Experimental Investigation of the Impacts of Fracturing Fluid on the Evolution of Fluid Composition and Shale Characteristics: A Case Study of the Niutitang Shale in Hunan Province, South China

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Received: 11 June 2020; Accepted: 26 June 2020; Published: 29 June 2020

Abstract: Hydraulic fracturing is a widely used technique for oil and gas extraction from ultra-low porosity and permeability shale reservoirs. During the hydraulic fracturing process, large amounts of water along with specific chemical additives are injected into the shale reservoirs, causing a series of reactions the influence the fluid composition and shale characteristics. This paper is focused on the investigation of the geochemical reactions between shale and fracturing fluid by conducting comparative experiments on different samples at different time scales. By tracking the temporal changes of fluid composition and shale characteristics, we identify the key geochemical reactions during the experiments. The preliminary results show that the dissolution of the relatively unstable minerals in shale, including feldspar, pyrite and carbonate minerals, occurred quickly. During the process of mineral dissolution, a large number of metal elements, such as U, Pb, Ba, Sr, etc., are released, which makes the fluid highly polluted. The fluid–rock reactions also generate many pores, which are mainly caused by dissolution of feldspar and calcite, and potentially can enhance the extraction of shale gas. However, precipitation of secondary minerals like Fe-(oxy) hydroxides and CaSO4 were also observed in our experiments, which on the one hand can restrict the migration of metal elements by adsorption or co-precipitation and on the other hand can occlude the pores, therefore influencing the recovery of hydrocarbon. The different results between the experiments of different samples revealed that mineralogical texture and composition strongly affect the fluid-rock reactions. Therefore, the identification of the shale mineralogical characteristics is essential to formulate fracturing fluid with the lowest chemical reactivity to avoid the contamination released by flowback waters.

Keywords: hydraulic fracturing; fracturing fluids; fluids-rock interaction; environmental implication
1. Introduction

Shale gas, as an unconventional resource, has been widely developed in the United States, Canada, China, and Argentina in the past decades to meet the increasing demands for geo-energy. China is the largest holder of shale gas resources worldwide, with estimates ranging from 12.8 to 31.2 trillion m³ [1–4]. In addition, more than two thirds of the estimated resources are stored in marine shales, in particular in south China. Therefore, the marine shale reserves have raised much attention.

The lower Cambrian Niutitang shale is a prolific gas play distributed in many places across South China, including Sichuan, Chongqing, Guizhou, Hunan, and Hubei provinces. This formation has been widely evaluated and analyzed over the past decade [5–10]: the Niutitang shale is mainly composed by quartz and clay minerals, which ranges from 35% to 77% and 6.2% to 37%, respectively. Carbonate and feldspar are also common in this formation, with ranges from 0% to 27% and 2% to 22%, respectively. The total organic carbon (TOC) ranges from 0.5% to 10% and the equivalent vitrinite reflectance (equal-Ro) ranges from about 1.5% to 4.6%. The thickness of this formation in Hunan Province can reach more than 300 m. Studies have showed that the Niutitang shale contains a very large quantity of shale gas resources. The achievements made in the analysis of pores and mineral composition in shale reservoirs [6,11–13] revealed the favorable pore systems for shale gas storage and a high brittleness that favors fracturing. More recently, wells targeting the Niutitang shale in the western Hubei province have already shown industrial gas flow [14].

However, due to the ultra-low porosity and permeability of unconventional reservoirs (e.g., shale and coal-bed methane reservoirs), horizontal drilling and hydraulic fracturing techniques are needed for effective extraction of these unconventional resources [15,16]. During the hydraulic fracturing process, from 7500 to 15,000 cubic metres of water along with specific chemical additives, which are acidic and oxidative, are injected into subsurface shale formations for one typical shale gas well [17,18]. From 5 to 85% of the injected fluid (generally 30–50%) flows back to the near surface and has a salinity three times greater than that of the initial water [19,20]. These flowback waters generally contain lots of toxic and radioactive elements (e.g., U, Pb, Sr), and therefore could lead to contamination of the surface water and shallow aquifers or accumulation of heavy metals in soil when spills and leaks occur [21,22]. There is much research evaluating the influence of shale gas development on groundwater quality in several shale regions in the U.S [23–26] and in the UK [27]. However, when it comes to China, the research is relatively rare. Although some scholars [28,29] have done research about the flowback waters of Longmaxi Shale in the Sichuan Basin, the Niutitang Shale, as a newly developed shale gas reservoir, has not received much attention yet. In addition, most of the research did not explain what caused the high salinity of flowback water. The geochemical interaction between shale and fracturing fluid, which affects not only physical properties of the shale but also the composition of the waters produced during shale gas production, is an important controlling factor [13] but rarely has been discussed [30]. Therefore, more studies about the geochemical processes between fracturing fluids and the shale are required to evaluate and minimize the potential environmental impacts.

