered when designing hydraulic fracturing operations because conventional wisdom dictates that kerogen is an unreactive and stable material. A change in functional group composition may also affect other properties of kerogen such as gas sorption capacity, which has been shown to vary with kerogen type and maturity.[43]

Our results suggest that changes in wettability occur when shale and specifically the organic matter within it is exposed to hydraulic fracturing fluid. ATR-FTIR results for the Marcellus kerogen isolate suggest that reaction with fracturing fluids containing kerosene and 2-ethyl hexanol causes addition of carbonyl or loss of aromaticity (or both). Consistent with these conclusions, RockEval data indicate that oxygen is incorporated into the kerogen structure following reaction with fracturing fluid. Although the alteration mechanism is different for Green River kerogen, it may also decline in hydrophobicity after reaction due to incorporation of oxygen/oxidation of the material, although this is more uncertain due to the loss of carbonyl groups.

These findings have important implications for alteration of shale and estimated ultimate recovery (EUR) during unconventional stimulation. Despite a lack of experimental justification, the assumption that kerogen is chemically stable over the timeframe of hydraulic fracturing has been implicitly built into modeling and prediction efforts.[44] However, small changes in organic functional group composition can have a substantial impact on kerogen wettability by water and oil.[9] Addition of carbonyl groups or loss of hydrophobic aromatic groups in the Marcellus kerogen will result in a more water-wetting rather than oil-wetting character, diminishing its capacity for hydrocarbon transport. Although it is unclear what volume of kerogen in shales would be affected by exposure to fracturing fluid, the fact that kerogen wettability and/or gas sorption capacity may change over time is important to modeling fluid transport through hydraulically fractured shales. This is true not only for modeling of oil and gas transport through organic conduits but is also relevant to other production issues such as poor recovery and trapping of injected solutions.[45]

4.3 Mechanisms of heavy metal mobilization

Based on the XRF and XRD results, the kerogen isolates contain remnant sulfide minerals that could not be removed during the extraction process. The presence of sulfides in the isolated kerogen biases the calculated enrichment factors, particularly for Fe and S, and likely for Se, Ni, Co, Zn and Cu. Even so, the enrichment factors provide insight into mass balance of metals within shales, particularly how enrichment of metals differs between the organic matter and associated sulfide minerals in these two shales. Notably, Green River shale has a significant portion of Fe associated with the organic fraction, as discussed in section 3.3, whereas the vast majority of Fe in the Marcellus shale is associated with the sulfide mineral fraction. In the Green River kerogen isolate, Fe(II) is likely sorbed to metal-binding functional groups such as carboxylates that are often present in immature kerogen but are absent in thermally mature organic matter.[20] Although Zn and Cu are potential trace elements found in sulfide minerals, their anomalously high concentrations in Green River experiment solutions indicate that they may also have been partially sourced from kerogen (**Figure 10**). Thus, there may be a propensity for divalent metal ions to sorb to relatively immature kerogen (Fe, Cu, and Zn, among others) and be mobilized after reaction with oxidized fluids. In contrast, the Marcellus kerogen has undergone more extensive organic maturation, resulting in the loss of oxidized metal-binding groups, and therefore loss of organic-associated metals.[46] Although the presence of S sinks could have potentially shifted the Fe:S ratio to higher values, the Fe:S trends observed in solution indicate that Fe must be at least partially sourced from organic matter even in the Marcellus reactors, since Fe:S ratios are higher than would be expected solely due to pyrite dissolution. If any other S sinks exist, the Fe:S ratio may have been shifted higher.

Iron:S (as well as Cu:S, *etc.*) ratios in solution were highest in the first 100 hours of reaction, suggesting that desorption of iron is a relatively rapid process. Solutions from the experiments in which kerogen isolates were reacted with fracturing fluid *vs.* water and hydrochloric acid showed similar Fe, S, and trace metal concentrations, indicating that the organic fracturing fluid additives do not enhance desorption relative to the pH ~2 water. Additionally, total Fe concentrations in solution were similar regardless of the presence of shale-sourced organic compounds. Although organic compounds did not appear to enhance the solubility of Fe(II), their presence did influence the oxidation state of solubilized Fe (**Figure 9**).

Bitumen has been shown to enhance the rate of oxidation of Fe by dissolved O_2,[2] especially at low pH where Fe oxidation is otherwise slow or completely inhibited. Moreover, the previously mentioned companion study[2] has shown that soluble bitumen is released from shale following exposure to fracturing fluid, which is mobilized by organic additives present in the fluid. This behavior is significant because an increase in the concentration of solubilized organic compounds was observed only in the Green River reactors, where Fe(III) was also observed. These findings strongly imply that oxidation of Fe(II) to Fe(III) in the Green River experiments was promoted by the liberated organics in the Green River kerogen isolate reactors.

Traditionally, contaminant metal(loid)s have been thought to originate solely from mineral dissolution or recrystallization.[47] However, results from our experiments suggest that kerogen may release substantial amounts of trace metals to flowback and produced waters. More work is needed to understand the relevance of these findings to field conditions. Compositions of injected fluids can also vary greatly depending on the operation, with some recycling of produced water for reuse. In this scenario, desorption could be impacted by higher ionic strength. Although we did not evaluate the reactions at high ionic strength in order to allow for close monitoring of mass balance, this work provides new insights into the mechanisms of mobilization of the contaminant inventory within kerogen during hydraulic fracturing.

