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Comparative geochemistry of flowback chemistry from the Utica/Point Pleasant and Marcellus formations

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ABSTRACT

Flowback/Produced fluid samples were collected from several wells from two Utica/Point Pleasant (UPP) sites (UPPW and UPPS) in Ohio, and one Marcellus (Marcellus Shale Energy and Environment Laboratory (MSEEL)) site in West Virginia over a period of approximately two years. Although these formations have different ages, depositional environments, diagenetic histories, and geochemical and mineralogical compositions (*i.e.* the UPP is significantly more carbonate rich than the Marcellus which is more siliceous), analysis of trends in fluid species over time shows that, overall, the TDS and major solubilized elements (Na, Ca, Cl) in the UPP and Marcellus brines are remarkably similar. Total dissolved solutes (TDS) in these brines ranged from approximately 40 to 250 g/L salt, and in general, concentrations increased with time elapsed since natural gas well completion and stimulation. The behavior of Na, Br, and Cl suggests that the produced water signatures from these formations are largely derived from the native formational brines which display evidence of originating from evaporated seawater. There is a strong correlation between Cl and Br, indicating that both species behave conservatively, and the similarity among each of these brines suggests no appreciable contribution of salt from halite dissolution because Br is excluded from the halite structure. Cl/Br ratios in the brines range from ~80 to 120 (mg/L/mg/L). Other elements, such as K, which readily reacts between fluids and ion exchange sites on clays, generally exhibit conservative behavior for an individual site, but show significant variations among each of the different well pads.

The concentrations of Sr and Ba vary dramatically among well sites, and increase with respect to Cl^- over time, suggesting increasing solubilization, presumably from desorption from clay minerals or dissolution of carbonates or sulfates from the source formation(s). The UPPW well site has very low Ba due to high-sulfate input fluid, which resulted in precipitation of barite/celestite in the brines. In contrast the UPPS well site had elevated Sr (~ 3500 mg/L), presumably due to the use of Sr-rich recycled brine used in hydraulic fracturing. The Marcellus site had the highest Ba concentrations (up to 10 g/L) and highest Ba/Sr ratios in the fluids, due to the high concentration of barium in the Marcellus target (~ 1000 ppm, as compared to ~200 ppm in the UPP). These observations suggest that solutes in the FP fluids are derived from native brines, water-rock interactions that have occurred over geologic time scales, as well as some contribution from contemporaneous reactions in the subsurface. The results also show that the composition of the injected fluid can influence flowback fluid chemistry and possibly production efficiency.

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1. Introduction

Within the last decade there has been a massive increase in oil and gas production from unconventional shale gas formations in the Appalachian Basin from hydraulic fracturing and directional drilling of the Devonian-age Marcellus Shale and the underlying upper Ordovician age Utica/Point Pleasant. For example, Geary and Popova (2017) report a roughly five-fold increase in natural gas production in Appalachia, from approximately 3 million cubic feet/day in 2012 to 15 million cubic feet/day in 2017. During that time, there have been nearly 11,000 new unconventional wells drilled in the state of Pennsylvania from 2004 to 2017, with natural gas production of 5.4 trillion cubic feet in 2017 (Jacobs, 2018). In West Virginia, there are approximately 2000 producing horizontal wells, most of which access the Marcellus Formation., that produced about 1.4 trillion cubic feet of gas in 2017 alone (West Virginia Department of Environmental Protection)(https://dep.wv.gov/oil-and-gas/databaseinfo/Pages/default.aspx). The Utica/Point Pleasant is of paramount importance for the development of hydrocarbons in eastern Ohio. As of 2020, there were 2526 producing horizontal shale wells in Ohio, most of which are located in the east and southeast part of the state. Total production from Ohio wells in 2019 was approximately 25 million barrels of oil and 2.5 trillion cubic feet of gas, per the ODNR Oil and gas website (ODNR) (http://oilandgas.ohiodnr.gov/) which has resulted in an economic outcome for the state.

With these hydraulic fracturing (HF) wells come the environmental problems associated with flowback/produced fluids, both in terms of water usage, and the complex chemistry of the fluids that return to the surface that need to be treated, reused, stored, or disposed. Kondash and Vengosh et al. (2015) report typical water usage per well for these unconventional reservoirs ranges from approximately 10 to 20 million liters, with only a small fraction of this volume returning to the surface over the life of the well. A more recent compilation (Scanlon et al., 2020) reports typical water usage on the order of 5 to 50 fold higher, reflecting longer laterals. However, these fluids have complex chemistries, with elevated concentrations of salts (10s to 100s of g/L), including very high levels of Sr, Ba, and Fe, toxic trace metals (especially Hg, As and Pb), naturally occurring radioactive materials (NORM), total ammonia, or organic compounds derived from alteration of hydraulic fracturing compounds or extracted from the formation (Abualfaraj et al., 2014; Akob et al., 2015; Balaba and Smart, 2012; Balashov et al., 2015; Barbot et al., 2013; Blauch et al., 2009; Blondes et al., 2020; Chapman et al., 2013; Chapman et al., 2012; Cluff et al., 2014; Dresel and Rose, 2010; Engle et al., 2016; Engle and Rowan, 2014; Engle and Rowan, 2013; Ferrer and Thurman, 2015; Freedman et al., 2017; Haluszczak et al., 2013; Harkness et al., 2015; Hayes and Severin, 2012; He et al., 2017; Jew et al., 2017; Kahrilas et al., 2016; Kondash and Vengosh, 2015; Kondash et al., 2017; Nelson et al., 2014; Oetjen et al., 2018; Rosenblum et al., 2017; Rowan et al., 2015; Tasker et al., 2020; Tasker et al., 2016; Hayes, 2009; Vengosh et al., 2015). In addition, these fluids host microbial populations that can impact biogeochemical reactions in the subsurface or in holding ponds or storage tanks (Akob et al., 2015; Booker et al., 2017; Borton et al., 2018b; Borton et al., 2018a; Daly et al., 2016; Evans et al., 2018; Mohan et al., 2014; Mohan et al., 2013; Mouser et al., 2016). Fluid chemistry affects well workings (pipelines, *etc.* by salt plugging or scaling from Sr-Ba sulfates or iron oxyhydroxides) and presents a waste-water disposal challenge.

The detailed characterization of these complex brines contributes to our understanding of rock properties and the consequences of fluid/rock interactions during the hydraulic fracturing process and beyond (during hydrocarbon production). Further, understanding produced and flowback chemistries will help inform industrial strategies for hydrocarbon recovery and subsurface science for predicting what will dissolve and precipitate in targeted mudrocks. In this study, we have characterized the flowback fluid/produced water chemistry from seven Appalachian basin hydraulic fracturing wells, five from two pads in eastern Ohio that are drilled into the Utica/Point Pleasant Formation, and two from West Virginia that are drilled into the Marcellus Formation, and have compared these data to the chemical and mineralogical composition of core samples from both units.

2. Geological setting

The Point Pleasant Formation in Ohio, which is most often targeted for hydraulic fracturing in the stacked Utica/Point Pleasant play (EIA, 2016) consists of interbedded light gray to black limestones, and brown to black organic-rich calcareous shale beds (Wickstrom, 2011, 2013). This interval, where it exists, is equivalent to the lower Clays Ferry Formation of Kentucky and the lower Indian Castle Shale of New York (Patchen and Carter, 2015). The average carbonate content is approximately 40 to 60%. As it extends northward beneath the Utica Shale it is described as being interbedded, fossiliferous limestone, shale and minor siltstone. The thickness ranges from <1 ft. in northwestern Ohio to 240 ft. in northern Pennsylvania (Patchen and Carter, 2015a, 2015b). The Point Pleasant Formation appears to have been deposited in part contemporaneously with the Trenton Limestone in northwestern Ohio, but also appears to have been deposited over the Trenton along portions of the platform margin to the southwest (Patchen et al., 2006).

The organic-rich Middle Devonian Marcellus Formation, and in particular the lowermost section, which is also a hydraulic fracturing target interval, is famous for generating copious quantities of natural gas (Milliken et al., 2013; Popova, 2017). In West Virginia, where hydraulic fracturing flowback/produced (FP) fluids were collected for this study, the Marcellus and overlying Mahantango formations together comprise the Hamilton Group. Ettensohn (1985) describes the depositional environment as “distal marine muds that accumulated under anoxic conditions.” These siliciclastic mudrocks were deposited in the Appalachian foreland basin during the Acadian Orogeny, and black shale units in the Marcellus Formation range in thickness from less than 50 ft in Ohio up to about 200 ft in northeastern Pennsylvania (Milici and Swezey, 2014). Debate is ongoing concerning the precise depositional controls and subsequent diagenetic imprints that prevailed to ultimately produce the organic-rich intervals. A geochemical study of the Marcellus in central Pennsylvania suggests that redox conditions fluctuated from anoxia during high stand sea-level conditions, to dysoxia during cycles of relative lowering of sea level. However, preservation of organic matter primarily occurred under anoxic conditions (Chen and Sharma, 2016; Wendt et al., 2015).

3. Methods

3.1. Water collection

Water used to generate the hydraulic fracturing fluids (input water), and hydraulic fracturing flowback/produced (FP) fluids were collected from seven wells in the Appalachian basin. Flowback fluids, usually referred to as the initial fluids returned to the surface, are thought to be composed predominately of the water used in the hydraulic fracturing process. Produced fluids, returned to the surface later when the well go into production, are thought to predominately reflect formation water. However, this terminology is often not well constrained because most Appalachian basin wells are “green completions” where production begins immediately and flowback and production are not sharply separated (O’Sullivan and Paltsev, 2012). Herein, we adopt the convention of Kondash et al., (2017) and refer to the brines that come up to the surface from hydraulic fracturing wells as FP fluids (flowback/produced fluids).

Five wells were located on two pads in eastern Ohio that access the Utica/Point Pleasant (UPP) Formation, while two wells were located approximately 30 km east of these wells near the city of Morgantown, West Virginia that access the Marcellus Formation (Fig. 1). The UPPW4 well is located near the southern border of Harrison County, Ohio, within the wet gas window of the UPP play. The UPPS1–4 wells are all located on the same pad approximately 50 km south of the UPPW4 in Monroe County, Ohio within the dry gas zone as informed by industry and others (Hohn et al., 2015). Depth to the targets in these locations are approximately 8550′ and 9650′ (~ 2575 m and 2940 m), respectively, and total well depths (true vertical depth plus lateral) range from approximately 17,000′ to 18,000′ (5180 m to 5486 m).