By conducting simulation experiments and studying the changes of fracturing fluid, mineral, and physical properties during the experiments, key reactions occurring during the fracturing process in the shale reservoirs can be extrapolated. In this study, the Niutitang shale samples from different depths were exposed to and reacted with fracturing fluids. The purposes of this article are: (1) to evaluate the release of major and minor cations and ions as well as trace metal contaminants during hydraulic fracturing, (2) to assess mineralogical and petrophysical changes of the shale during shale gas production, and (3) to investigate the key reactions between the shale samples and fracturing fluids. If the reactions that release metals can be identified, steps to minimize those reactions could be taken, making the flowback waters less toxic, radioactive, and easier to be treated.
2. Materials and Methods

2.1. Samples and Fracturing Fluid

Samples were cored from an exploration well drilled in Anhua County, Hunan Province (Figure 1). Two groups of samples from different depths were used in the experiment, one from a depth of about 80 m and the other from a depth of about 795 m, to investigate the influence of the initial shale mineral compositions and physical properties. The information about initial shale samples is presented in Table 1. The fracturing fluid used in our experiments was from a chemical company called Rong Sheng Chemical Co., Ltd. and this kind of fracturing fluid has been used for shale gas exploitation in field. It contains 99.7 wt% water, 0.15 wt% guar gum, 0.03 wt% acid (mainly acetic acid and hydrochloric acid), 0.01 wt% pH adjustor (NaOH, NaHCO₃), and some other additives like K⁺ and Ca²⁺ salts. In each reactor, approximately 8 g of shale sample was exposed to 50 mL fracturing fluid. Most of the shale samples were powder samples, ground to between 100 to 200 mesh, and others were thin sections, for which the main purpose was to provide a surface for field emission scanning electron microscope (FE-SEM) observation.

![Sample Site and Shale Distribution](image)

**Figure 1.** Location of the shale gas well in Anhua (the red spot), where the samples were obtained. The blue area represents the distribution of Lower Cambrian Niutitang Formation in South China (Modified from [31]).

2.2. Experiment Design

During the hydraulic fracturing process, there is a shut-in period (several days to several weeks), which is hypothesized to be the main stage of reactions between shale and the injected fluid. A part of the fracturing fluid flows back to the surface during shale gas production, but it is estimated that more than 50% of the fracturing fluid remains underground and continues to react with the shale [32,33]. Therefore, two sets of experiments with different timescales were designed. One group of experiments was conducted for two weeks, referred to as short-term experiments. The other group of experiments was conducted for one year, referred to as long-term experiments. Each group had two series of experiments, in which samples from different depths (Table 1) were used to investigate the impact of shale characteristics on fracturing process. The purpose of short-term experiments (S1 and S2 series) is to simulate the initial stage of fluid injection into shale formation for hydraulic fracturing, i.e., the main stage of reaction, while that of the long-term experiments (S3 and S4 series) is to investigate the interactions between fracturing fluid that remains underground and the shale reservoirs over a long time.
The short-term experimental temperature was adjusted to 50 °C to simulate the reservoir temperature and minimize the difference between the experimental and field results, while the long-term experimental temperature was difficult to be strictly controlled and we adopted the annual average local temperature (about 20 °C). The temperature of long-term experiments could have an effect on experimental results, but it can still provide insights into the investigation of the geochemical reactions between shale and fluids. The experiments were conducted at atmospheric pressure rather than reservoir pressure, but the influence of pressure on the interactions between fracturing fluid and shale is much smaller than that of temperature [15,34].

The fluid samples were taken at certain intervals, i.e., 12 h, 24 h, 48 h, 3 days, 6 days, 10 days, and 15 days for short-term experiments and 15 days, 30 days, 90 days, 180 days, and 360 days for long-term experiments, to trace the evolution of fracturing fluid compositions. Solids were collected at the end of experiments, dried at 75 °C for 24 h and then analyzed to assess the mineralogical and petrophysical changes after being exposed to fracturing fluid.

Table 1. Mineral composition and physical property of initial shale samples.

| Sample | Quartz | Feldspar | Calcite | Pyrite | Clay | TOC | Porosity | Density |
|--------|--------|----------|---------|--------|------|-----|----------|---------|
| S1 a   | 67.9   | 12.0     | nd      | 10.7   | 9.3  | 3.1%| 9.4      | 2.51    |
| S2     | 65.7   | 11.5     | 3.9     | 7.1    | 11.9 | 8.6%| 0.7      | 2.72    |
| S3     | 65.5   | 12.1     | nd      | 9.4    | 13.0 | 2.7%| 9.7      | 2.46    |
| S4     | 66.8   | 11.6     | 3.2     | 6.9    | 11.4 | 8.3%| 0.8      | 2.70    |

* Sample 1 (S1) and sample 3 (S3) are from 80 m, while sample 2 (S2) and sample 4 (S4) are from 795 m. Samples S1 and S2 are used in short-term experiments, while S3 and S4 are used in long-term experiments.