5. Conclusions

This study provides, to our knowledge, the first quantitative evidence for kerogen alteration when exposed to hydraulic fracturing fluid. When organic additives were present in the fracturing fluid, both Green River and Marcellus kerogen isolates were altered, though with differing trends. A minor amount of the Green River kerogen isolate was solubilized, and ATR-FTIR analysis indicates the remaining isolate lost carbonyl groups. The Marcellus kerogen isolate, however, appeared to have either gained carbonyl or lost aromaticity and increased in average aliphatic chain length. Hydrophobic functional groups were lost in the Marcellus isolate and hydrophobic character was potentially lost in the Green River isolate due to oxidation, suggesting that shale organic matter of various compositions and maturities may become more hydrophilic in the presence of fracturing fluid. This study also demonstrates that trace metals can be mobilized from immature organic matter due to desorption. There is strong evidence that Fe bound directly to organic carbon was desorbed from the Green River kerogen isolate and that this process happened within the first few hours of reaction. In contrast, Fe(II) is present mostly in pyrite in Marcellus kerogen and thus is not available for rapid desorption. This observed desorption may also apply to other divalent metal ions, such as Zn(II) and Cu(II). Additionally, the same magnitude of desorption occurred independent of which organic fracturing fluid additives were present, suggesting that pH and not the presence of organic additives was the primary control over the release of sorbed metals from kerogen in these experiments. These results are summarized in **Table 2**.

The results of this investigation are an important step in evaluating hydrocarbon and fracturing fluid transport and hydrocarbon production following unconventional stimulation, as kerogenic pore networks are the dominant pathways of hydrocarbon transport within shale reservoirs. A shift toward more hydrophilic behavior is expected to reduce the transport of hydrocarbons through the organic pore network. The results are also important in determining the role that kerogen plays as a contaminant source in shale reservoirs. The different starting compositions of the relatively aliphatic Green River and the more aromatic Marcellus kerogens certainly influence the extent and direction of alteration. Although possible alteration mechanisms are proposed, additional studies using a wider array of shales in addition to the two distinctly contrasting kerogens used here will help explain how kerogen type and thermal maturity influence patterns of alteration. Furthermore, it would be helpful to explore additional techniques to identify the extent of kerogen alteration. In particular, it would be informative to maintain the spatial context of kerogen within the rock structure For example, a recent study utilized a novel ATR-FTIR technique that lowered spatial resolution to about one micron, which allowed the authors to study the distribution of kerogen in the Marcellus shale and map the functional group composition.[48] Such a technique would allow for the examination of reacted kerogen *in situ*, providing information on the fraction of kerogen that will undergo exposure to fracturing fluid and thus experience alteration. Finally, additional work is needed to understand the impact that a change in wettability would have on shale transport properties.

Acknowledgements

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Supporting Information

Supporting Information includes additional material discussing X-ray diffraction methods (used to confirm kerogen purity), kerogen isolate purity, and more detail on ATR-FTIR results.

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Tables and Figures

Chemical	Purpose	Percent of Total Mass
Water	Base fluid	99.7570
Ethylene glycol	Scale inhibitor, iron control, breaker	0.0190
Kerosene	Friction reducer	0.0240
Guar gum	Dry gellant	0.0290
2-Ethyl hexanol	Corrosion inhibitor	0.0004
Glycol ether	Corrosion inhibitor	0.0004
Polyethylene glycol	Biocide	0.0200
Hydrochloric acid	Acid	0.1480

Table 1. Synthetic fracturing fluid composition, representative of fluids used in the Marcellus formation.[25]

Experiment	CH_3:(CH_3+ CH_2)	Carbonyl: Aromatic	TOC	OI	Metals
Green River, Fracturing fluid (“F”)	Little/no change	Decrease	Small portion (<1%) C content of the sample mobilized	Slight increase	Some mobilization of metals from pyrite, although Fe:S and ratios of other metals to S are higher than would be expected due to solely pyrite dissolution; Significant Fe(III) in solution.
Green River, Water and Hydrochloric Acid (“W”)	Little/no change	Decrease	Much less than the “F” reactor	Slight increase	Some mobilization of metals from pyrite, although Fe:S and ratios of other metals to S are higher than would be expected due to solely pyrite dissolution.
Marcellus, Fracturing Fluid (“F”	Decrease	Increase	Not detected	Increase	Significant mobilization of metals from pyrite, although Fe:S and ratios of other metals to S are

					higher than would be expected due to solely pyrite dissolution.
Marcellus, Water and Hydrochloric Acid ("W")	Increase	Increase	Not detected	No change	Significant mobilization of metals from pyrite, although Fe:S and ratios of other metals to S are higher than would be expected due to solely pyrite dissolution.

Table 2. Summary of important findings.