Input water samples for the UPPW4 well were collected from a nearby water reservoir about 1 km south of the well pad as well as from a tank on the well pad that was used store water before it was mixed with the hydraulic fracturing additives. Samples were collected from both the reservoir and the tank three times over approximately 20 days while hydraulic fracturing was occurring for the UPPW4 well. Input water for the UPPS wells were sourced from several freshwater bodies located near the well pad, as well as treated recycled flowback fluids from nearby hydraulic fracturing wells. Samples of both of these fluids were collected from two holding tanks on the well pad nine times over one month during hydraulic fracturing to characterize representative compositions of the water used to generate the hydraulic fracturing fluids that were injected into these wells.

The Marcellus wells are part of a more extensive multidisciplinary study on hydraulic fracturing (Marcellus Shale Energy and Environment Laboratory MSEEL, (Carr et al., 2017; Hakala et al., 2018; Moore et al., 2018; Phan et al., 2020, Phan et al., 2019; Pilewski et al., 2019; Sharma et al., 2018; Song et al., 2018; Wilke et al., 2015; Ziemkiewicz, 2018; Ziemkiewicz and He, 2015). Depth to the target at these locations, is approximately 7500 ft (2300 m) and the total length of these wells are approximately 13,000 ft (4000 m). The two wells (MIP 3H and MIP 5H) are located a few km from West Virginia University along the Monongahela River, which is the source of the water used for hydraulic fracturing. River water samples were collected twice near the start of hydraulic fracturing for the MIP 3H and MIP 5H wells respectively.

Water sample collection procedures varied at the different sampling sites, and also differed depending on whether the wells were in flowback or production mode. In general, large water volumes were collected in 5 gal carboys from spigots on the phase separator, and these samples were processed and preserved for analysis as soon as possible (tens of minutes to several hours) to minimize changes that might occur as a result of oxidation. Water temperature was not measured within the well as part of this study, however temperatures measured at the time of collection from the separator ranged from approximately 30 to 40 °C. Brine samples for geochemical analysis were filtered through a 0.45 μm capsule filter into 60 mL LDPE Nalgene bottles that were filled to the brim to minimize air in the head space. Samples for cation and metal analysis were acidified with trace metal grade nitric acid to a final concentration of ~2% HNO_3.

FP fluid samples from the wells were collected periodically over time. Initially samples were collected daily or every few days in the first few weeks of flowback, and then the intervals for sample collection decreased (monthly to several months) as the volume of fluids produced declined over time. FP fluids from the UPP wells were collected over a period of approximately 18 months in total, though sampling in the last year was limited, as well production decreased and brine production was more sporadic. The MIP 3H and 5H were sampled over a period of approximately two years.

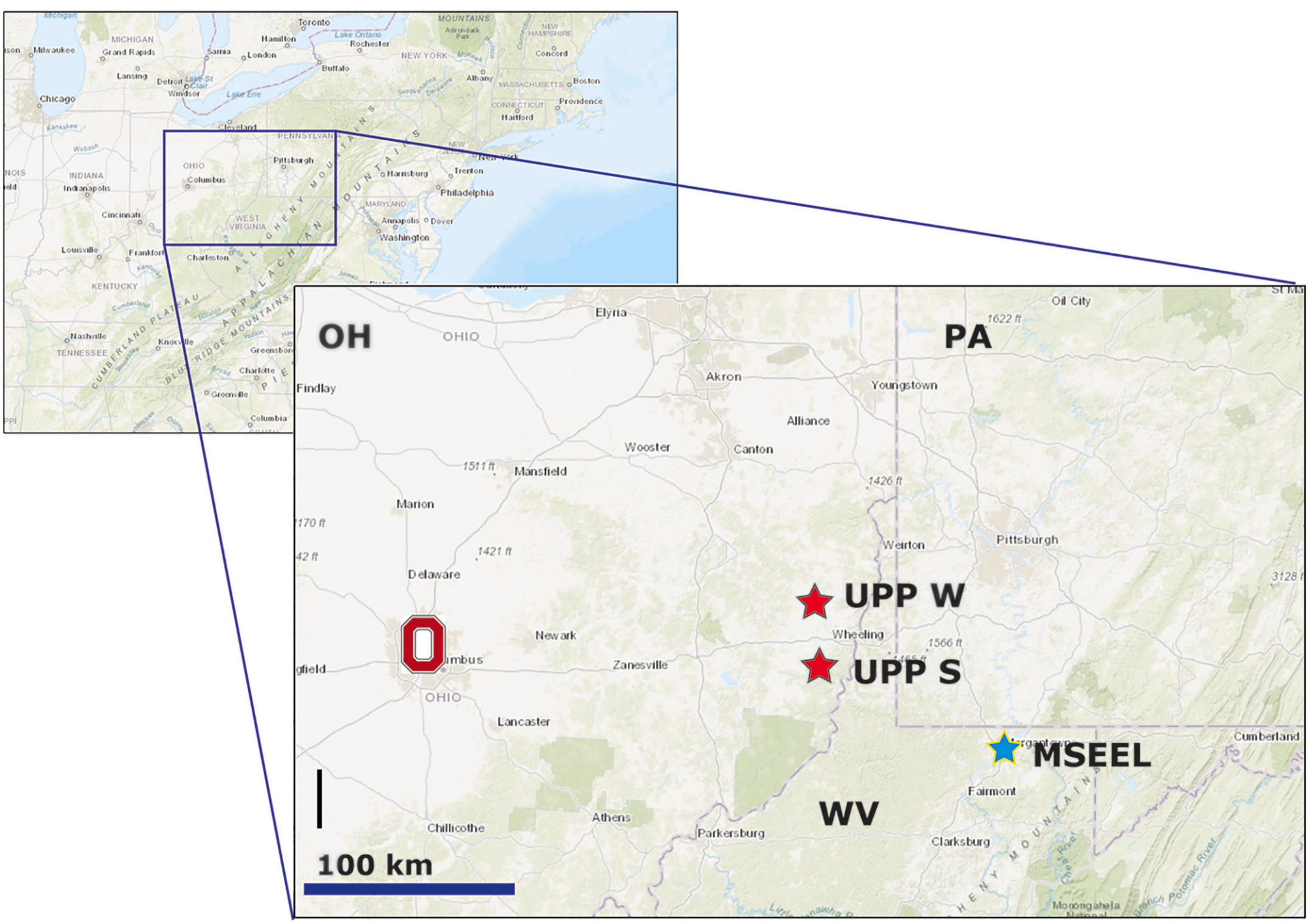

Fig. 1. Map of the field sites. UPPW and UPPS site in the Utica/Point Pleasant and MSEEL MIP 3H and 5H in the Marcellus formation.

3.2. Water analysis

Water samples collected from the field sites were analyzed for various constituents. Anion analysis (F^-, Cl^-, Br^-, NO_3^-, SO_4^{2-}, $S_2O_3^{2-}$, PO_4^{3-}, and organic acids including acetate, formate and oxalate) were analyzed using a Dionex ICS 2100 ion chromatograph. Flowback/produced fluid samples were diluted by a factor of either 101- or 1111-fold using MilliQ water (18 megaΩ) before analysis. Analytical precision was determined from replicate analysis of samples and/or standards and was generally within 5% for most analytes. However, error was greater for species with concentrations close to detection limits (typically a few 10's of ppb). Accuracy was determined by analysis of a commercial check standard, and a USGS inter laboratory check sample. The accuracy for major anions (F^-, Cl^-, Br^-, NO_3^-, SO_4^{2-}) was generally within 10%, though more typically within 5%, of the reported or most probable value for these species.

Major and trace metal analyses were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES) using either a Perkin Elmer Optima 3000DV or 4300DV ICP-OES. Trace metals were also analyzed by using inductively coupled plasma mass spectrometry (ICP-MS) using either a Perkin-Elmer Sciex ELAN 6000 Inductively Coupled Plasma Mass Spectrometer or a ThermoFinnigan Element 2 Inductively Coupled Plasma Sector Field Mass Spectrometer. Samples were diluted by a factor of 100- to 10,000-fold with 1% nitric acid to decrease salt content and lower metal concentrations to within the working range of the instruments. Accuracy and precision were estimated by analyzing a commercial check standard and USGS inter-laboratory comparison sample, as well as multiple replicate analysis of samples and standards. Samples for ICP-MS analysis were also spiked to 10 ppb Indium which was used as an internal standard to correct for matrix effects when necessary.

Suspended material and precipitates in the raw water were analyzed from selected samples. A few milliliters of sample volume were filtered onto a 47 mm polycarbonate filter with either 0.2 or 0.4 μm pore size, and then the filter was rinsed with a few milliliters of milliQ water to remove excess salt. The filter was allowed to air dry, and then a section of the filter was affixed to an aluminum stub using carbon tape, coated with Au-Pd using a Denton Desk V precious metal coater, and imaged using an FEI Quanta FEG field emission SEM equipped with a Bruker EDX detector. Samples were imaged using both secondary and back-scattered electron detectors to determine detailed surface morphology and differences in chemistry.

Sulfur isotope analysis of dissolved sulfate was conducted on samples that contained sufficient sulfate for analysis, primarily the UPPW4 well. Dissolved sulfate samples were collected in a 1 L polyethylene bottle with no headspace and then vacuum filtered through a 0.45 μm PCM filter. The sample was then acidified to pH 2–3 with 1 M solution of HCl to remove any carbonate as CO_2 and then heated at 90 °C for 1 h, continuously stirring. After this step, 5–10 mL of 20% $BaCl_2$ was added to the sample to precipitate out solid $BaSO_4$ precipitate which was then dried and homogenized (Révész et al., 2012). Samples were stored in 2 mL plastic centrifuge tube and sent to University of Arizona's Environmental Stable Isotope Facility for analysis of δS_{SO4} on an Elemental Analyzer coupled to a Finnigan Delta Plus mass spectrometer. Reproducibility and accuracy were monitored by duplicate analysis of samples and internal lab standards, previously calibrated to international standards, and were better than 0.2‰ for $\delta^{34}S$. All $\delta^{34}S$ isotope values are reported in per mill relative to the Vienna Cañon Diablo Meteorite international isotope standard.

3.3. Rock analysis

Eight core plug samples were obtained from the UPPW1 well, which is on the same well pad as the UPPW4 (from which flowback samples were collected). The core plugs were collected from core that was recovered during drilling. Cuttings were obtained from the UPPW4 well for a separate study (Wells, 2015). In addition, eight sidewall core samples from the MSEEL Marcellus MIP 3H well were collected after the well was drilled, but before hydraulic fracturing occurred. No core samples were obtained from the UPPS location. Thin sections were prepared from all of the core samples, and these, along with core chips (fragments broken along natural fractures), were analyzed using a Quanta 250 FEG scanning electron microscope (SEM) equipped with a Bruker EDX detector for characteristic X-ray microanalysis. Together, and along with ThermoFisher software, these tools provide the analytical platform for quantitative evaluation of mineralogy by Scanning Electron Microscopy (QEMSCAN®). Mineralogy was also determined with powder X-ray diffraction analysis using a Malvern PANalytical X'Pert Pro X-ray diffractometer. Details of rock, mineral and pore structure analysis of these samples are the subject of other studies (Sheets et al. in prep; Sharma et al., 2018; Song et al., 2018). Here we focus only on the core that represents, at least in part, samples located at the depths in close proximity to the hydraulically fractured target rocks. Offcuts from thin section preparation of core samples from the UPP and Marcellus formation were also analyzed at Washington State University (WSU) for bulk rock analysis by XRF and ICP-MS. Details of the analytical methods used at WSU are described in Johnson et al. (1997).