2.3. Analytical Technique

Fluid samples were measured using inductively coupled plasma-optical emission spectrometry (ICP-OES: ICAP7400 Radial from Thermo Fisher Scientific, Waltham, MA, USA) and inductively coupled plasma-mass spectrometry (ICP-MS: iCAP RQ from Thermo Fisher Scientific, Waltham, MA, USA). ICP-OES was used to determine the concentrations of major cations, e.g., Mg, Ca, and Fe, while ICP-MS is more accurate in measuring minor cations and trace elements, e.g., Al, Pb, U, Sr, and Ni. The concentrations of dissolved anions like sulfate ion were measured by ion chromatography (IC: ICS-1500 from DIONEX, Sunnyvale, CA, USA). In addition, the pH of the fluid was also analyzed and recorded using AZ8685A type pH meter.

The mineral composition of the powder samples was analyzed using an X-ray powder diffractometer (XRD: Advance D8 from Bruker, Billerica, MA, USA). The porosity was measured with a mercury intrusion meter. Observation of thin sections by FE-SEM coupled with energy-dispersive spectroscopy (EDS) (FE-SEM: MIRA3 LMH from TESCAN, Czech Republic + EDS: X-MAX20 from Oxford Instruments, Abingdon, UK) was performed to provide supplementary information to assess the mineralogical and petrophysical changes of the shale.

3. Results and Discussion

3.1. Aqueous Inorganic Geochemistry

3.1.1. Evolution of pH and Fluid Composition

The initial pH of all groups of experiments is 6. However, the pH values show different variation trends with the increase of reaction time. The pH values of the S1 series drop rapidly in the first 24 h and then become relatively stable. Afterwards, the pH values show small fluctuations around 3.5 (Figure 2a). Concerning the S2 series, the pH values decrease very slightly in the first 24 h, followed by a slow rise to the 72 h, and remain relatively stable at about 6.0 afterwards (Figure 2a). The changes of pH in S3 and S4 series are generally close to those in the short-term experiments. In S3 series the pH values decrease and stabilize at about 3.5, while in S4 series the pH remains close to 6.5, which is
consistent with the results of short-term experiments (Figure 3a). However, after nearly three months, the pH of both long-term experiments begins to rise slowly (Figure 3a).

The concentrations of the major ions, i.e., Ca\(^{2+}\), Mg\(^{2+}\), Fe\(^{3+}\), Al\(^{3+}\), and SO\(_4^{2-}\), show significant differences between the two sets of short-term experiments. In the S2 series, Ca\(^{2+}\) is released into the fracturing fluid to the greatest extent among all of the measured ions. Ca increases rapidly in the first 72 h, reaching the maximum value of 140 mg/L, and after that the concentrations of Ca\(^{2+}\) remain stable (Figure 2b). For the S1 series, the Ca\(^{2+}\) concentrations increase to a maximum value of 40 mg/L in the early stage, which is much less than that of the S2 experiments (Figure 2b). The trends of Mg\(^{2+}\) release into the fluids are similar to those of Ca\(^{2+}\). In both S1 and S2 experiments, the concentrations of Mg\(^{2+}\) increase within the first 72 h and are a little higher in S2 series (Figure 2b).

The situation of the concentrations of Fe\(^{3+}\) and SO\(_4^{2-}\) is different from that of Mg\(^{2+}\) and Ca\(^{2+}\). For the S1 experiments, the concentrations of Fe\(^{3+}\) and SO\(_4^{2-}\) increase greatly within the first 24 h, after which they are maintained at approximately at 470 mg/L and 2400 mg/L respectively (Figure 2c). The concentrations of aqueous Fe\(^{3+}\) and SO\(_4^{2-}\) in the S2 experiments increase slightly with a maximum value of 8.5 mg/L and 124 mg/L, respectively (Figure 2c). The trend of aqueous Al\(^{3+}\) is similar to that of Fe\(^{3+}\). In the S1 experiments, the concentrations of Al\(^{3+}\) increase from less than 1 mg/L to about 85 mg/L within 72 h, while those of the S2 series are always low (Figure 2d).

The changes of concentrations of Ca\(^{2+}\), Mg\(^{2+}\), Fe\(^{3+}\), SO\(_4^{2-}\), and Al\(^{3+}\) in long-term S3 and S4 experiments are similar to those of the short-term S1 and S2 experiments. The fluids of the S4 experiments contain much more Ca\(^{2+}\) and Mg\(^{2+}\), but the increase of Fe\(^{3+}\), SO\(_4^{2-}\) and Al\(^{3+}\) is far less compared to S3 (Figure 3).

