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Mineralogical and Physical Changes that Control Pore-Scale Shale-Gas Properties

Adam D. Jew^{1,2}, Anna L. Harrison^{1,2}, Andrew M. Kiss², Megan K. Dustin¹, Claresta Joe-Wong¹, Dana L. Thomas¹, Katharine Maher¹, Gordon E. Brown Jr.^{1,2}, David Cercione³, and John R. Bargar²*

¹ Department of Geological Sciences, Stanford University, Stanford, CA, 94305, United States

² Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA, 94025, USA

³ National Energy Technology Laboratory, Strategic Center for Natural Gas and Oil, Pittsburgh, PA, 15236, USA

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Summary

Chemical reactions between hydraulic fracture fluids and oil/gas shales can increase or decrease rock porosity depending on a number of factors. For example, acidic fracture fluids increase porosity through dissolution of minerals, particularly carbonates. In contrast, oxidative dissolution of pyrite caused by oxic fracture fluids releases Fe(II), which when oxidized precipitates as Fe(III)-(hydr)oxides that occlude pores and pore necks, resulting in a loss of porosity. Depending on the mineralogy and organic content of the host shale, the rate of Fe(III) oxidation/precipitation and the type of solid phase precipitated can vary markedly. This study used a combination of laboratory- and synchrotron-based methods to monitor these changes in four oil/gas shales with highly variable mineralogy and organic matter.

Introduction

Hydraulic fracturing of unconventional shales has been an important addition to the energy portfolio of the United States. Though this practice has been highly successful, a significant amount of oil/gas resources remain in shales that have been hydraulically fractured [1]. While a large amount of the research on unconventional shale plays has focused on the geophysical aspects of the shale deposits, alteration of the rock due to chemical reaction has received comparably little attention. Geochemical reactions in the subsurface can either increase porosity/permeability through mineral dissolution or decrease porosity/permeability as secondary minerals precipitate in the system. The impact of these alterations on long term hydrocarbon production is a first-order question that remains unanswered. This project lays the foundation to address this problem.

Methods: We investigated the mineralogical, geochemical, and physical changes of four shales with varying mineralogy and organic contents [Marcellus shale (NY), Barnett shale (Central TX), Eagle Ford shale (South TX), and Green River shale (CO)] (**Table 1**) following reaction with a synthetic fracture fluid based on the fracture fluid composition used by the National Energy Technology Laboratory (NETL) in Marcellus Shale Gas Well E, located in Greene Co., PA (**Table 2**). This fracture fluid formulation is standard for the majority of the Marcellus shale gas plays.

Whole rock (cm-scale) samples and samples ground to sand-sized particles (150-250 μm) were reacted at 80°C and ~1.5 atm for various incubation times (3-weeks, 3-months, and 6-months). Solution samples were periodically taken to measure pH, total organic carbon, and cation concentrations, with special focus on aqueous Fe(II) and Fe_{tot} concentrations. Following reaction the solid samples were analyzed using synchrotron-based μ -computed tomography (μ -CT) imaging, synchrotron-based x-ray fluorescence (XRF) mapping coupled with x-ray absorption near edge structure (XANES) spectroscopy, and bulk Fe K-edge extended x-ray absorption fine structure (EXAFS) spectroscopy to identify the presence and location of Fe(III)-bearing secondary mineral phases. Detailed results on fluid and solid chemistry are provided in Jew *et al.* [2] and Harrison *et al.*[3]. Here, we present additional results regarding porosity changes as observed with synchrotron-based μ -CT.

Table 1: Bulk mineralogy of unreacted shale samples used in reactors. All mineral species are normalized to 100%. Error is $\leq 0.5\%$ [2].