4. Results and discussion

4.1. Rock composition

The bulk rock composition (major elements as weight percent oxides and SrO and BaO in ppm) for three sample depths closest to the hydraulic fracturing target for the UPP W site and the MSEEL site are given in Table 1. Additional data are given in Table S1.

The bulk rock mineralogy of the Utica/Point Pleasant hydraulic fracturing target (~ 8500 ft. at this location) is dominated by calcite, illitic clay, and quartz. Within the rock fabric, calcite is present both as fossil skeletal (f) and matrix (m) grains. The grain size varies, and among the fine calcite particles (1 s to 10s of μm in length scale) that comprise the finely-laminated matrix, several other clay and silt-sized minerals are dispersed, including albite, dolomite, chlorite (chamosite), pyrite, and Ca-phosphate (Fig. 2a). Within the matrix zones are silt- to clay-sized materials with angular—possibly detrital and perhaps locally reworked—fragments of calcite, quartz, illitic clay, albite, and small fossil tests. In terms of both texture and mineral composition, this sample and others of the Point Pleasant and underlying Lexington Limestone are best described as calcisiltites.

In contrast, bulk mineralogical analysis of core samples from well

Table 1
Major element composition of UPP and Marcellus Shale samples normalized to 100% after loss on ignition (LOI).

Formation	UPP	UPP	UPP	Marc Top	Marc Mid	Lower Marc
Depth ft	8492	8529	8550	7451	7509	7543
Major Elements (Weight %):						
SiO_2	38.4	52.0	34.5	65.7	71.8	63.8
TiO_2	0.53	0.71	0.45	0.71	0.64	0.44
Al_2O_3	10.2	13.4	9.37	17.6	14.9	11.1
FeO[a]	4.05	3.65	3.05	9.14	4.91	7.64
MnO	0.07	0.05	0.05	0.03	0.01	0.02
MgO	2.07	2.18	2.87	1.49	1.45	1.13
CaO	41.0	23.8	46.6	0.76	1.86	12.3
Na_2O	0.62	0.93	0.66	0.45	0.55	0.52
K_2O	2.34	3.03	2.07	4.09	3.70	2.98
P_2O_5	0.76	0.36	0.42	0.09	0.13	0.11
Trace Elements ppm:						
BaO ppm	218	273	204	1110	1040	1170
SrO ppm	1320	979	1960	133	148	417

[a] Fe assumed to be as FeO. Additional bulk rock data are given in Table S1.

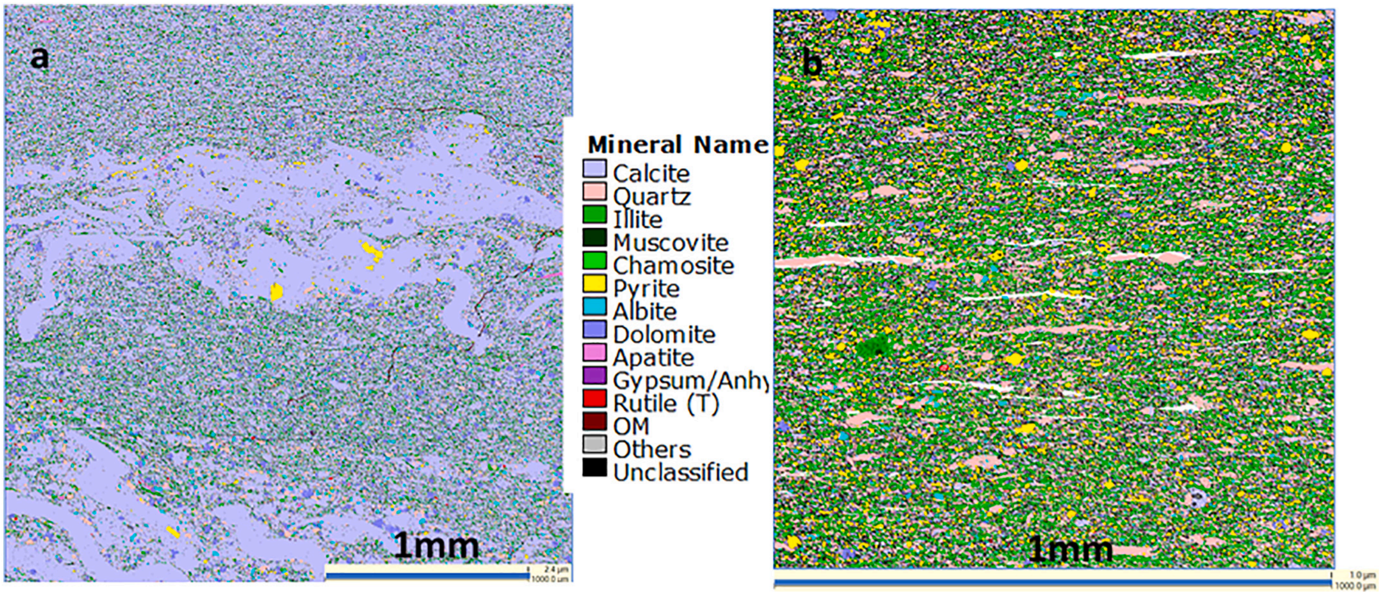

Fig. 2. a (left) and b(right) QEMSCAN mineral maps of hydraulic fracturing targets (scale bar = 1 mm). Lavender shades are carbonates, green shades are phyllosilicates, pale pink is quartz, cyan is albite, yellow is pyrite, and fuchsia is apatite. a) 3 × 3 mm^2 region of polished thin section of calcite-dominated (69.7%) Point Pleasant (depth 8550′). Most organic matter (OM) is finely intercalated with illite and too small to be resolved with QEMSCAN. b) 1 × 1 mm^2 region of Lower Marcellus (depth 7543′). Illite (25.7%) and quartz (25.2%) dominate the mineralogy. Pyrite also is abundant in this field (8.8%) compared to the Point Pleasant (0.9%). The black unclassified pixels (22.5%) represent the complex clay fraction, and include grain boundaries, including the finest-grained OM intercalated with illitic clay, barite, pyrite, REE phosphates, sphalerite (ZnS) and a U-Ti phase, as identified by EDX spot analysis. This Marcellus interval is a very OM-rich siliciclastic mudrock with minor carbonate, and the large OM macerals are replaced by quartz to varying degrees. The same mineral legend applies for both maps except for OM, which is dark brown in the Point Pleasant image a) and white in Lower Marcellus b).

MIP 3H shows that Marcellus core is composed primarily of siliciclastic mudstones with interbedded carbonates. Of the four sidewall cores sampled within the Marcellus, three organic matter (OM)-rich mudrocks (Marcellus Top (depth 7451′), Middle Marcellus (7509′) and Lower Marcellus (7543′), the hydraulic fracturing target (Fig. 2b) are composed of phyllosilicates (illitic clay and chlorite), quartz, pyrite, alkali feldspar, with minor carbonate.

Small chips of the core samples were broken off along natural fractures or cleavages and analyzed by SEM. Salts, primarily halite and calcium sulfate (either gypsum or anhydrite) were present in samples from both the UPP and Marcellus formations. However, from these analyses it is not clear if the salts observed were present *in situ* in the core, if they reflect brine that had evaporated after the core had been collected, or if they represent salt contamination into small fractures from drilling mud (Fig. 3). These phases were not observed in thin sections. However, thin sections were cut and polished wet, thus any readily soluble salt would have dissolved during processing. Barite, celestite, and barite-celestite phases were observed in both the broken core chip samples, and in the polished thin sections. In addition, elevated concentrations of major elements from solutes measured in the FP Fluids (predominately Na, Ca, Cl, S, P, and Sr) were detected by EDXS spot analysis of organic blebs within the shales, or in porous Ca-phosphate phases (Fig. 3d), suggesting that either salt precipitates or brine was present in these phases, and may represent a significant source of solutes in the flowback fluids.

5. Results-water

5.1. Concentration trends

The flowback fluids from these three locations (seven wells in total) have a remarkably similar chemical composition despite the different lithologies, and each has a composition that is distinct from, though affected by, the composition of the fluids injected into the wells (Fig. 4). The fresh to brackish waters used to produce the hydraulic fracturing fluids have relatively low total dissolved solids (TDS) ~ 1.5 g/L or less, but vary in composition. For instance, the lake water that was used for hydraulic fracturing of the UPPW4 well was a Ca-Mg-SO_4 water with a SO_4^{2-} concentration of ~900 mg/L. Surface waters in this area of Ohio frequently have a chemical composition that reflects the legacy of coal mining and this site is located in close proximity to reclaimed mining areas. The freshwater used for hydraulic fracturing of the UPPS wells had a TDS of ~100 mg/L and SO_4^{2-} concentrations less than 25 mg/L. The surface water used for hydraulic fracturing of the MIP 3H and 5H wells sourced from the Monongahela River had a Ca-Na-SO_4 composition with a TDS of approximately 300 mg/L and SO_4^{2-} of approximately 130 mg/L.

The FP fluids from all the wells studied can be described as Na-Ca-Cl brines with TDS concentrations ranging from approximately 40 to 250 g/L. In general, TDS of brine compositions from these three sites follow similar trends, increasing rapidly in the first few weeks to months of flowback, and then much more slowly, eventually becoming approximately constant over time (Fig. 5 and Fig. S1) as the volume of FP fluids decrease. This behavior has been observed frequently in hydraulic fracturing sites, and is thought to represent dilution of the *in situ* brine with the relatively fresh hydraulic fracturing fluid followed by the slower release of the natural formation water over prolonged periods of time (Balashov et al., 2015; Barbot et al., 2013; Blauch et al., 2009; Capo et al., 2014; Chapman et al., 2012; Phan et al., 2020; Timofeeff et al., 2006). However, there were exceptions to this behavior. Several of the UPPS wells have elevated Cl and Ca concentrations in the first day of flowback which reflects the dense $CaCl_2$ brine that is used to fill the well during the shut in period, after hydraulic fracturing but prior to the start of flowback (Figs. 5 and 6). In general, TDS is highest in the UPPS wells that were fractured with input fluids sourced in part from other recycled flowback fluids. The TDS is generally lower in the Marcellus wells over similar time periods. This relationship holds true for Cl, Br, and most of the cations measured, except for Ba which is elevated in the Marcellus site as compared to the Utica/Point Pleasant.