The variation of major elements in the two sets of experiment indicates that the main reactions that occurred in these sets of experiments are different. In the analyzed shale, the main Fe and S bearing phase is pyrite, which can be easily oxidized. During the process of pyrite oxidation, sulfuric acid is generated [35]. The tremendous increase of Fe\(^{3+}\) and SO\(_4^{2-}\) within 24 h in the S1 experiments indicates a great generation of sulfuric acid, which results in the rapid drop of pH in the first 24 h. However, in the S2 experiments the increase of Fe\(^{3+}\) and SO\(_4^{2-}\) is much less and that could account for the slight pH decrease with the first 24 h. The Ca\(^{2+}\) and Mg\(^{2+}\) are mainly released by dissolution of carbonate minerals including calcite [CaCO\(_3\)] and dolomite [Ca, Mg (CO\(_3\))\(_2\)]. They can act as a pH buffer. In the S2 experiments, the finding of much higher concentrations of Ca\(^{2+}\) and Mg\(^{2+}\) suggests that the main reaction is dissolution of carbonate minerals, which leads to the slow rise of pH in the first 72 h. The slight decrease in the first 24 h caused by pyrite oxidation and the following rise caused by calcite dissolution in the S2 experiments also indicates that the dissolution of calcite is probably triggered by the sulfuric acid generated by pyrite oxidation.

The case of S3 and S4 experiments is similar to the short-term experiments. The main reaction that occurred is pyrite oxidation in S3 and carbonate mineral dissolution in S4. The slight rise of pH after 3 months (Figure 3a) might be caused by clay minerals. The reaction between fracturing fluid and clay minerals would generate some substances that affect pH like silicate ions which are alkaline after hydrolysis [36], causing the rise of pH of the solutions. Furthermore, after a long duration of experiments, the emergence of microorganisms and the degradation of some organic matter [15] will also have an impact on the evolution of the fluids, making the situation more complicated and unpredictable.

In the shale, the Al-bearing minerals include clay minerals and feldspar. According to the results of XRD analysis of shale samples (Table 2), the main source of Al in our experiments is feldspar. The content of feldspar in the S1 and S3 experiments is reduced by about 30% while in the S2 and S4 experiments there is almost no change of feldspar content. The different degrees of feldspar dissolution are mainly caused by pH, as feldspar can be corroded more easily under acidic conditions than under neutral conditions. Clay minerals also affect the release and transport of ions in shale. Many exchangeable ions attach to the surface of clay minerals, and when in contact with fluid, they are separated and diffused into water, which therefore influences the release of ions [18]. Previous studies also have revealed that under acidic conditions clay minerals like illite release more Si and Al than under neutral and alkaline conditions [37], which could also contribute to the different results.
of the S1(3) and S2(4) experiments. However, to what extent clay minerals will affect the release of ions is not clear yet and further study is needed.

Figure 2. pH (a) and concentrations of Ca$^{2+}$ and Mg$^{2+}$ (b), Fe$^{3+}$ and SO$_4^{2-}$ (c), and Al$^{3+}$ (d) in short-term experiments.

Figure 3. pH (a) and concentrations of Ca$^{2+}$ and Mg$^{2+}$ (b), Fe$^{3+}$ and SO$_4^{2-}$ (c), and Al$^{3+}$ (d) in long-term experiments.
3.1.2. Trace Elements and Contaminant Release

A major environmental concern is that hydraulic fracturing may lead to pollution of underground or surface waters [21]. It has been reported that the fluid recovered during hydraulic fracturing contains many toxic or radioactive metals, e.g., As, Sr, Pb and U, most of which are released from the shale reservoirs through dissolution of shale minerals or degradation of organic matter [38–40]. In this study, the concentrations of trace metals were analyzed to evaluate their source and amount of release.

As shown in Tables 3 and 4, the concentrations of most of the metals are much higher in the S1 experiments than in S2. For example, the concentrations of Ni in the S1 experiments reach a maximum value of 4500 μg/L, while in S2 experiments it only reaches about 170 μg/L, far less than in S1. In addition, in both series of experiments, these metal elements are released into fluids within 24h rapidly and remain relatively stable. The concentrations of these elements in S3 and S4 series are similar to the short-term experiments (Tables 5 and 6). A very similar phenomenon is also exhibited by Fe³⁺ and SO₄²⁻, which are also much higher in the S1 experiments and released in the first 24h. The similarity indicates that pyrite is the main source of metal elements in shales, which is consistent with the observation of previous studies [41,42]. Heavy metals can be incorporated into pyrite by different surface processes, including precipitation, co-precipitation, chemical or physical adsorption, ionic replacement, or redox reactions between dissolved cations and the surface of pyrite [42–45]. For example, Co and Ni can substitute for the Fe(II) in pyrite due to their similar ionic radii [46], and elements (e.g., Cr, Pb, and Zn) that have higher water-exchange reaction kinetics than Fe(II) form metallic sulfides and co-precipitate with pyrite [47]. When pyrite is oxidized, the incorporated metals are released along with Fe³⁺ and SO₄²⁻, leading to the different results of the experiments.

### Table 2. Mineral compositions of shale samples recovered after experiments.

| Sample | Quartz | Feldspar | Pyrite | Clay | Calcite |
|--------|--------|----------|--------|------|---------|
| S1     | 76.2   | 9.5      | 4.7    | 9.5  | nd      |
| S2     | 69.9   | 11.2     | 6.3    | 12.1 | nd      |
| S3     | 74.3   | 8.8      | 4.5    | 12.2 | nd      |
| S4     | 71.0   | 12.2     | 6.1    | 10.3 | 0.4     |

*: nd = non detected.