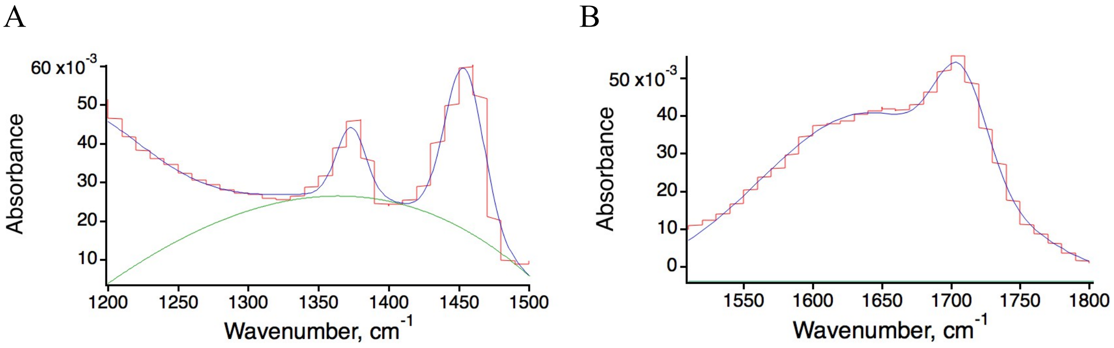

Figure 1. Example fits of ATR-FTIR spectra from Green River kerogen isolate reacted with fracturing fluid. In each panel, the actual spectrum is shown in red, fits are overlain in blue, and background is shown as green. A) Region of 1200-1500 cm^{-1} B) Region of 1500-1800 cm^{-1}, where the background is negligible and not shown.

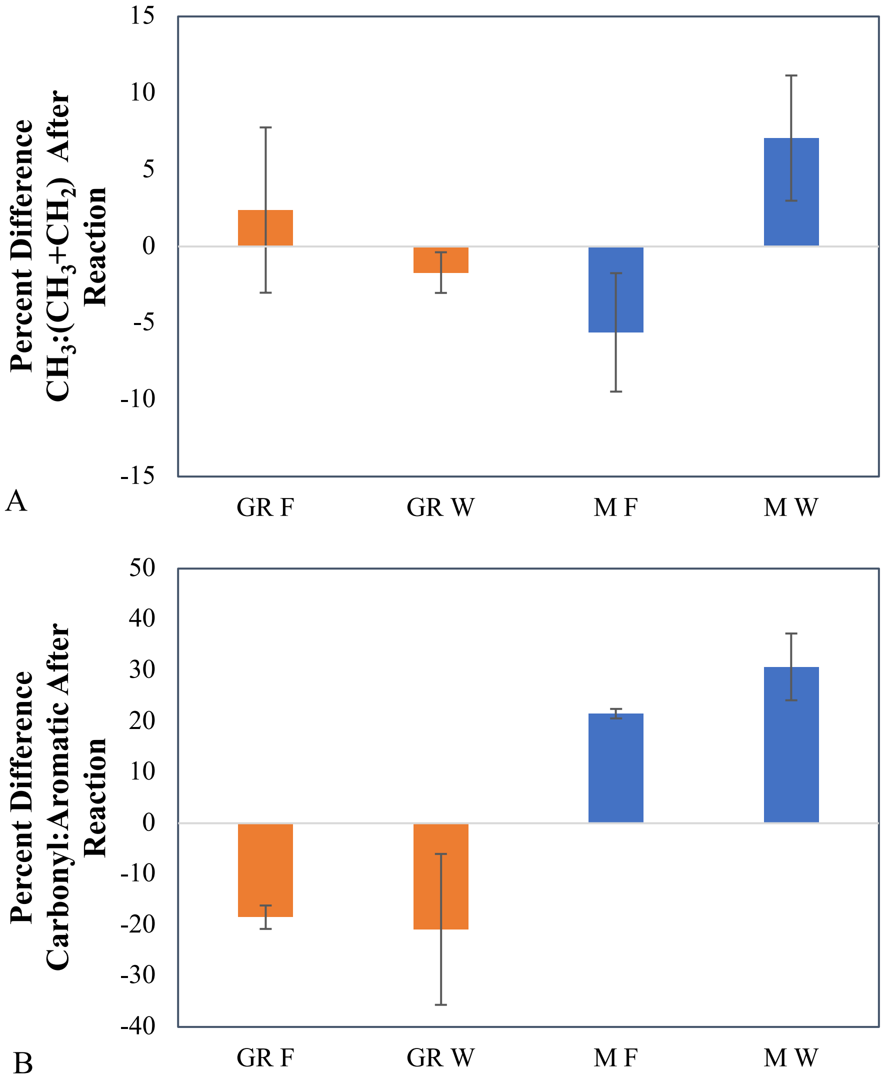

Figure 2. Percentage differences (100*(reacted sample – unreacted sample)/reacted sample) calculated for (A) CH_3 bending:(CH_3+CH_2) bending ratios and (B) carbonyl stretching:aromatic stretching ratios. GR denotes Green River kerogen isolate experiments and M denotes Marcellus kerogen isolate experiments. Experiment descriptions are shortened from fracturing fluid reactors (F), and water and hydrochloric acid only reactors (W). Functional group ratios were calculated by areas under the representative peaks, based on the multipeak fitting feature of the Igor Pro software package. Ratios used for the reacted and unreacted samples are the averages of duplicate analyses, with the error bars representing the variation in the duplicate reacted samples.