The Marcellus wells, particularly the MIP 5H well, exhibited more

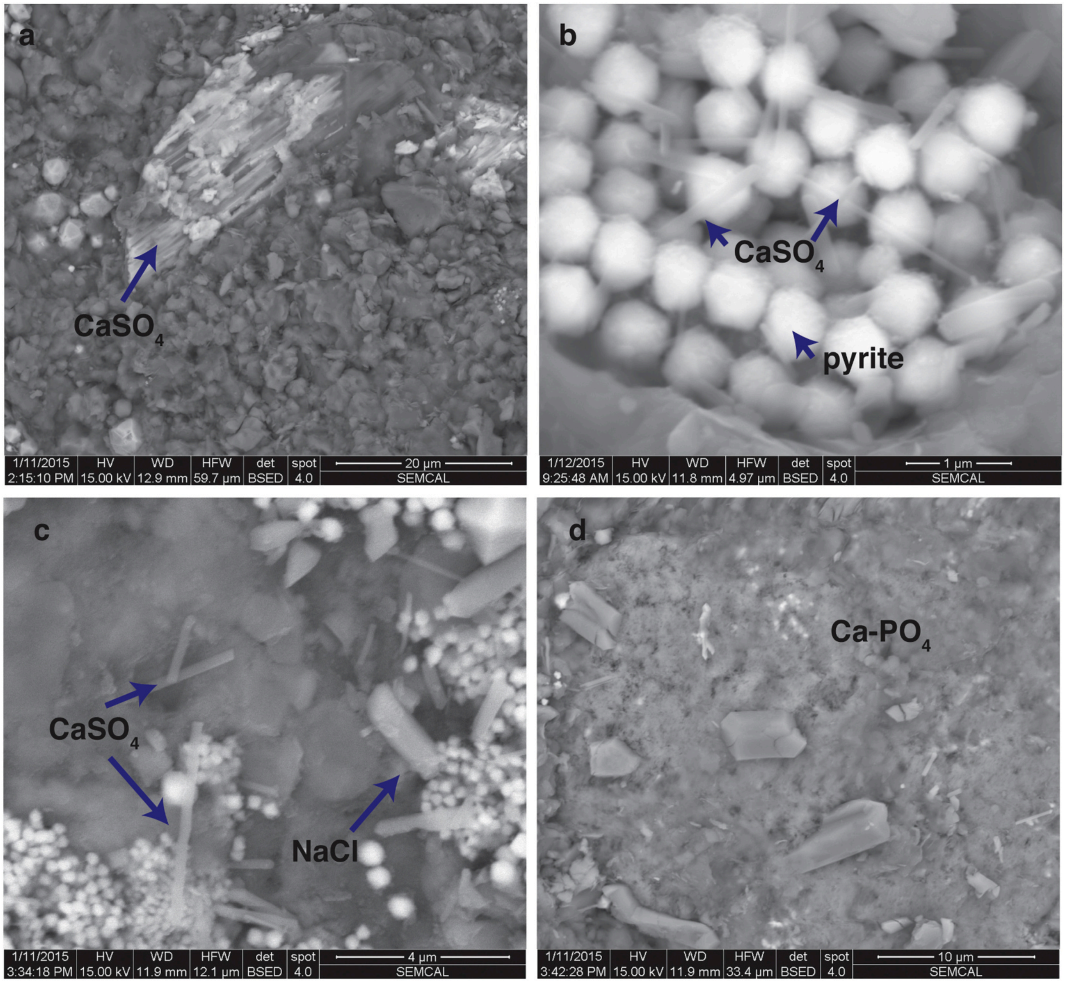

Fig. 3. SEM of salts in core chips from the UPP W site. a) Gypsum precipitates within the rock matrix, b) needles of $CaSO_4$ phase on the surface of framboidal pyrite. C) Salts of both NaCl and $CaSO_4$ on a fractured surface. d) Ca-phosphate phase with salts.

variability in dissolved solute concentrations over time. For example, MIP 5H well showed a twofold increase in TDS for the brine sample collected at day 462 compared to the samples collected in the months before and after. This variation in the TDS of the MIP wells in part reflects how the wells were managed, because gas production had to be decreased in response to municipal demand (Ziemkiewicz, 2018; Ziemkiewicz and He, 2015) and the wells experienced periods where gas production was either throttled back or wells were completely shut in.

In contrast to the geochemical behavior exhibited by most species in water, dissolved SO_4^{2-} concentrations show very different trends. In the UPPW4 well the SO_4^{2-} concentration is elevated, though still considerably lower than the input fluids (~ 900 mg/L) and decreases with time to undetectable levels (few ppm). The $\delta^{34}S$ of SO_4^{2-} increased almost linearly with decreasing SO_4^{2-} in the FP fluids from the UPPW4 well (Fig. 7). Dissolved SO_4^{2-} in the UPPS wells varied considerably in the first month after flowback, and then concentrations were low to undetectable for the remainder of the study. Although SO_4^{2-} was relatively high in the input fluids used for the MIP wells (~ 130 mg/L), concentrations were low to undetectable in the FP fluids (only a few mg/L).

Most of the major elements in these brines (*e.g.*, Na, Cl, Br, Ca, Mg, Sr) follow similar trends and have similar ion ratios in solution, suggesting that they behave conservatively and are controlled by similar geochemical processes (Figs. 5 and 6). The strong correlation between Cl and Br among the brines from all the natural gas wells suggests that there was no appreciable contribution of dissolved Na and Cl from halite dissolution, because Br is excluded from the halite structure (Engle and Rowan, 2014; Engle and Rowan, 2013; McCaffrey et al., 1987). However, all of the wells do exhibit a small decrease in the Cl/Br ratio over time, which may reflect some contribution from halite dissolution during the earlier stages of flowback (Fig. 8 and Fig. S2). Halite was observed in SEM images of core chips from both the UPP W4 and MIP 3H wells at depths close to the target (Fig. 3). The UPPW4 and the MIP 3H and 5H wells have higher Cl/Br in the first few weeks to months (~ 95 to 110) when flowback volumes were higher, and lower ratios (~ 75 to 95) after several months, which may reflect a change in the source of the salts, either from encroachment of brine from adjacent formations, or the slower release of native brines from capillaries (Balashov et al., 2015). The same decreasing Cl/Br trend was not as apparent in the UPPS wells. However, the fluid for the hydraulic fracturing at this site was composed of ~5 to 20% recycled flowback fluids from nearby well sites, and these excess salts may be masking the small changes in the composition observed in other sites. There is also a strong correlation between Na and Cl (or Br), with Na/Cl ratios of approximately 0.33 to 0.38 (wt:wt) for the UPPW4, 0.35 to 0.44 for the UPPS and 0.35 to 0.47 for the MIP wells (Fig. 8). The source of Na, Cl and Br was examined using the isometric log ratio (ilr)-based approach (Engle and Rowan, 2014; Engle and Rowan, 2013) to distinguish between halite dissolution and evaporation of paleo seawater. The parameters Z_1 and Z_2 were calculated and compared to the results depicted in Engle and Rowan (2014) (their Fig. 5). Where

$$Z_1 = \frac{1}{\sqrt{2}} ln \frac{[Na]}{[Cl]}$$

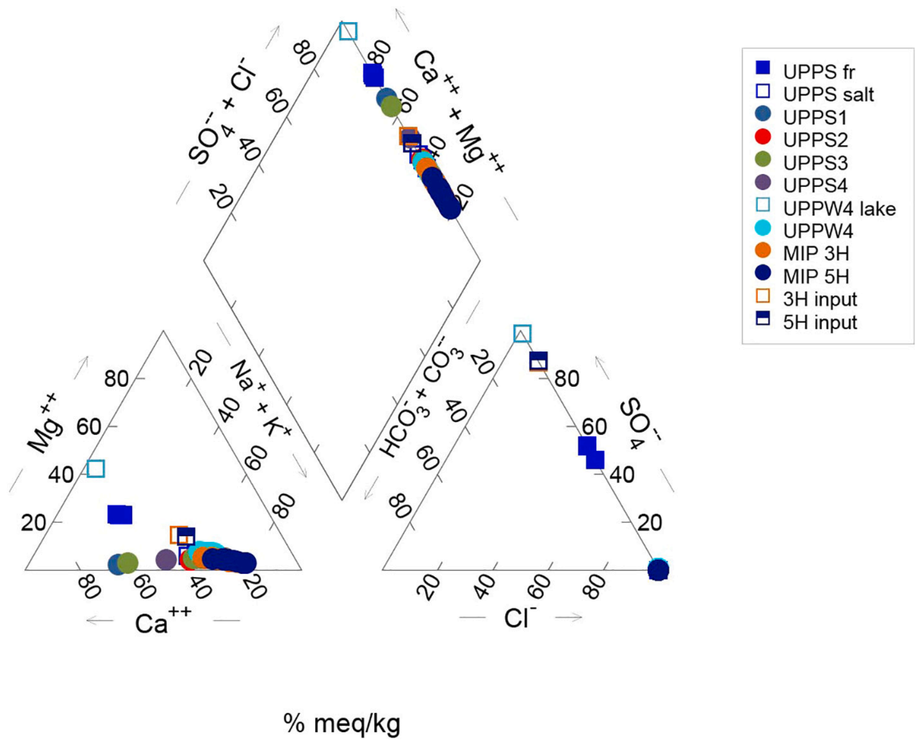

Fig. 4. Piper diagram of flowback fluids and input fluids from two sites in the Utica/Point Pleasant Shale in eastern Ohio (UPPW4 and UPPS1_4) and the MIP 3H and 5H in the Marcellus formation in West Virginia.

$$Z_2 = \frac{\sqrt{2}}{\sqrt{3}} ln \frac{([Na][Cl])^{0.5}}{[Br]}$$

Our UPP and Marcellus data plot along the same trajectory shown as the day 5–90 data for Marcellus flowback fluids, plotting along or above the trend for modern seawater evaporation (McCaffrey et al., 1987) which suggests that these ions are primarily derived from evaporated seawater (Fig. 9). Similar values were reported by Blondes et al. (2020) for Utica Shale samples collected from Ohio and Pennsylvania. However, because their measured TDS values were lower than expected (~ 214 to 283 g/L) for seawater evaporation, they suggest that either the brine is diluted with a lower Na brine, or that Na is removed either by precipitation or ion exchange post evaporation.