### Table 3. Concentrations (μg/L) of trace metals in short-term fluid sample of S1.

| S1   | Cr   | Co   | Ni   | Cu   | Ba   | Pb   | U    | Sr   |
|------|------|------|------|------|------|------|------|------|
| 0 h  | 1.6  | 0.2  | 2.3  | 7.2  | 29.4 | 1.5  | 1.4  | 84.9 |
| 12 h | 535  | 445  | 3320 | 5000 | 48.6 | 17.68| 65.5 | 94.9 |
| 24 h | 421  | 445  | 3240 | 4230 | 50.6 | 15.32| 56.8 | 99.0 |
| 48 h | 482  | 596  | 4110 | 5220 | 43.6 | 14.48| 60.4 | 113 |
| 72 h | 400  | 591  | 4040 | 5090 | 39.0 | 14.68| 61.3 | 111 |
| D6   | 438  | 576  | 4312 | 5796 | 29.2 | 1.44 | 51.4 | 116 |
| D10  | 91   | 529  | 4509 | 6257 | 127  | 1.2  | 48.1 | 102 |
| D15  | 573  | 555  | 4016 | 5283 | 26.9 | 2.2  | 42.9 | 110 |
In source experiments, isotopes of energies are expected to degrade in the study.

Although trace metals, such as Ba, U, and Sr, are more abundant in the S2 and S4 experiments than in S1 and S3 (Tables 3–6). However, Ba, as an element released from pyrite dissolution, is predicted to have greater concentrations in the S1 and S3 experiments. Considering the much higher concentrations of SO$_4^{2-}$ in S1, this could be caused by the precipitation of BaSO$_4$. The source of U is more complicated. A study on Marcellus shale shows most U is held in silicate minerals and about 20% is hosted in carbonate minerals [38]. Another study states that U is often found in association with organic matter because they can form complexes in low-energy environments [42]. In this study, the concentrations of U are higher in the S2 and S4 experiments. This indicates that the source of U in our experiments can be the organic matter, which is also higher in S2 and S4 (Table 1). In S4 experiments, there is a great increase of U concentration after 3 months. This could be a result of the degradation of organic matter in shale, a phenomenon observed by Marcon et al. (2017) [15]. The concentrations of Sr exhibit an initially rapid increase for both the S1 and S2 experiments and reach their maximum values at about 72 h. This temporal trend is comparable to the observed behavior of Ca and Mg, indicating that the main source of Sr can be the carbonate minerals. Sr isotopes can be used as a tracer of fluid-rock interactions to help identify sources and flow paths of flowback and produced waters, but the Sr released from carbonate minerals dissolution can influence the composition and must also be taken into consideration [35,48,49].

Although only some trace metals were investigated, the fracturing fluid recovered after experiments belongs to Class IV and V water according to GB/T 14848-2017 “Groundwater Quality Standard”, which means highly polluted and chemical toxic water. The elevated concentration of these metals is attributed to several acid-base and oxidation-reduction processes. Among these processes, attention should be paid to pyrite oxidation because it is the main source of heavy metals.
and the sulfuric acid generated by it can also trigger carbonate minerals and feldspar dissolution. By minimizing the oxidation of pyrite, the concentrations of these toxic and radioactive elements can also be controlled.

3.2. Geochemical Changes in Shale

3.2.1. Dissolution of Minerals in Shale

The investigation of the element concentration in the fluids shows that many elements in the water sample increased to a certain degree, which reflects the dissolution of minerals in shale. The changes of mineral composition in shale samples are determined by XRD and FE-SEM coupled with EDS.

The pyrite dissolution has always been of concern because it can release trace heavy metals. Therefore, it is important to understand the extent of pyrite reaction in order to constrain the release of contaminants. The comparison between the XRD results of initial samples (Table 1) and recovered samples (Table 2) reveals that in the S1 and S3 series of experiments the pyrite is significantly reduced by up to more than 50%, while in S2 and S4 the pyrite content changes very little. The images of short-term chip samples observed by FE-SEM exhibited similar results to that of XRD. In the S1 experiments, the pyrite is obviously corroded, but in the S2 experiments the pyrite remains relatively stable (Figure 4). The results of XRD and FE-SEM analysis in shales are consistent with that of ions analysis in fluids. There are two possible reasons for this different result: (I) The pyrite content is relatively higher in S1, where the mean value is approximately 10%, and a small amount of pyrite particles can be observed on the surface, while in S2 the pyrite content is about 6–7% and relatively lower; (II) The degree of weathering of the two groups of samples differs from each other due to different sampling depths. The sampling position of S1 is about 100 m and closer to the surface, resulting in the vulnerability to groundwater erosion and a greater porosity (Table 1). As shown in FE-SEM images, there are many cracks observed on the surface of pyrite crystals in S1, which may be caused by weathering (Figure 4a, Figure 5). The S2 samples were taken from the shale formation 800 m deep. Therefore, due to the pressure of the overlying strata, the structure of S2 shale formation would be less weathered and have fewer pores compared to S1 (Table 1). The pyrite grains in S2 are also better preserved and cracks do not develop on the surface (Figure 4d and 5). The loose structure and cracks in S1 provide more area exposed to fracturing fluid, leading to a greater degree of reactions.