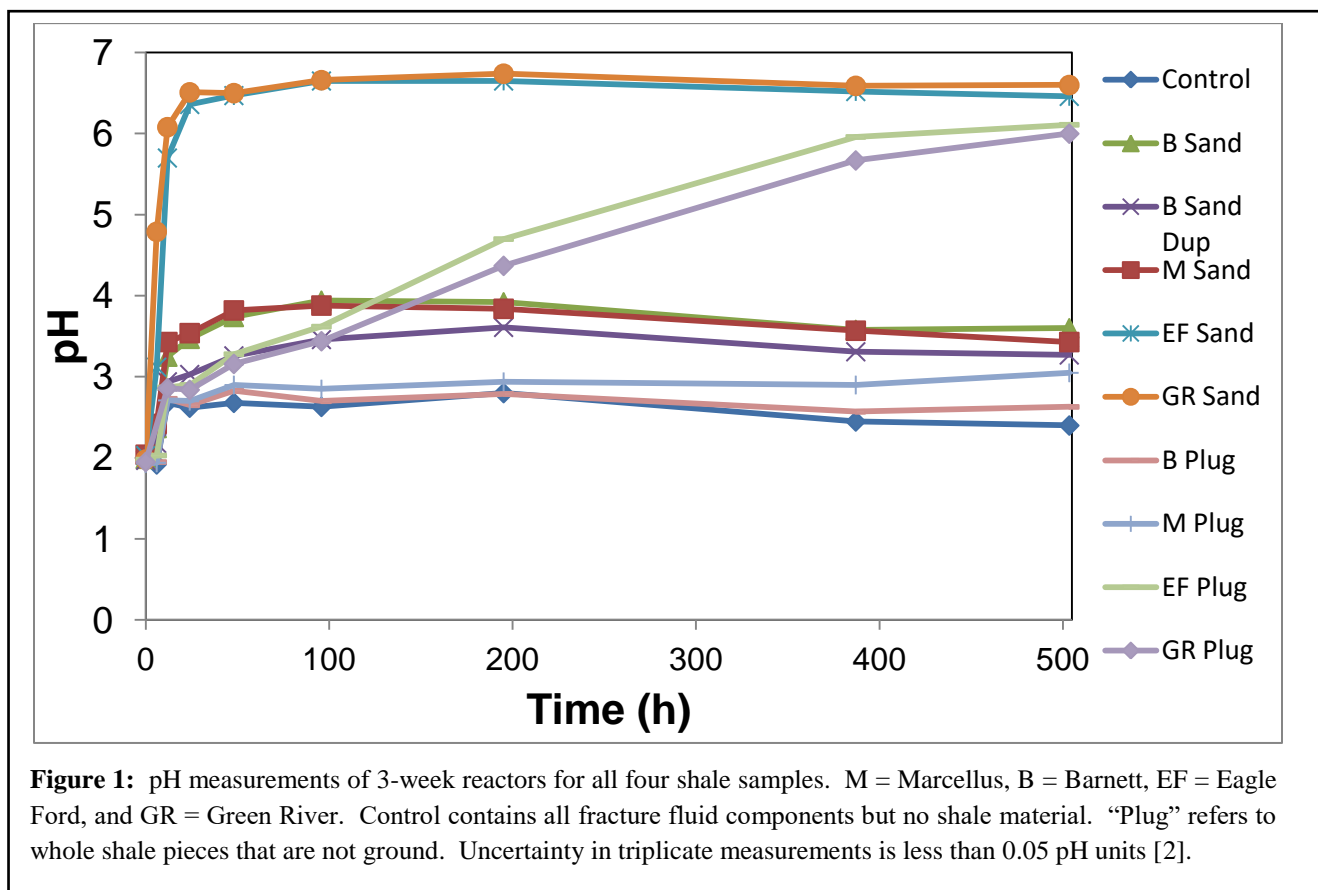
Sample	Quartz	Calcite	Dolomite	Illite	Kaolinite	Pyrite	Feldspar	Analcline	Total C (wt.%)
Barnett	44.2	8.2	X	40.6	X	2.1	4.9	X	16.0
Marcellus	42.2	11.6	1.1	35.0	X	6.4	3.7	X	6.0
Eagle Ford	25.2	64.5	X	X	7.6	2.7	X	X	4.4
Green River	31.4	23.2	28.9	X	X	X	8.0	8.5	12.7

Table 2: Fracture-fluid composition used in experiments based on reported additives used at Marcellus Shale gas Well E. Polyethylene glycol represents more than 60% of the total biocide introduced into Well E. Solution pH = 2.0.