The Ca to Cl trends, except for the first few samples that were contaminated with the dense $CaCl_2$ brine, all fall on the same trend line, although the Ca/Cl ratio measured in FP fluids shows a small but systematic increase (~ 10%) over time (Fig. 8c). The Mg *versus* Cl plot (Fig. 6) shows that the FP fluids from the UPPW4 site have elevated Mg, suggesting some solubilization of Mg from either the Mg-calcite cement which is interleaved or laminated with the illitic clay, or from dolomite. Mg concentrations in the rock near the UPP target are approximately 50% to twice as high in the UPP as compared to the Marcellus.

Other elements, such as K, generally exhibit conservative behavior for an individual well site, with concentrations increasing approximately linearly with Cl in the FP fluids, reflecting dilution of the original brine by the relatively fresh hydraulic fracturing fluids. However, there is significant variation among the three well pads, suggesting that differences in the geochemical and mineralogical composition of the formation exerts control on the indigenous brine fluid chemistry (Fig. 6g). K concentrations are substantially lower in FP fluids in the Marcellus wells where the lithology is more siliceous (and clay rich) than the carbonate dominated UPP sites. Engle and Rowan (2014) noted considerable spatial variability in K concentrations from Marcellus flowback brines collected throughout Pennsylvania and West Virginia. They suggest that *in situ* K concentrations in the subsurface brines were controlled by diagenetic alteration of clay minerals (smectite to illite to chlorite), partitioning K into the solid phase. This is consistent with K concentrations in the core samples that are approximately 50% to twofold higher in the Marcellus than in the UPP (Table 1), reflecting the higher concentrations of illite/smectite and K-spar in the Marcellus.

Compared to concentrations of most major elements, the concentrations of Sr and Ba from the three sites are significantly different, resulting from variation in the lithology (both bulk and mineralogical composition), and the fluids used for hydraulic fracturing (Fig. 5). The Sr *versus* Cl plot (Fig. 6e) shows that the Marcellus and UPPS wells fall along a similar linear trend which could reflect a simple mixing and dilution of the indigenous brine with the injected fluids. On the other hand, the Sr for the UPPW4 follows a trend that is parallel but lower in concentration, suggesting either overall lower Sr concentrations in the formation (brine or rock), Sr is in a phase that is unreactive, or that Sr is removed from the brine during hydraulic fracturing. Sr concentrations in flowback fluids from the UPP sites are approximately twofold higher than those in the MSEEL fluids.

Whole-rock elemental analysis of core shows that Sr is abundant in the UPPW (1000 to 2000 ppm SrO, Table 1). EDX spot analysis reveals Sr distributed in the carbonate cement, in strontianite ($SrCO_3$) (occasionally observed as thin rims on carbonate fossils), in fossil tests, in phosphate phases and as barite-celestite crystals, all of which could be solubilized to some extent in the brine or in the hydraulic fracturing fluids which are in disequilibrium with the newly exposed mineral surfaces. Sr concentrations in the MSEEL rock are considerably lower (~ 130 to 400 ppm SrO) and were detected primarily by EDX spot analysis of barite phases.

The most significant variation in chemistry for these three well sites was observed for Ba. In contrast to what has been observed for many Appalachian basin hydraulic fracturing sites, where the concentration of Ba can be upwards of 20 g/L in flowback brines (Akob et al., 2015; Barbot et al., 2013; Rowan et al., 2015), Ba concentrations in the FP fluids from the UPPW4 well were relatively low, on the order of 10s to 100 s of mg/L, and do not exhibit the same systematic trends with Cl as

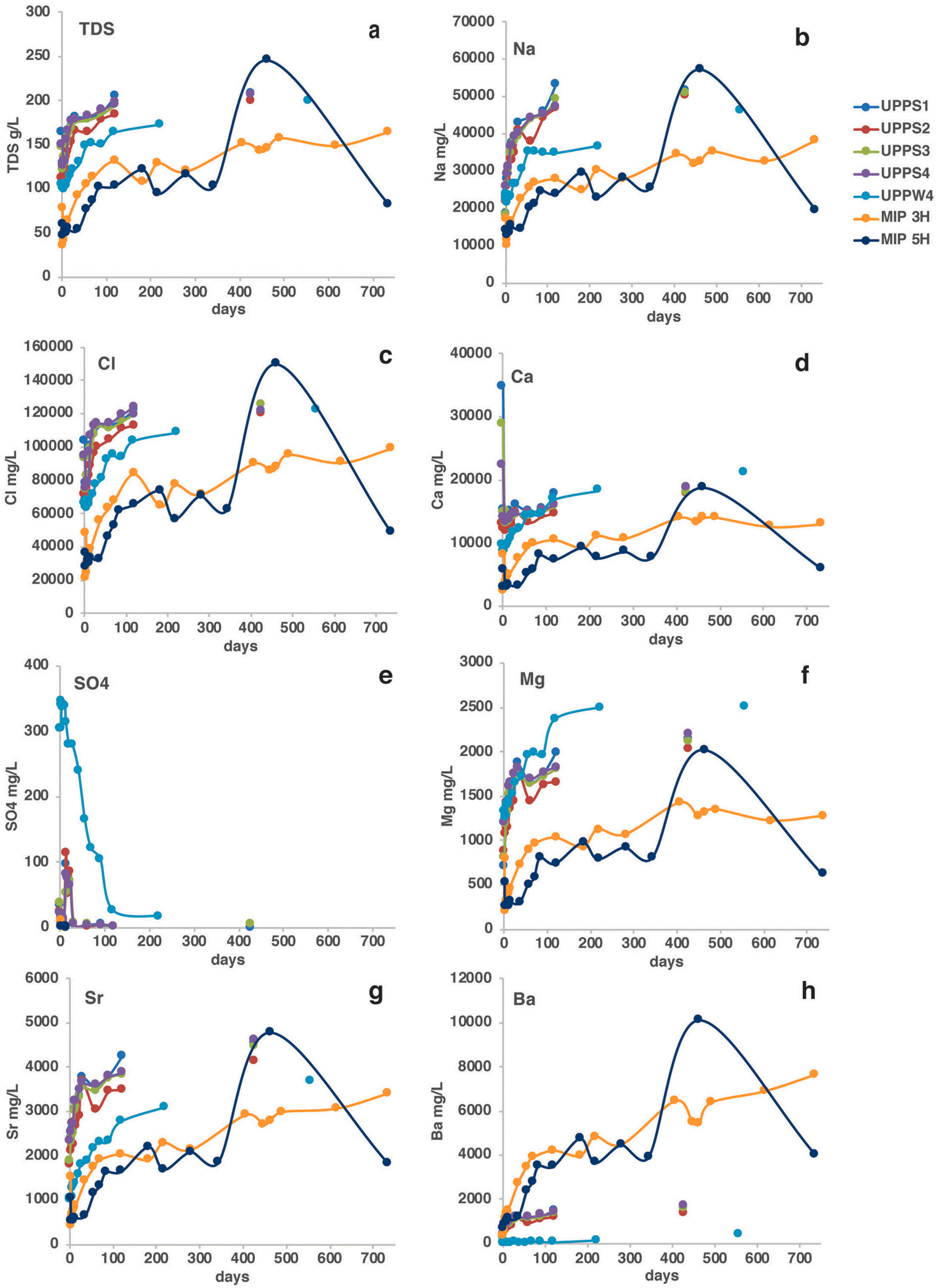

Fig. 5. Evolution of flowback composition over time a) TDS, b) Na, c) Cl, d) Ca, e) SO4, f) Mg, g) Sr and h) Ba.

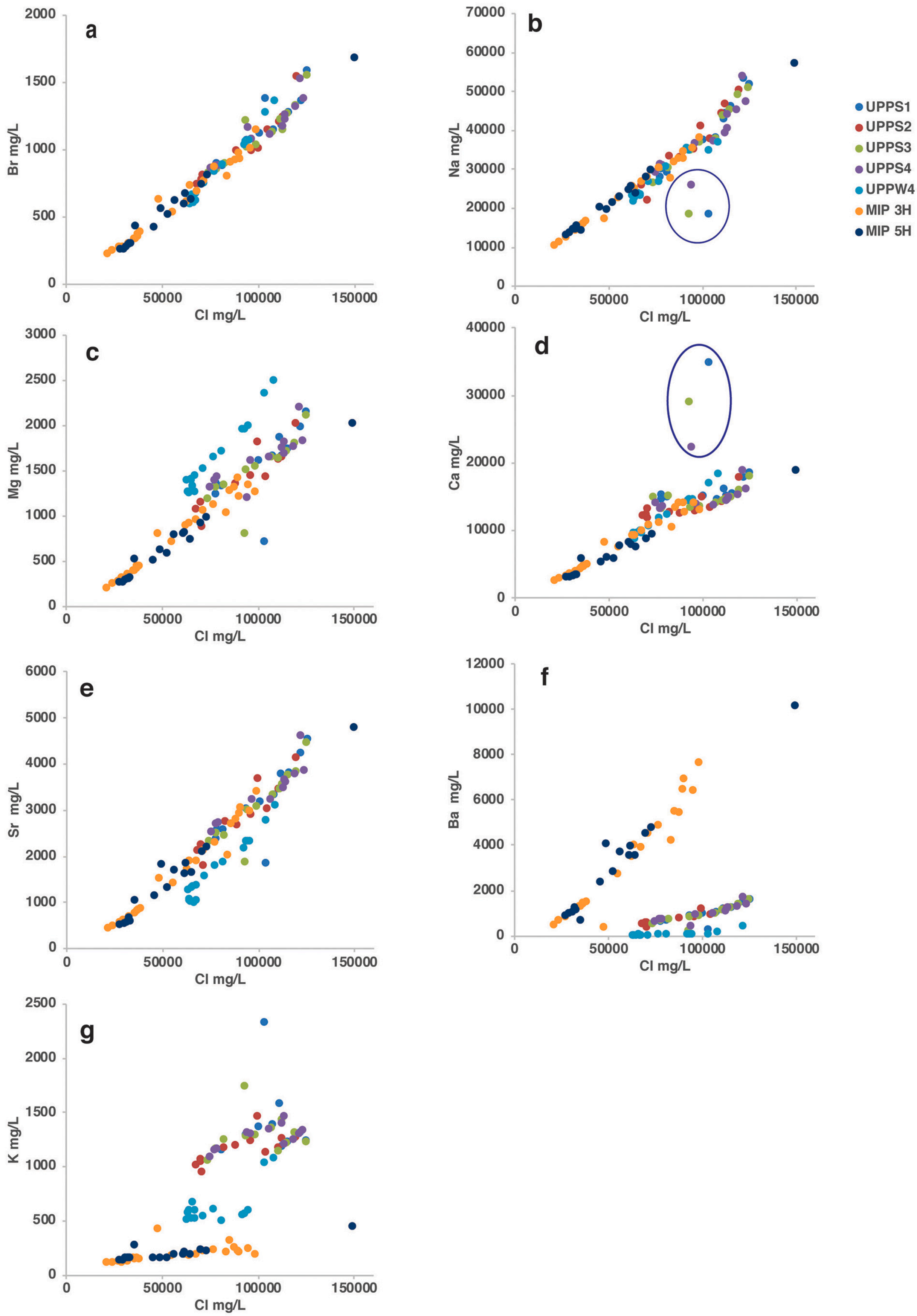

Fig. 6. Concentrations of species in flowback fluids compared to Cl. The outliers highlighted in Fig. 6b and d reflect the heavy $CaCl_2$ brine that was pumped into the well during the shut in period.