XRD analysis also shows that the pyrite content is similar between the long-term and short-term experiments. This indicates the inhibition of pyrite dissolution over time. One potential explanation is the surface of pyrite being covered by the precipitation of secondary minerals (Figure 4c), preventing pyrite from contacting the fluid. Another possible reason is that the oxidants in fracturing fluid, namely dissolved oxygen and chemical additives, are exhausted. This study is conducted under open conditions, so exhaustion of oxidant is not a main factor constraining pyrite dissolution. However, at field scale during hydraulic fracturing operation, this may not be the case. Considering the highly reducing conditions underground, limited dissolved oxygen and chemical additives without supplement [35], and a relatively large amount of pyrite in shale, the pyrite reaction would be limited seriously by the oxidant supply. However, due to the high rock to fluid ratio in the field, even only a little dissolution of pyrite would alter the fluid composition greatly [35].
Figure 4. SEM images taken to compare shales before and after experiments. (a) is a pyrite grain observed in the S1 initial sample. (b) and (c) are images taken after 5 days and 10 days of reaction respectively. The pyrite was corroded in the middle, where the cracks developed. After 10 days, the surface of the pyrite was covered by precipitates, which may inhibit pyrite dissolution. (d), (e) and (f) are images of S2 sample. No cracks were observed on the surface of the pyrite in the initial sample (d). After 5 days (e) and 10 days (f) of reaction, the pyrite grain did not change significantly. (g), (h) and (i) are images of calcite in S2 sample. After reaction, the calcite was severely dissolved.

The XRD analysis of shales following the reaction confirms a reduction of calcite content in the S2 and S4 experiments. The calcite content in the initial samples is about 4% on average, while there is almost no calcite in samples after the experiments (Tables 1 and 2). The initial content of calcite in S1 and S3 is very low, which may be caused by groundwater erosion, leading to relatively lower Ca\(^{2+}\) concentrations in the fluids. The calcite dissolution is also observed on the surface of S2 thin section by FE-SEM, which is not found on the surface of S1 (Figure 4). In addition, the decline of feldspar content in S1 and S3 experiments is also observed (Tables 1 and 2). The feldspar content decreases about 30% after experiments. However, in S2 and S4, it remains unchanged. On the surface of S1 section, dissolution of minerals, which are very likely to be feldspar according to EDS analysis, has been observed (Figure 6). This difference is mainly caused by the different pH values, which depend on the amount of pyrite oxidation.
Figure 5. SEM images of pyrite grains in two samples. In S1, the pyrite grains are fragmented and many cracks develop, while in S2 the pyrite grains are better preserved. This phenomenon may show that S1 has been weathered.

Figure 6. SEM images of dissolved surfaces of minerals at different magnification (a), (b), showing the formation of a depression. (c) The EDS analysis of the mineral residues revealed that the main components were K, Al, Si and O, indicating that the dissolving minerals are very likely to be feldspar.
3.2.2. Precipitation of Secondary Minerals

Pyrite is the main source of aqueous Fe\(^{3+}\) and SO\(_4^{2-}\), therefore theoretically the molar ratio of Fe\(^{3+}\) to SO\(_4^{2-}\) should be close to 0.5. The deviation between the actual ratio and the theoretical value indicates the precipitation of secondary minerals which removes one ion preferentially [30]. Based on the measured SO\(_4^{2-}\) concentration, the iron concentrations produced from the dissolution of stoichiometric pyrite are calculated (Figure 7a). Measured Fe concentrations in both the S1 and S2 experiments are less than calculated Fe concentrations, which is indicative of the removal of Fe by precipitation of Fe-bearing phases. In addition, the saturation indices of Fe(III)-bearing phases are calculated (Figure 7b). All the saturation indices are greater than 0, indicating that the fluid is supersaturated for these Fe(III)-bearing phases. What we observed in this study is consistent with the conclusion that the oxidative dissolution of pyrite is accompanied by precipitation of secondary Fe(III)-bearing (hydr)oxide phases [50]. During the precipitation of these secondary (oxy)hydroxide phases, some trace metals like U and Pb are likely to be adsorbed at the surface of or co-precipitate with these minerals [51,52]. This may account for the downward trend of concentrations of U and Pb after about 72 h in the S1 and S2 experiments (Tables 3 and 4), indicating that the precipitation of Fe(III)-bearing (hydr)oxide can restrict the migration of some toxic metals.