Ingredient	Purpose	By Mass	Percentage of Ingredient (wt.%)
Water	Base Fluid	1995.6674 g	99.783%
Ethylene Glycol	Scale Inhibitor, Iron Control, Breaker	0.4113 g	0.021%
Kerosene	Friction Reducer	0.4815 g	0.024%
Guar Gum	Dry Gellant	0.5807 g	0.029%
2-Ethyl hexanol	Corrosion Inhibitor for Acid	0.0093 g	0.0005%
Glycol ether	Corrosion Inhibitor for Acid	0.0031 g	0.0002%
Polyethylene glycol	Biocide	0.3974 g	0.020%
Hydrochloric acid	Acid	2.4493 g	0.122%

Results: For carbonate-poor shale samples (Marcellus and Barnett), solution pH rose slightly from a starting value of 2.0 to pH < 4.0 within 48 hours and remained steady for the remainder of the experiments at all incubation times (**Figure 1**). However, carbonate-rich samples (Eagle Ford and Green River) buffered the solution pH to circum-neutral within the first 48 h of reaction (**Figure 1**). Due to lower surface area compared to the sand-sized particles, the neutralization of the acidic fracture fluid for the whole rock samples occurred more slowly over the span of three weeks (**Figure 1**). μ -CT imaging of Marcellus (**Figure 2**) and Green River (**Figure 3**) shale samples showed a

significant difference in the porosity development of the samples. The Marcellus shale showed the development of worm holes and surface roughness, while the Green River sample had a much more uniform reaction rim with clear development of a secondary porosity network. Quantitative XRD results indicate that calcite was preferentially dissolved in all four samples. In the case of the Green River sample, there was no detectable loss of dolomite. The intimate grain-scale co-location of the calcite and dolomite in the Green River samples resulted in a reaction rim where calcite was preferentially dissolved while dolomite was left behind. XRD analyses confirmed that in Barnett and Marcellus samples essentially all of the calcite was dissolved, while for Eagle Ford and Green River, less than half of the total mass of carbonate minerals was dissolved. These images (**Figures 2 and 3**) show a significant increase in porosity in the shale samples.