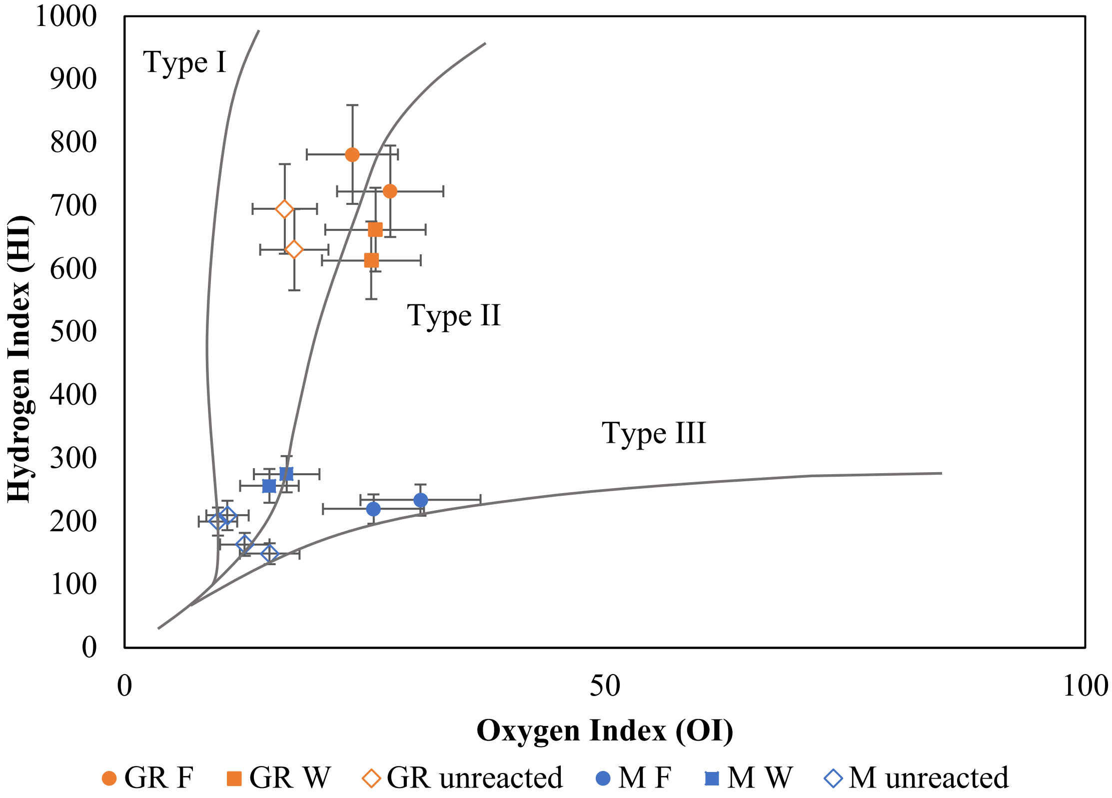

Figure 3. Psuedo-Van Krevelen diagram showing results for Green River and Marcellus samples. GR denotes Green River kerogen isolate experiments and M denotes Marcellus kerogen isolate experiments. Experiment descriptions are shortened from fracturing fluid reactors (F), and water and hydrochloric acid only reactors (W). Gray lines denote the general maturation pathways of kerogens of different Types. The Green River shale contains Type I kerogen and the Marcellus shale contains Type II kerogen.