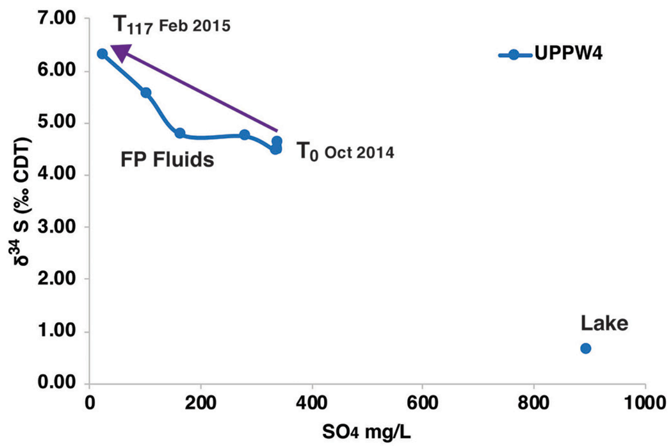

Fig. 7. $\delta^{34}S$ of SO_4^{2-} in FP fluids and input fluid (lake) at the UPPW4 location.

observed for the other sites (Fig. 5h, Fig. 6f). Analysis of suspended material in the UPPW4 FP fluid shows abundant Sr-bearing barite crystallites (Fig. 10), indicating at least some removal of Sr from the fluids, and removal of most of the Ba is due to sulfate-rich water used for the hydraulic fracturing fluids. Although some of the barite/celestite observed in suspension in the FP fluids could be a residual from the drilling fluids, its composition and morphology are distinctive from what was observed from the analysis of cuttings from a UPP well on the same well pad (Wells, 2015). Additionally other minerals from the formation or from the drilling fluids were not abundant in suspension in the FP fluids, indicating that the barite/celestite precipitated from the brine. Ba concentrations in FP fluids from the UPPS wells are higher than those from the UPPW wells, ranging from approximately 200 to 1600 mg/L, and show a strong correlation with Cl (Fig. 6 f). The Ba:Sr ratio in these brines increased over time, from ~0.1 to 0.35, and are higher than the Ba:Sr in the UPPW core samples (~ 0.1, Fig. 11 and Fig. S3). The highest concentrations of Ba (up to ~10 g/L) were measured in brines from the MSEEL site (Fig. 6 h Ba), and have Ba:Sr ratio of approximately 2:1 (wt:wt). In comparison, the geochemical and mineralogical analysis of the rocks near the MSEEL target show Ba in excess of 1 g/kg and Ba:Sr ratios ranging from approximately 3:1 to 7:1 with abundant barite identified by both SEM and XRD analysis.

6. Geochemical controls on the source of dissolved salts

Several studies of FP fluids attempt to better understand the geochemical processes that are occurring in the subsurface during hydraulic fracturing and production (Blauch et al., 2009; Phan et al., 2020; Rosenblum et al., 2017). In general, relationships among the brine chemistry (input, FP fluids and formation), bulk rock chemistry, and sources of the solutes is not well understood for many hydraulic fracturing systems (Birkle, 2016; Lu et al., 2017). Integrating input and flowback fluid analysis with whole core elemental and mineralogical analysis helps shed light on the source(s) of specific elements observed in produced water chemistries. This is especially useful when comparing

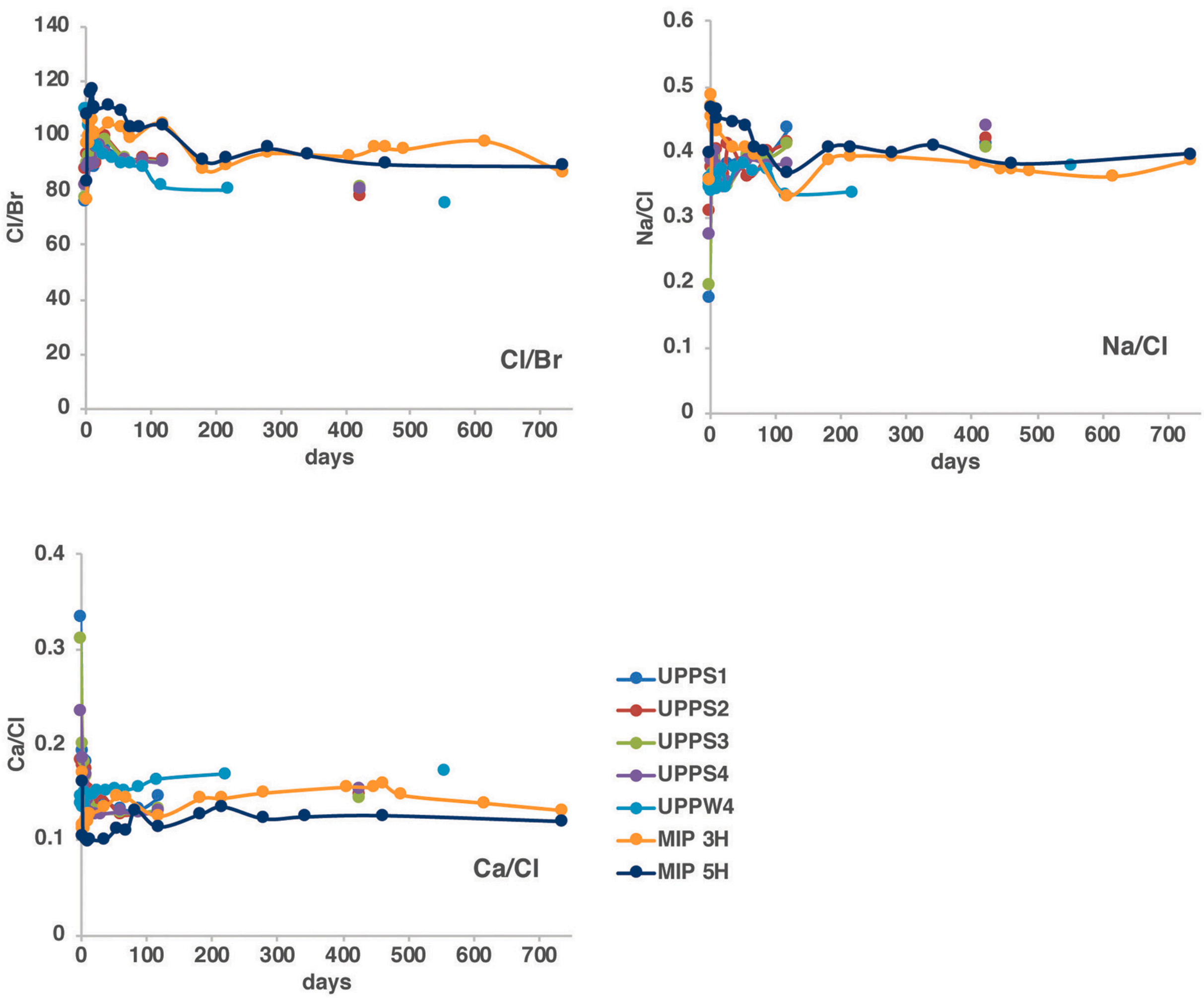

Fig. 8. Cl/Br, Na/Cl and Ca/Cl ratios (mg/L/mg/L) for FP fluids from the seven wells.

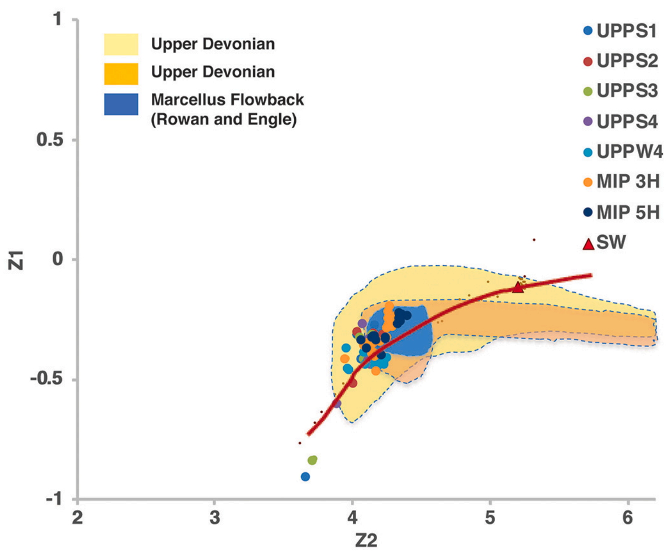

Fig. 9. Isometric log ratio plot redrafted after Engle and Rowan (2013, 2014) with our data superimposed. The yellow and orange shaded areas represent the range of brine compositions from the Upper and Lower Devonian formations. The area shaded in blue represents Marcellus flowback from Engle and Rowan (2014). The red line represents modern seawater evaporation pathway (McCaffrey et al., 1987) and the red triangle is modern seawater. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

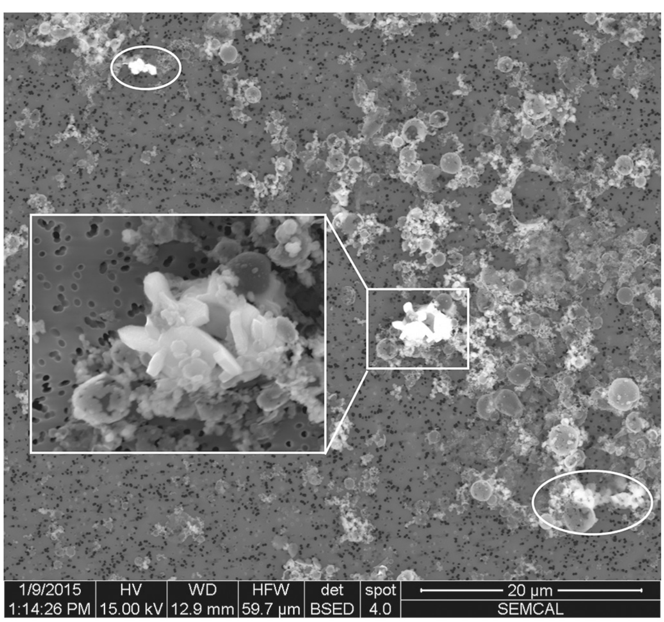

Fig. 10. SEM images of solid phases collected on a filter from FP fluids from the UPPW4 well approximately three months after flowback started. The bright phases in the BSE images are barite-celestite (Sr-bearing barite) - Insert shows the euhedral barite-celestite crystals from the SE detector. The small hollow spheres, ~ 2 to 5 μm in size, are capsules that held compounds used in hydraulic fracturing. The small particles (generally less than micron sized aggregates) are predominately iron oxyhydroxide phases.

two very different hydraulic fracturing targets—the carbonate-rich Utica/Point Pleasant and silicate-rich Lower Marcellus. Another goal is to determine how porosity and permeability may control the extent to which the fluids interact with the formation and in turn undergo modifications.