Considering the high concentration of SO\(_4^{2-}\) in these experiments, there is a high probability of barite (BaSO\(_4\)) and gypsum (CaSO\(_4\)) precipitation. The saturation indices (SI) are calculated and presented in Table 7. The SI of barite in both experiments is greater than 0, which means the fluid is supersaturated for BaSO\(_4\). Considering that the concentrations of SO\(_4^{2-}\) are much higher in S1 than in S2, the Ba concentrations in S2 would be predicted to be lower, but in fact they are relatively high. At the surface of SEM thin sections of both S1 and S2 experiments, highly crystallized secondary minerals are observed, which are confirmed to be CaSO\(_4\) by EDS (Figure 8). Most of the gypsum crystals observed are accumulated on pyrite grains, which may be caused by the higher concentration of SO\(_4^{2-}\) near the pyrite that is being oxidized. However, the SI of CaSO\(_4\) is below 0, indicating that CaSO\(_4\) is undersaturated (Table 7). Therefore, the gypsum crystals observed in our experiments might be precipitated during the drying process of SEM samples. Nevertheless, during the process of hydraulic fracturing in field, due to the much higher shale to fluid ratio, the precipitation of CaSO\(_4\) is very likely to occur. Gypsum is a common scale mineral and difficult to dissolve. The precipitation of gypsum has the potential to occlude the pores or throats in shale and thus affect the exploitation of shale gas.

| Minerals  | 24h  | 48h  | 72h  | D6   | D15  | D30  | D90  | D220 | D360 |
|-----------|------|------|------|------|------|------|------|------|------|
| Barite in S1&3 | 0.36 | 0.29 | 0.25 | 0.12 | 0.11 | 0.11 | 0.07 | 0.05 | 0.05 |
| Gypsum in S1&3 | -1.67 | -1.44 | -1.43 | -1.08 | -1.18 | -1.46 | -1.51 | -1.57 | -1.52 |
| Barite in S2&4 | 0.52 | 0.39 | 0.48 | 0.38 | 0.44 | 0.69 | 0.84 | 0.54 | 0.69 |
| Gypsum in S2&4 | -1.21 | -1.17 | -1.22 | -1.22 | -0.98 | -1.8 | -1.85 | -2.01 | -1.83 |
Figure 7. (a) and (b) are images of the comparison between stoichiometric and actual Fe concentrations in short-term and long-term experiments respectively. (c) Saturation indices of secondary Fe(III)-bearing phases versus reaction time in the experiments. All the saturation indices were greater than 0, which means the fluid is supersaturated for all these secondary Fe(III)-bearing phases.
Figure 8. SEM images of the CaSO₄ precipitates observed on the surface of samples in both experiments. (a) and (c) are images of S3 and S4 respectively. (b) and (d) are magnified images of the red zones of (a) and (c) respectively. The main elements in the crystals (the yellow spots) are Fe, S and Ca through EDS analysis, which suggests a high potential of gypsum precipitates.

3.2.3. Alteration of Porosity

During the process of hydraulic fracturing, mineral dissolution generates pores, and the precipitation of secondary minerals may cause pore blockage, which could influence the long-term productivity of shale gas wells. Therefore, it is necessary to investigate the alteration of porosity.

On the surface of the S1 thin sections recovered after experiments, many discrete holes about several microns in diameter are observed through FE-SEM, which are not found in the original sample (Figure 9). Most of these pores are isolated, and the microscopic image shows the dissolution of minerals clearly. The unstable minerals like feldspar and some clay minerals are dissolved, while the more stable minerals like quartz remain undissolved. However, in the S2 experiments, the reacted samples observed through SEM are not much different from the intact sample (Figure 10). Although pores are observed on the surface of S2 thin sections, there are much less of them than in S1. But many irregular pores generated by calcite dissolution are observed in S2, forming a mottled texture over the calcite residue (Figure 11). Unlike other isolated pores, these pores are interconnected and have a high potential to affect the transportation of fluid. The porosity of shale before and after the experiments is also measured (Table 8). The initial porosity of S2 is 0.8%, and after a reaction between shale and fluid, the porosity increased to 1.1%. The initial porosity of S1 is 9.7%, which is much higher than that of S2. After experiments, the porosity increased to 20.0%, which is twice that of the original sample. As shown in Figure 6, the EDS analysis of the mineral residues remaining in the discrete pore
reveals that the pores may be caused by feldspar dissolution, which explains the great difference between S3 and S4 experiments.

Table 8. Measured porosity of initial samples and recovered samples.

| Samples     | Porosity (%) | Density (g/cm³) |
|-------------|--------------|-----------------|
| Initial S3  | 9.7          | 2.46            |
| Recovered S3| 20.0         | 2.18            |
| Initial S4  | 0.8          | 2.70            |
| Recovered S4| 1.1          | 2.68            |

Figure 9. SEM images showing changes of porosity in S3 from time 0 to 360 days. On the surface of the initial sample, no pores were observed, while after exposure to fracturing fluid, many discrete holes were generated.