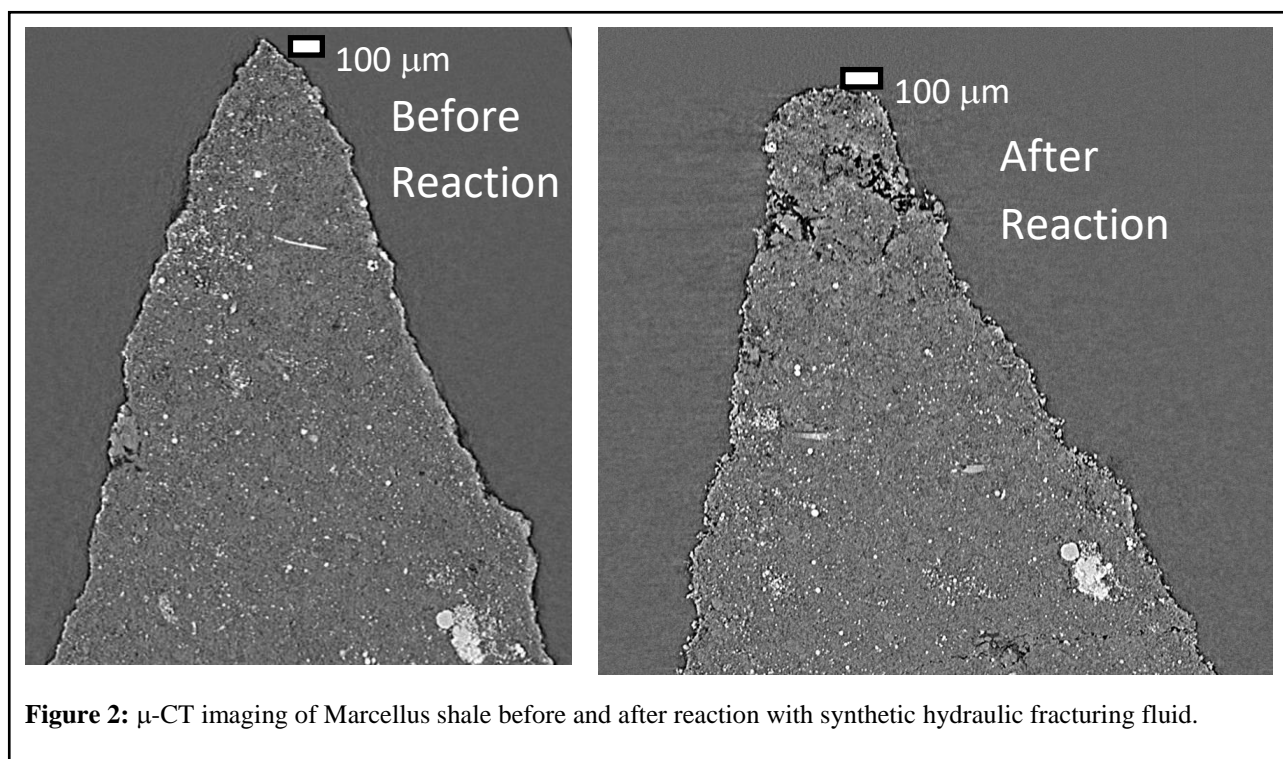
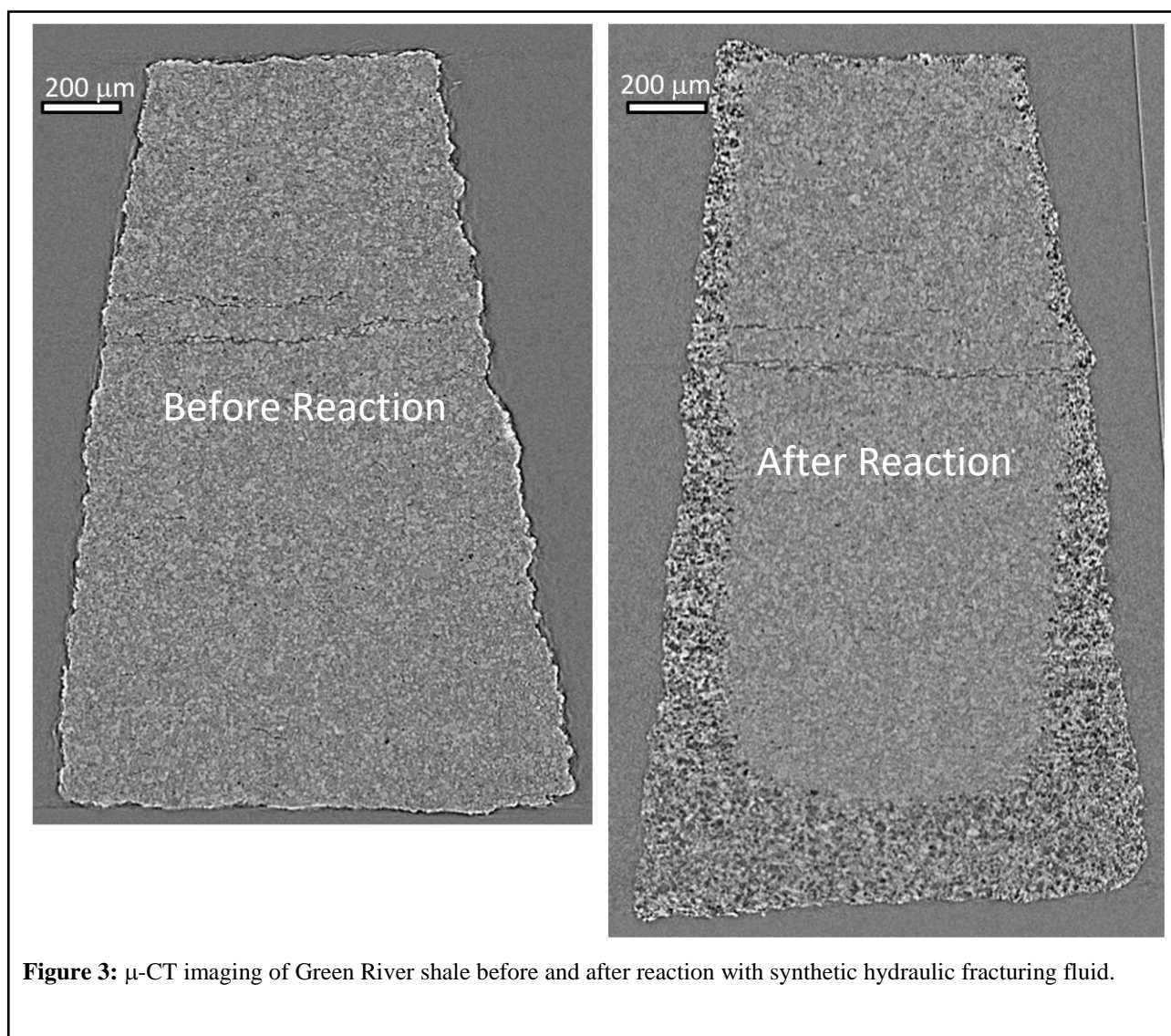