The UPP and Marcellus formational brines have elevated salt content (from 10s to 100 s of g/L) and have a chemical composition that is derived from evaporated seawater. However, their compositions are distinct from that of the original fluid due to geochemical processes that have occurred over geologic time, including dolomitization, sulfate reduction, and ion exchange reactions. Both Ba and Sr are reported in high concentrations relative to other major ions in natural waters from many hydraulically-fractured lateral wells sampled in the Appalachian basin. Additionally, the injection of relatively fresh water, hydraulic fracturing chemicals, oxidizing species (both in the frac fluid chemical mix and in the input fluids (dissolved O_2, NO_3, SO_4^2, other oxidizers) as well as microbial populations into the subsurface has the potential to induce geochemical reactions that are not simply the dilution of the *in situ* brine or dissolution of readily soluble salts (Lu et al., 2017).

The primary sources of dissolved salts for these FP waters are thought to be derived from both subsurface 'salt' (solid phase) and dilution of subsurface indigenous brines. Salts (either dissolved or solid phase) in these formations include both primary solutes (derived from the original formation brine) and allochthonous solutes (dissolved salts from brines that infiltrated pores and fractures from the adjacent stimulated zones). For example, while the brines can be *in situ* within the target formation (occurring either as free brine or capillary-bound fluid in micropores), or they can encroach from the adjacent zones due to an increase in fracture density and porosity produced during hydraulic fracturing (Balashov et al., 2015; Renock et al., 2016). Estimates of fracture propagation show that the fracture networks can extend for meters to tens of meters, though fractures of hundreds of meters have been reported (Davies et al., 2012). Fractures extend in any direction along the lateral, inducing migration of brines through these previously impermeable zones. Studies of Marcellus flow back brines have concluded that the dissolved salts in FP fluids are derived from Appalachian brines in the shale or the surrounding formations (Balashov et al., 2015; Chapman et al., 2012; Dresel and Rose, 2010; Engle et al., 2016; Engle and Rowan, 2014; Haluszczak et al., 2013; Rowan et al., 2015), with little evidence for dissolution of evaporite salts.

However, fewer studies consider that the solutes in the FP fluids can be derived from contemporaneous (during hydraulic fracturing and flowback) brine-rock interaction, either from the dissolution of primary rock, oxidation of reduced species or adsorption-desorption reactions in the subsurface (Engle and Rowan, 2014; Landis et al., 2018b; Lu et al., 2017; Phan et al., 2020; Renock et al., 2016). Injection of the relatively fresh fluids, mixed with complex organic compounds, and a host of oxidizing species (O_2, NO_3^-, SO_4^{2-}, as well as compounds such as persulfate and peroxide additives) into newly opened fractures creates an environment where the fluids are potentially out of equilibrium with the newly exposed rock surfaces. Analysis of the changes in composition over time can be used to infer possible mechanisms occurring in the subsurface and to differentiate between dilution of *in situ* brines and other geochemical reactions that would either contribute to or remove solutes from the flowback fluids. These latter mechanisms are essential because they can result in changes in rock porosity and permeability, which can, in turn, impact gas production and well integrity over time (Harrison et al., 2017; Lu et al., 2017; Sharma et al., 2020).

The strong correlations among most of the major constituents in the brines with conservative species such as Cl or Br, suggest that *in situ* brine composition in these formations is diluted by the relatively fresh input fluids used in hydraulic fracturing. The large scale temporal changes can be described by diffusion of brines residing in micropores to the more extensive fracture network generated by hydraulic fracturing (Balashov et al., 2015). The Na-Cl-Br (ilr) plot is consistent with the observations of Engle and Rowan (2014), Engle and Rowan, 2013) and Rowan et al. (2015) indicating that the high saline brines from both the UPP and Marcellus formations are derived from evaporated paleoseawater. However, the small but systematic decrease in the Cl/Br ratio over time suggests a potential contribution from halite dissolution in early stages of flowback, increasing contributions from brine with a different composition during the later stages of flowback, another source

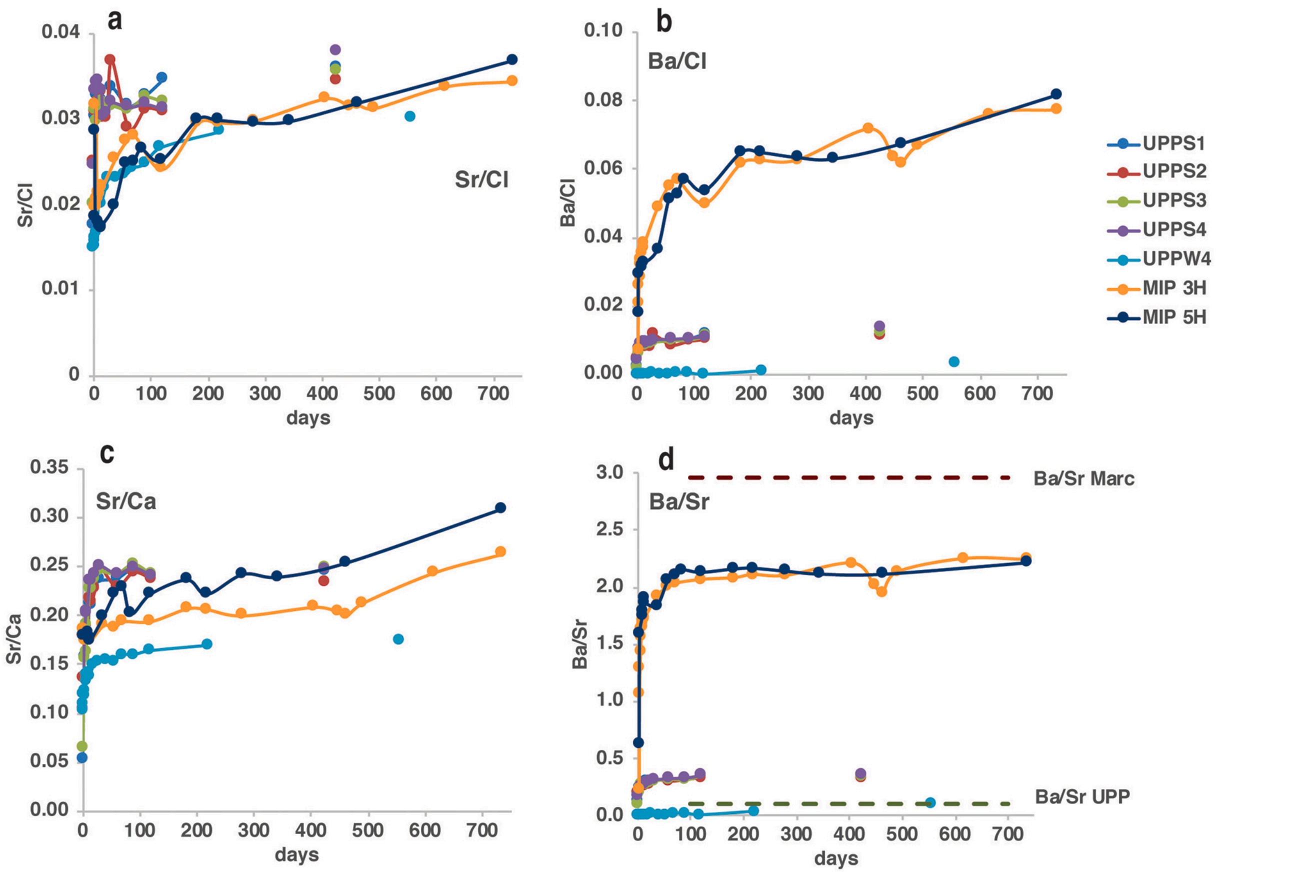

Fig. 11. a) Sr/Cl, b) Ba/Cl, c) Sr/Ca and d) Ba/Sr (mg/L/mg/L) in the wells. The dashed lines in 11d represent the Ba/Sr ratio (wt/wt) for the bulk rock analysis.

of either Cl or Br, or a change in the mechanism of Cl/Br release from the micropores.

The differences observed for K and Mg when comparing the UPP and Marcellus flowback fluids may reflect diagenetic alteration of the rock. The lower K concentrations in flowback brines for the more siliceous clay-rich Marcellus reflect illitization, whereas the slightly elevated Mg in the brine for the UPP reveals diagenetic reactions with carbonates. The overall lower Mg/Ca ratio (wt/wt) in the brines, ~ 0.13 to 0.15 for UPPW, 0.08 to 0.12 for UPPS and 0.08 to 0.11for the MIP brines compared to ~3.1 for modern seawater, reflects the previous dolomitization and to some extent illitization that had occurred over geologic time. However, the strong correlation between these elements and Cl or Br and the relatively constant metal/Cl ratio over time in the FP fluids indicates that the concentrations of these species in the FP fluids are primarily controlled by mixing and dilution of the *in situ* brine with the hydraulic fracturing input fluids during hydraulic fracturing and flowback.

However there is evidence of geochemical reactions that are occurring contemporaneously with hydraulic fracturing or flowback that would result in changes to the FP fluid composition, particularly for SO_4^{2-} and the divalent cations (Ca^{2+}, Sr^{2+} and Ba^{2+}).

6.1. Sulfur chemistry

The geochemistry of sulfur in hydraulic fracturing systems is complicated because sulfur redox chemistry can be mediated by both biological and abiotic reactions. Sulfate concentrations in subsurface brines and flowback fluids are typically low compared to seawater ratios of other soluble salts because under oxidizing conditions, evapoconcentration will result in gypsum precipitation, while under reducing conditions, sulfate is reduced to sulfide and forms sedimentary pyrite. Pyrite and sulfate minerals (barite-celestite endmembers or solid solutions) are common in both the Marcellus and UPP formations in our samples, while other S-bearing phases (gypsum/anhydrite, sphalerite and S-bearing organic blebs) were observed less frequently. The introduction of low ionic strength oxidizing hydraulic fracturing input fluids can promote the dissolution of sulfate minerals and oxidation of sulfides to sulfate, which in turn can exert control over both Sr and Ba geochemistry due to the low solubility of barite-celestite minerals.