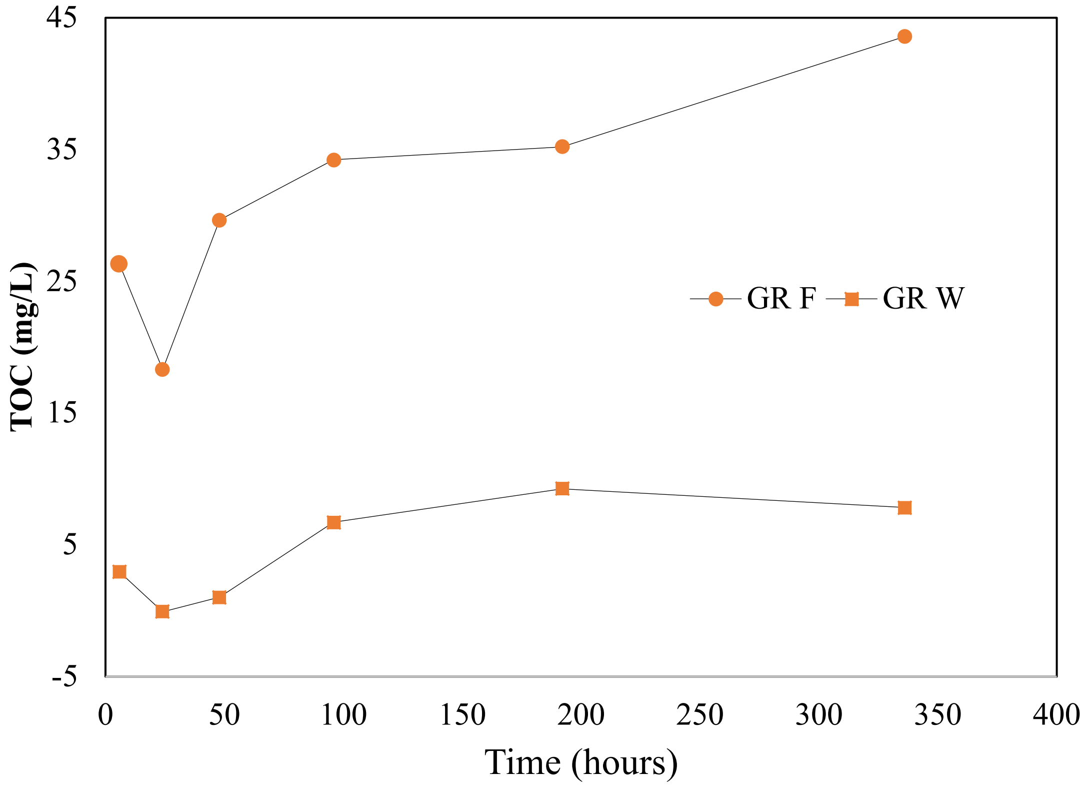

Figure 4. Total organic carbon (TOC) in solution for Green River experiments. TOC was not above background for any Marcellus experiments and so is not shown in this plot. Experiment descriptions are shortened from fracturing fluid reactors (F) and water and hydrochloric acid only reactors (W). Measurement error for TOC is 3%.

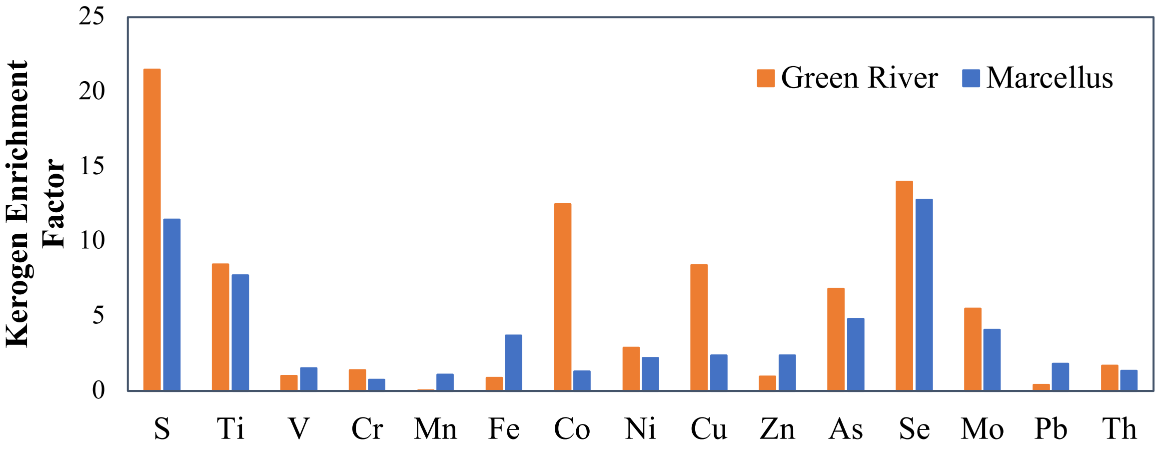

Figure 5. Concentrations of elements in the unreacted isolated kerogen fractions (which contain some pyrite and quartz) divided by the concentrations in the respective bulk shales.