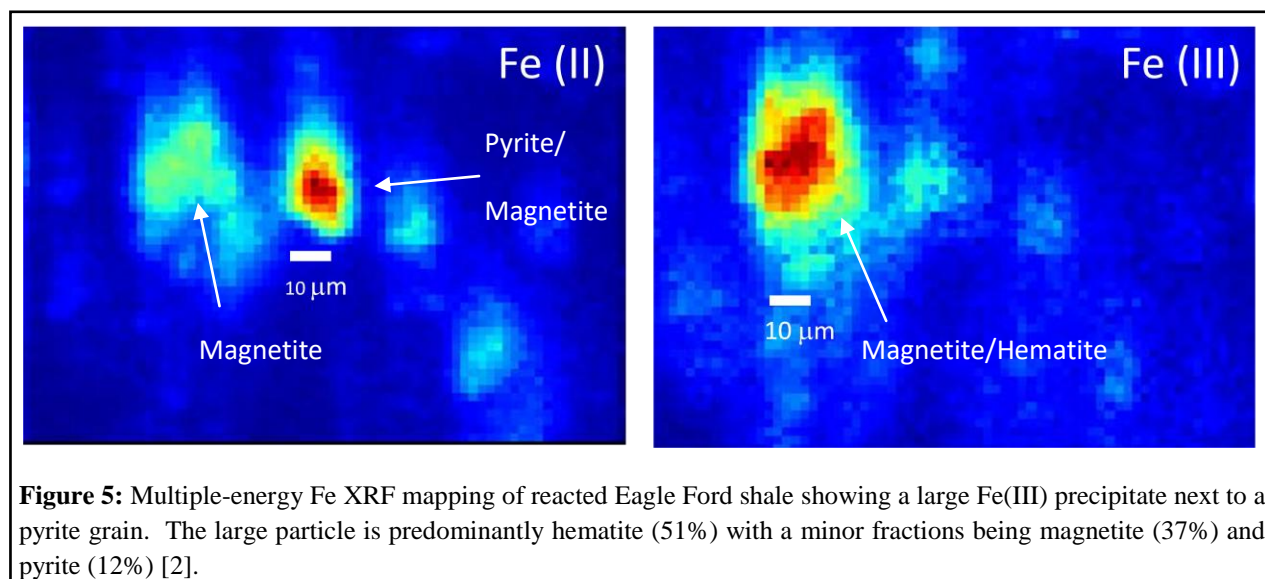
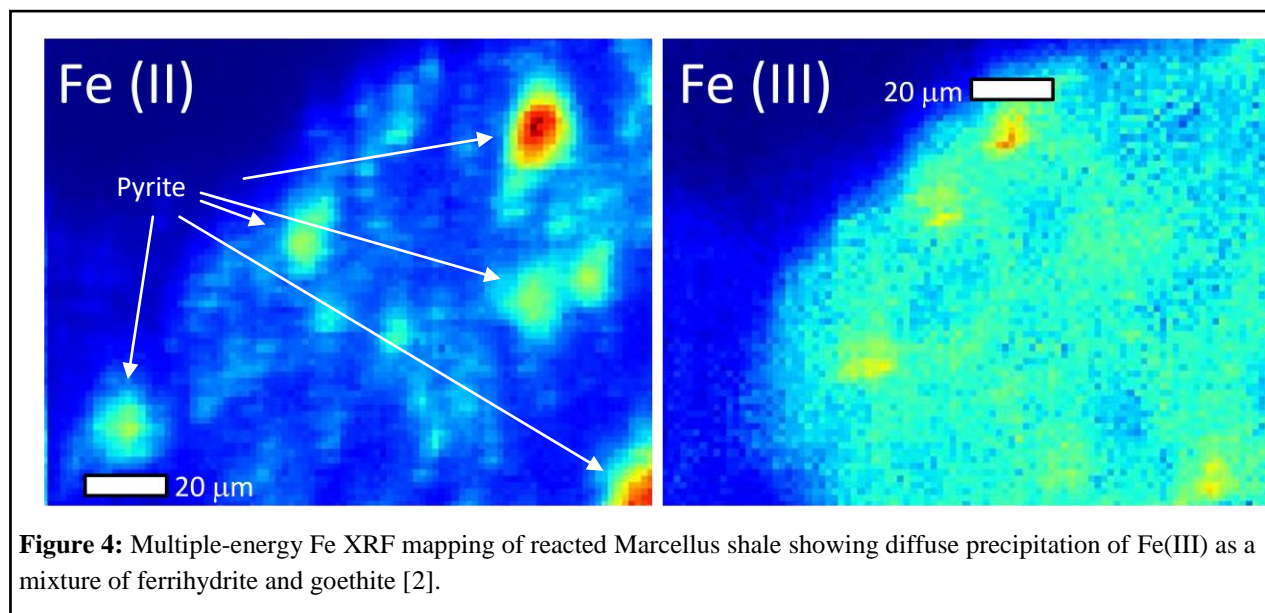