At the UPPS site, there is evidence of sulfate release to FP fluids in the early stages of flowback, as there was a pulse of SO_4^{2-} in the FP fluids from the four wells that varied in the first few weeks, and concentrations were elevated compared to any of the measured input fluids, from 10s to ~100 mg/L SO_4^{2-}. This strongly suggests that either sulfate phases were dissolved by the relatively low ionic strength hydraulic fracturing input fluid or sulfide minerals were oxidized, either biotically (by the *in situ* or injected microbial communities) or abiotically from the addition of oxidizing agents in the fracturing fluids. Analysis of microbial communities in these fluids show that microbes capable of metabolizing sulfur compounds are common (Booker et al., 2017; Cluff et al., 2014; Daly et al., 2016). Experimental studies with shale samples conducted at both ambient and *in situ* temperatures and pressures suggest pyrite oxidation can occur in the early stages of hydraulic fracturing (Harrison et al., 2017). However, the Marcellus and UPPW4 site exhibited a different trend. When sulfate was present in the water used to make hydraulic fracturing fluids, there was a rapid decrease in SO_4^{2-} concentrations in the FP fluids. This trend has been observed for numerous sites and has been attributed to *in situ* microbially mediated sulfate reduction (Engle and Rowan, 2014).

$$C_6H_{12}O_6 + 3SO_4{}^{2-} \rightarrow 3H^+ + 3HS^- + 6HCO_3{}^-$$

Sulfur isotope analysis of the UPPW4 waters are consistent with this interpretation (Fig. 7), with increasing $\delta^{34}S$ corresponding to decreasing SO_4^{2-} over time in the FP fluids. However, studies of microbial populations from this well do not show evidence of active sulfate reducing bacteria in the FP fluids (Booker et al., 2017; Daly et al., 2016) but instead have revealed the presence of other microbes capable of mediating different sulfur redox chemistry.

6.2. Alkaline earth chemistry

There is a small but systematic increase in the Ca/Cl ratio in FP fluids in both the UPPW and MIP wells over time in these systems, particularly for the more carbonate-rich UPP formation, indicating dissolution of a Ca bearing phase (Fig. 8c Ca/Cl) during hydraulic fracturing and flowback. The hydraulic fracturing input fluids have added dilute HCl and other complex organic compounds that could promote the dissolution of calcite, increasing the Ca concentrations in FP fluids compared to other constituents.

Phan et al. (2020), Phan et al., 2019) have conducted major and trace element and isotopic analysis of FP fluid samples from the MIP wells collected in concert with the ones in our study. They have demonstrated an increase in the Ca/Na and Sr/Na ratios, and an increase in dissolve U along with a shift in the $^{87}Sr/^{86}Sr$ in the early produced water samples that they attribute to either the dissolution of carbonate cements or the Cherry Valley formation. However, there are other potential sources of Ca, particularly in the UPP formation. In particular, trace Ca-bearing phases (Ca-phosphates and gypsum/anhydrite) that are more abundant in the UPP target compared to the Marcellus. These are only minor contributors to the total Ca concentrations in the rock ($P_2O_5 \sim 0.42$ wt% in the UPP and ~ 0.1 wt% in the Marcellus), but their increased reactivity compared to calcite or dolomite suggests that they may contribute disproportionately to the total Ca flux to the brine (Welch et al., 2015). In experiments, Ca is preferentially dissolved from both UPP and Marcellus core samples primarily from the dissolution of carbonates leading to an increase in porosity (Welch et al., 2020, (Dieterich et al., 2016; Lu et al., 2017; Moore et al., 2018; Pilewski et al., 2019).

More significant changes were observed for Sr and Ba in the FP fluids reflecting differences in lithology, bulk composition, rock reactivity and differences in the hydraulic fracturing input fluids between the UPP and Marcellus sites. The Sr concentration in the FP fluids correlate with Cl, but are elevated approximately two orders of magnitude compared to seawater ratios (modern seawater Sr/Cl = 0.000412 (g/kg/g/kg) compared to 0.02–0.035 for FP fluids (Chester, 2003). Sr concentrations in the FP fluids from the UPP and Marcellus are elevated compared to both Mg and *Ca*. For example, Sr/Ca and Sr/Mg are 0.019 and 0.0062 in seawater compared to 0.15–0.25 and 1.5–3.0 for FP fluids. Respectively. Sr concentrations increase exponentially with salinity in deep basin brines (Kharaka and Hanor, 2003) due to buffering reactions with carbonate, sulfate, and silicates minerals.

For example, diagenetic alterations of carbonate phases over geologic time would result in the exclusion of the larger Sr ion from the crystal structure and enrichment in the brine (Engle and Rowan, 2014). The Sr/Ca and Sr/Cl ratios in FP fluids increase over time following a trend similar to what has been observed for solute concentrations, where in the first few days to weeks of flowback these ratios increase quickly and then more slowly over the months to years of flowback ((Fig. 10 Sr/Ca and Sr/Cl). This suggests that if carbonates are dissolving in the subsurface during hydraulic fracturing and flowback, the larger Sr^{2+} ion would be preferentially solubilized from the mineral. Calcite cements in the UPP contain Mg and Sr, as measured by EDX spot analysis, and Sr-rich rims on fossil tests also are observed in the UPP rocks and are possible candidates for such solubilization of strontium.

Additionally, Ca phosphate phases including apatite and a poorly crystalline Ca phosphate/carbonate OM mixture (collophane) are abundant in the UPP target rock and also contain Sr as measured by EDX. Within the UPP, these phases are of silt to sand-sized aggregates of nanoscale grains and appear very porous compared to the surrounding rock matrix, providing higher surface area preferential reactivity (Fig. 3). In the UPP core samples, Sr has also been observed as nearly pure celestite ($SrSO_4$) and as barite-celestite solid solution crystals.

The same trends in Sr/Ca and Sr/Cl for FP fluid were also observed for the Marcellus. However, Sr concentrations in the Marcellus rocks were much lower (Table 1), as was the abundance of carbonate minerals (Fig. 2, Table 1). Other than in barite-celestite crystals, Sr was not detected by EDX spot analysis, which suggests perhaps Sr is preferentially solubilized from barite-celestite crystals leaving the more insoluble barite behind (Hanor, 2000). Similar trends were observed for the evolution of Sr in other Marcellus FP brines (Capo et al., 2014) where both Sr concentrations, and $^{87}Sr/^{86}Sr$ increased over time. However, the isotopic composition remained ‘constant’ before Sr concentrations plateaued indicating that the more radiogenic Sr was sourced from ion exchange reactions with clays.

The concentrations of Ba in flowback fluids are of environmental interest because they are elevated (10s of mg to 10s of g/L), especially with respect to other major ions in natural waters. In addition, radium can substitute for Ba, thus reactions that control Ba can exert control over naturally occurring radioactive material (NORM) in these fluids. Elevated concentration of Ba-rich fluids can result in mineral scale as barite and negatively impact natural gas well performance (Landis et al., 2018a, 2018b; Renock et al., 2016). Barbot et al. (2013) noted that there was considerable spatial variability of Ba concentrations in FP fluids from hydraulic fracturing of the Marcellus Formation in Pennsylvania, with relatively high values in the northeast and trending downward to the southwest corner of the state in a trend that corresponds to maximum burial depth and increasing thermal maturity. The highest Ba/Cl ratios (6–8.4%) found in northeast Pennsylvania are comparable to the later stage Ba/Cl measured in our West Virginia Marcellus FP fluids. Just across the border in southwest Pennsylvania, the Ba/Cl in less mature Marcellus FP fluids ranged from 0.25 to2.5%, in the same range as we observe for the UPPS wells. Blondes et al. (2020) noted that Ba concentrations in the FP fluids from the Utica Shale play varied from approximately 1000 to 3000 mg/L in Pennsylvania, and had considerably lower values, 10 to 100 mg/L in FP fluids from Ohio.

The geochemical controls on Ba in FP fluids differed significantly among the three sites. At the UPPW well, where the SO_4^{2-} concentration of the input fracking fluid was elevated ($\sim$ 900 mg/L SO_4^{2-}) Ba concentrations were initially very low, only a few to few 10's mg/L, and only increased substantially once SO_4^{2-} was depleted. Geochemical modelling to determine mineral saturation and demonstrates *in situ* formation of barite within the well, which was confirmed by analysis of suspended material (Welch et al., 2020). However, Ba concentrations measured within the UPPS and Marcellus wells show geochemical behavior that is more typical of hydraulic fracturing, increasing systematically over time with the other dissolved salts. Ba increases with respect to Cl, especially in the early stages of flowback, suggesting a reaction with the formation mineral assemblages is releasing Ba to the FP fluid solution. Barite and barite-celestite were observed in both formations, and were particularly abundant in the Marcellus target formation, however, the kinetics of barite dissolution are notably slow (Hanor, 2000; Ouyang et al., 2017; Zhen-Wu et al., 2016), and SO_4^{2-} was generally not detected in the high Ba fluids, thus dissolution of barite is probably not a significant source of dissolved Ba. The increase in Ba/Cl ratio in the Marcellus and UPPS FP fluids, and the noted decrease of Na/Cl in the fluids over time, suggest ion exchange reactions with clays are a major source of the Ba (Kravchenko et al., 2014; Ouyang et al., 2017; Renock et al., 2016). Experimental studies on shale samples from the Marcellus Formation showed that approximately 5 to 25% of the available Ba could be solubilized by ion exchange reactions, and Ba concentrations in the supernatant increased with ionic strength (Renock et al., 2016). Similarly, our sequential extraction experiments with the UPP rocks (Welch et al., 2020) showed that approximately half of the readily soluble Ba was extracted in the ion exchange extraction step, suggesting that ion exchange reactions with clays could readily solubilize Ba from the formation (Chikkamath et al., 2020; Eylem et al., 1990; Renock et al., 2016).

7. Conclusions

The primary mechanisms controlling the observed water chemistry in FP fluids include 1) dilution of an evaporated seawater fluid by input hydraulic fracturing fluid; 2) long-term geochemical and diagenetic processes (including recrystallization, dolomitization, illitization and sulfate reduction) that result in differences in *in situ* brine composition, and 3) contemporaneous geochemical processes that result from water-rock interaction of brine, oxidizing input fluids and microbial communities with newly exposed fracture surfaces. Of these, the first two processes are the primary mechanisms for controlling both the composition and concentrations of solutes in FP fluids. However, *in situ* geochemical reactions during hydraulic fracturing can be profoundly important for impacting well integrity and gas production during the lifetime of the well because these reactions can have direct impacts on porosity and permeability over a range of scales by affecting dissolution/precipitation and ion exchange reactions.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemgeo.2020.120041.

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