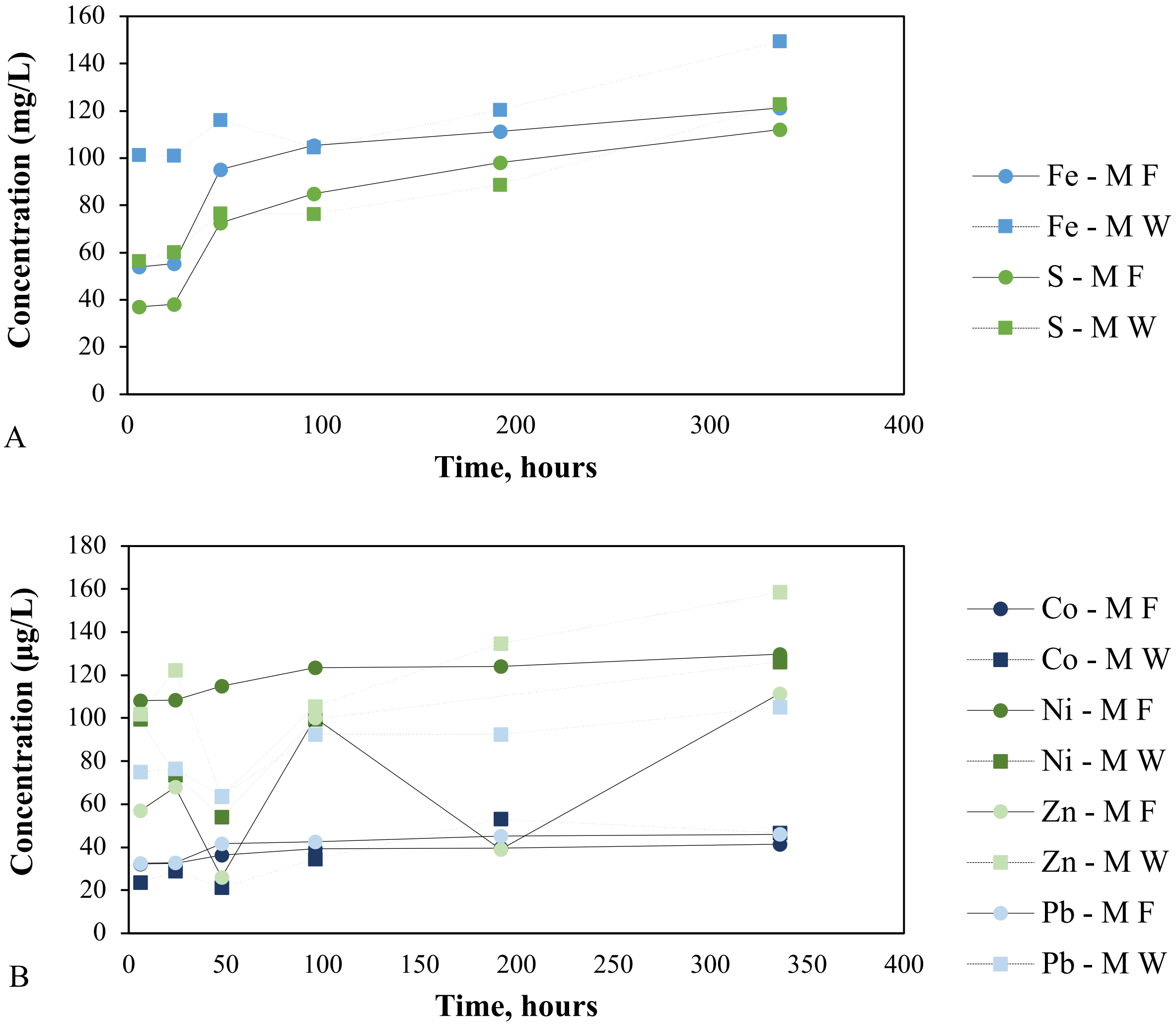

Figure 6. Concentrations of selected A) major and B) trace elements in solution for the Marcellus kerogen isolate and fracturing fluid reactor, as measured by ICP-OES and ICP-MS, respectively. Uncertainty in triplicate analyses is <8%.

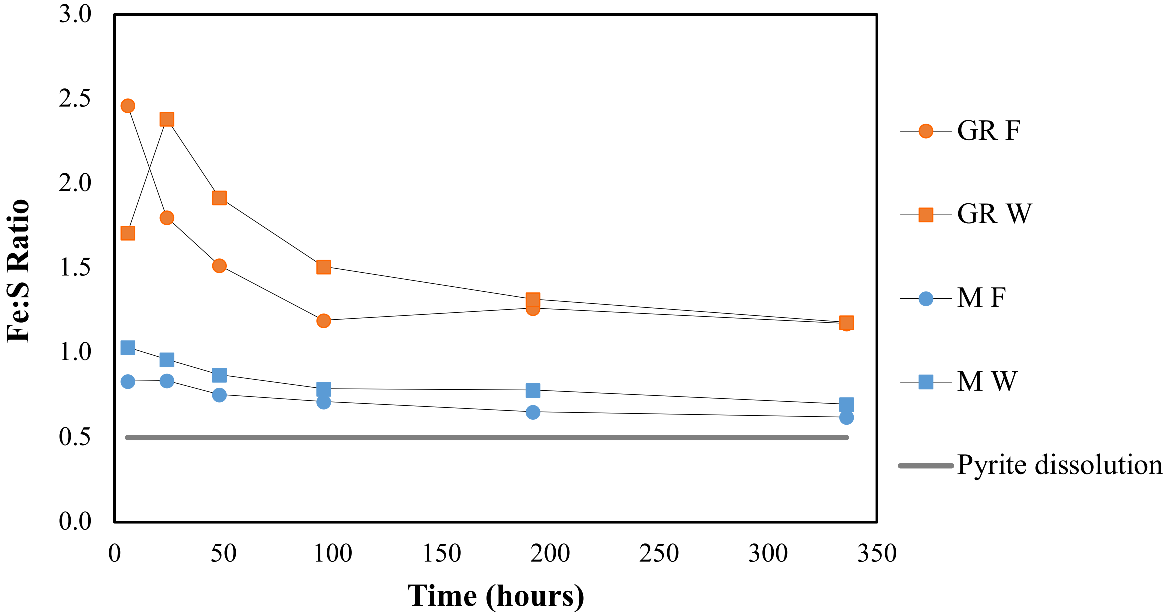

Figure 7. Fe:S ratios in solution. Total Fe and S concentrations were measured by ICP-OES, and verified by UV-Vis (Fe) and IC (SO_4^{2-}). GR denotes Green River kerogen isolate experiments and M denotes Marcellus kerogen isolate experiments. Experiment descriptions are shortened from fracturing fluid reactors (F), and water and hydrochloric acid only reactors (W). The gray line represents the stoichiometry that would be expected solely due to the dissolution of pyrite. Uncertainty in triplicate samples is <8%.