As shown in Figure 4c, the surface of pyrite grain in S1 is covered with a layer of precipitates, part of which develops on cracks and blocks them. In S2, on the surface of calcite residue after dissolution, some black substances are observed (Figure 4i), which are not found in initial samples. Although the composition of these precipitates was not determined, they all act to occlude pores to some extent. In addition, gypsum crystals developed in pores are also observed (Figure 11). Although this crystal is very small and cannot block the pore in our experiments, it shows that pores occluded by CaSO₄ are very likely to occur in the field. It is known that even slight changes in porosity can affect the permeability of the rock [52,53], but the effect of the porosity blockage on fluid transport and long-term productivity of shale gas is not clear yet and needs further study.

According to the results of our experiments, there are several key geochemical reactions caused by the fluid during the fracturing process. When shale is exposed to fracturing fluid, the first reaction is the oxidation of pyrite, during which a large amount of metal elements and sulfuric acid are released, resulting in acidification of the fracturing fluid. The acidic fracturing fluid dissolves carbonate minerals, which tends to neutralize the pH of the solution and generate pore networks. Subsequently, if the shale is not abundant in carbonate minerals, the feldspar is also dissolved due to the vulnerability to acidic solution, which generates many pores and increase the porosity greatly. At the same time, some secondary minerals are also precipitated. For example, Fe(OH)₃ precipitates at a pH greater than 3.7, and very high concentrations of SO₄²⁻ cause precipitation of CaSO₄ and BaSO₄.
that may occlude the pores and affect the transportation of hydrocarbons, and ultimately influence of the recovery of shale gas.

![Figure 10](image1.png)

**Figure 10.** SEM images illustrating changes of porosity in S4. Although several pores were observed, there was no big difference between the initial and recovered samples.

![Figure 11](image2.png)

**Figure 11.** A gypsum crystal developed in a pore in S2, which shows the possibility of gypsum blocking pores.

### 4. Conclusions and Field Implication

This study reveals that the exposure of shale to hydraulic fracturing fluid causes a series of reactions that are strongly affected by the mineralogy and physical properties of the shale. Fracturing fluid can erode the relatively unstable minerals in shale like calcite and pyrite, thus influencing the evolution of fluid composition. In pyrite-rich shale formations with a loose structure, the pH of fracturing fluid decreases due to the greater extent of pyrite dissolution, while in carbonate mineral-rich shale reservoirs with a tight structure, pyrite dissolves less and calcite can act as a pH buffer,
leading to the smaller pH change. The dissolution of these minerals in shale generates porosity, which can increase the shale permeability and then probably enhance hydrocarbon transport. But the precipitation of secondary phases blocks pores or cover cracks, affecting the exploitation of shale gas. Mineral dissolution also releases many trace metal contaminants into fracturing fluid that are highly likely to contaminate surface waters after being brought to the surface by flowback or produced water. Therefore, treatment and monitoring of flowback and produced water are essential for safe disposal or re-use. However, some of the metal contaminants are removed from solution through adsorption by or co-precipitation with secondary phases, which therefore can mitigate migration of contaminants to some extent.

The dissolution of minerals is also related to the additives in fracturing fluid, so the degree of pollution can be minimized by adjusting the composition of solution. The precipitation of secondary Fe-(oxy)hydroxide and the adsorption of metal contaminants would be both enhanced at higher pH. Therefore, the use of low pH fracturing fluid in carbonate mineral-poor shale reservoirs requires more treatment of flowback and produced water and is not suggested. The dissolution of pyrite is mainly due to oxidants in fracturing fluid. The utilization of fracturing fluid with a lower content of oxidants could minimize the release of trace metal contaminants and formation of secondary phases. However, the effect of the high underground pressure and lower temperature in long-term experiments on the reactions between shale and solution, which may impact mineral dissolution and precipitation, has not been characterized in this case and requires further studies. Furthermore, during the process of shale gas production in field, the formation waters in reservoirs typically contain high concentrations of ions. These formation waters may affect the saturation state of secondary minerals and the adsorption of trace metal, which also requires further investigation. Despite the drawbacks, our experiments confirmed that a series of reactions between shale and fluid can be induced, and understanding these processes and their effects on shale gas production can help us to predict the geochemical changes during exploitation and minimize the contaminants.

Author Contributions: Conceptualization, J.T. and Q.L.; Investigation, J.T., G.L., R.H., and L.L.; Resources, J.T. and Q.L.; Data Curation, J.T. and G.L.; Writing—Original Draft Preparation, G.L.; Writing—Review & Editing, J.T., G.L., L.L., and J.D.; Supervision, J.T., L.L., and Q.L.; Funding Acquisition, J.T. and L.L. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by the National Natural Science Foundation of China grant number 41872151, the Innovation driven Project of Central South University grant number 502501005, Natural Science Foundation of Hunan Province, grant number 2019JJ50762, and China Postdoctoral Science Foundation, grant number 2019M652803.

Conflicts of Interest: The authors declare no conflict of interest.

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