Figure 2: μ -CT imaging of Marcellus shale before and after reaction with synthetic hydraulic fracturing fluid.

Reactor experiments containing fracture fluid without HCl showed that no Fe was released from the shales for all four shale types, indicating that acid is required to release Fe from the shale. Analysis of XRD and Fe K-edge EXAFS data of the samples before and after reaction indicate that pyrite is the primary source of released Fe in these systems [2]. EXAFS spectroscopy indicates that a significant amount of Fe in these samples (upwards of 33%) is in the form of Fe(II) bound directly to C in kerogen-rich regions. This form of Fe was found to be surprisingly stable in the presence of fracture fluid. In the presence of dissolved O_2 , Fe(II) released from pyrite dissolution was oxidized and precipitated as Fe(III)-(oxyhydro)oxides, reducing pore volume. In shales with poor pH buffering capacity (Barnett and Marcellus), Fe(III)-(oxy)hydroxide precipitate as diffusely distributed ferrihydrite and goethite coatings covering the surface of pores and fractures (**Figure 4**). In contrast, when pH buffering capacity is high, in the case of carbonate-rich shales (Green River and Eagle Ford), Fe precipitates as large grains of hematite and magnetite close to pyrite grains (**Figure 5**). These different types of precipitation behavior imply different shale alteration patterns in the subsurface depending on carbonate content and fluid composition.



Oxidation of Fe(II) by O_2 is strongly pH dependent, with relatively fast rates at near-neutral pH and orders of magnitude slower oxidation at low pH [4]. Consequently, the low pH of the Marcellus and Barnett reactors was expected to retard or inhibit the oxidation of Fe(II) and subsequent precipitation of Fe(III)-(oxyhydr)oxides (**Figure 1**). In spite of this expectation, ferrihydrite and goethite precipitation was clearly observed (**Figure 4**). Reactors containing fracture fluid, Fe(II), and bitumen extracted from either Marcellus or Green River shale showed that the bitumen can accelerate the oxidation of Fe(II) even at low pH [2]. Thus, because organic compounds common to fracturing fluids are capable of readily extracting bitumen from oil/gas shales [5-6], regardless of the pH of the solution in the subsurface, precipitation of Fe(III)-(oxyhydr)oxides is still likely and can alter porosity.



Conclusion: Our work shows that the reaction of hydraulic fracturing solution with unconventional oil/gas shales of different pH buffering capacity produces different mineralogical, geomechanical, and geochemical products. The dissolution of carbonate grains and the subsequent precipitation of Fe(III)-bearing phases can cause both increases and decreases in the porosity of the shale matrix. Though fracture fluid additives inhibit precipitation of Fe(III)-bearing solids, the extraction of bitumen from the host shale can severely impact the effectiveness of these chemicals. Our results stress the importance of considering organic additives and shale organic compounds as controls on iron scale precipitation in shale formations. It is evident that geochemical reactions in hydraulically fractured shales have the potential to significantly impact production rates and overall recovery in unconventional hydrocarbon systems.

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