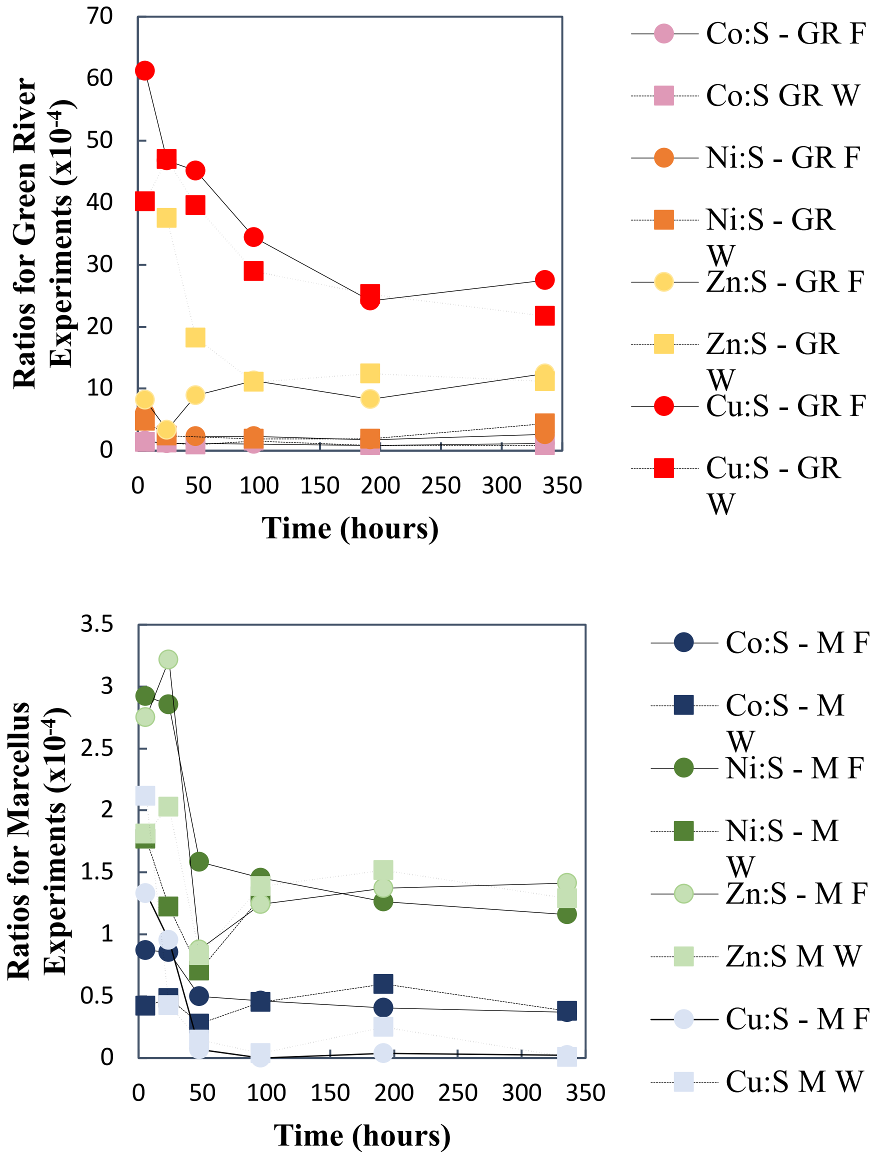

Figure 8. Metal:S ratios for Green River (A) and Marcellus (B) fracturing fluid reactor experiments. Metals were measured by ICP-MS and S was measured by ICP-OES. Trends generally mirror the trend seen for Fe:S ratios. Uncertainty in triplicate samples is <8%.

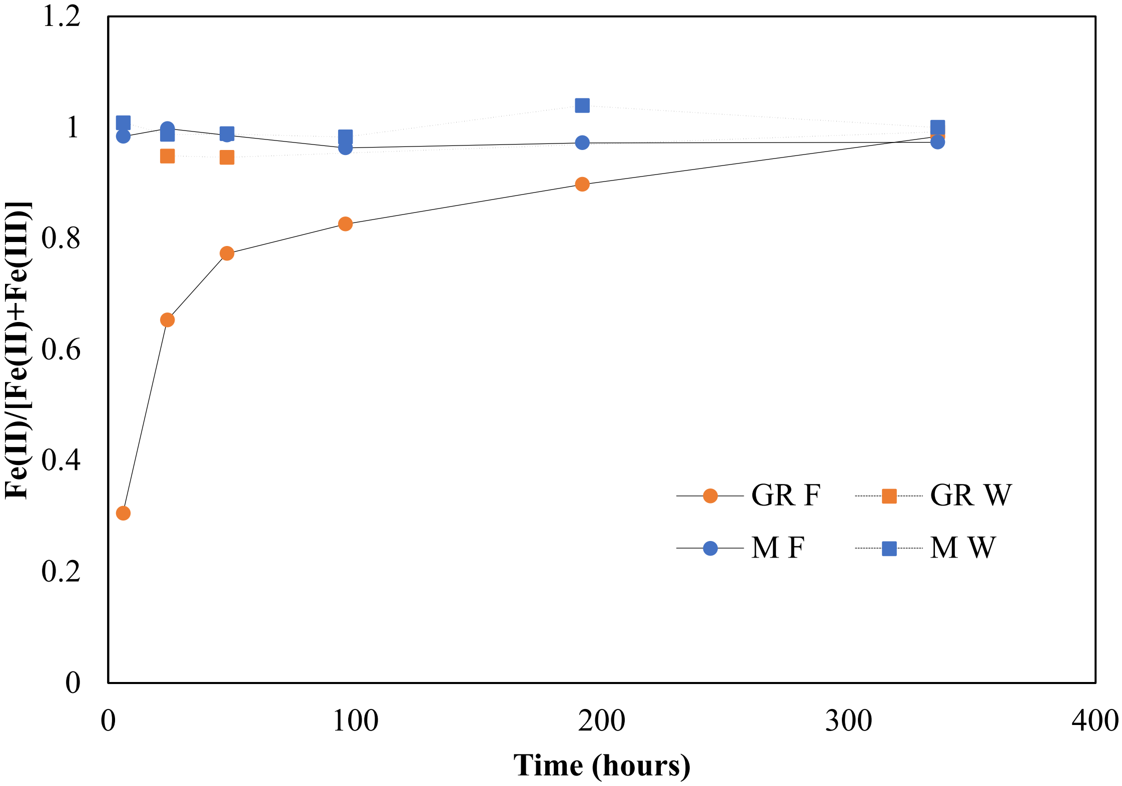

Figure 9. Fraction of total Fe present as Fe(II) in solution, as measured by UV-Vis with the ferrozine method. GR denotes Green River kerogen isolate experiments and M denotes Marcellus kerogen isolate experiments. Experiment descriptions are shortened from fracturing fluid reactors (F), and water and hydrochloric acid only reactors (W). Note that the Green River water and HCl only reactor results plot at nearly 100% Fe(II) throughout the duration of the experiment. Measurement error is <3%.

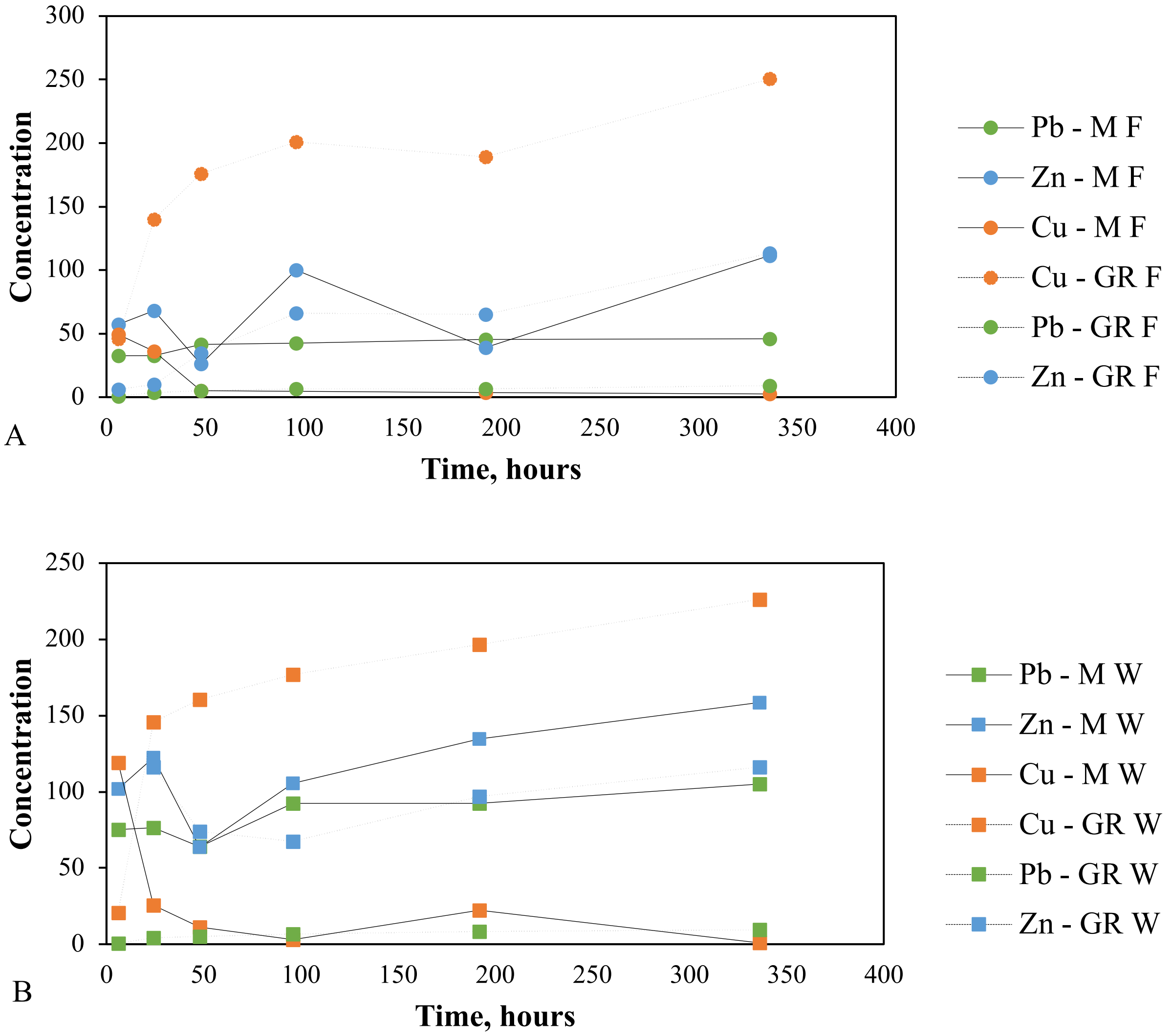

Figure 10. Trace metal concentrations in solution during kerogen isolate experiments with A) fracturing fluid reactors and B) water and hydrochloric acid reactors, as measured by ICP-MS. The Pb data are representative of other trace element data (i.e. Ni, Co). Zn and Cu represent two notable exceptions to these trends. Uncertainty in triplicate analyses is <8%.