

Geochemistry and metal release from Marcellus Shale and surrounding rock formations

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Abstract

High total dissolved solids as well as high concentrations of anions and alkaline earth metals (Cl, Ba, and Sr) are contaminants of concern in wastewaters produced from unconventional oil and gas wells. These contaminants are thought to originate from migrated formation brines and/or shale mineral dissolution and mixing with hydraulic fracturing fluids. Understanding intra- and inter-geologic unit metal composition and contaminant release is important in assessing the origin of produced oil and gas wastewaters. To study intra- and inter-geologic unit metal composition, Marcellus Shale samples, Utica Shale samples, and their overlying and underlying confining units were collected from multiple cores at varying depths (428-5163 ft. below ground surface). Samples from surrounding formations, i.e. Salina Group, suspected of hosting the original brine that subsequently migrated into other units were also collected. Samples were characterized by sequential extractions. Extractant solutions were analyzed for anions (IC) and cations (ICP-MS). Marcellus Shale and Utica Shale samples should experience similar elemental mobilization since they may receive migrated formation brines from the same rock formation, the Salina Group. Rock dissolution and mixing with hydraulic fracking fluids may play a larger role in high elemental mobilization than formation brines. Interestingly, Utica Shale samples experienced more elemental mobilization than Marcellus Shale samples in anions and cations such as Br, Cl, and Na.

Introduction

Unconventional oil and gas production is steadily growing in the United States due to the use of directional drilling and hydraulic fracturing techniques. Natural gas is pursued for several reasons, such as the reliability of U.S. natural gas supply over the delivery system of imported fossil fuel, the high energy content of natural gas (about 30 kJ/m³ or 1000 Btu/ft³), and the clean-burning nature of natural gas (Kargbo et al., 2010). Figure 1 (Appendix) shows the locations of U.S. shale basins that bear natural gas. Due to the vast natural gas resources in formations such as the Marcellus Shale and Utica Shale, technically recoverable natural gas from U.S. shales is more than 1,744 trillion cubic feet (Kargbo et al., 2010). The Marcellus Shale formation alone—

which extends across the states of New York, Pennsylvania, Ohio, Maryland, and West Virginia—holds between 128 and 516 trillion cubic feet of natural gas (Pennsylvania, 2012). Relying on production techniques such as directional drilling and hydraulic fracturing, increasing unconventional oil and gas production can have the potential for economic growth and environmental benefits (Kargbo et al., 2010; Dale et al., 2013). However, research on these production techniques and the gas-producing, geologic formations of interest is important for developing safer production practices and addressing public health concerns (Soeder et al., 2014).

Hydraulic fracturing, a.k.a. “fracking”, is an unconventional oil and gas production technique that produces fractures in the rock formation that stimulate the flow of natural gas or oil, increasing the volumes that can be recovered (EPA & OEAAEE, 2015). Fractures are created by pumping large quantities of fluids at high pressure down a wellbore and into the target rock formation (EPA & OEAAEE, 2015). These fracking fluids commonly consist of water, chemical additives that open and enlarge fractures within the rock formation, and a proppant that holds the fractures open (GWPC, 2016). The additives may include varying percentages of the following: acid, breaker, bactericide, clay stabilizer, corrosion inhibitor, friction reducer, gelling agent, scale inhibitor, and surfactant (NYSDEC, 2011). The proppants (i.e. sand, ceramic pellets, or other small incompressible particles) hold open the newly created fractures (EPA & OEAAEE, 2015). Once the injection process is complete, the internal pressure of the rock formation causes fluid to return to the surface through the wellbore (EPA & OEAAEE, 2015).

Injected hydraulic fracturing fluids that return to the surface within the first two weeks after stimulation by fracturing are collectively called the “flowback” water (Haluszczak et al., 2013). Fracking fluids that flow from the well after the initial two-week period are “produced” waters (Haluszczak et al., 2013). Typically, ten to fifty percent of the injected fluid is returned to the surface via well casing (USEPA, 2012; Vidic et al., 2013). Flowback water contains the original or degraded additives as well as constituents mobilized from the formation (Wang et al., 2015). These can include a number of metals, metalloids, dissolved organics, and hydrocarbons (Gregory et al., 2011). Table 1 (Appendix) shows a typical range of concentrations for common constituents in flowback and produced waters from natural gas development in the Marcellus Shale (Gregory et al., 2011). Naturally occurring salts, radionuclides, and other elements will also appear in flowback water, which is suspected to occur because of subsurface mixing between the injected fracking fluid and salty waters or brines present in the formation (Abualfaraj et al., 2014). Barium and radium have been found to strongly correlate with total dissolved solids (TDS) (Renock et al., 2016). Barium concentrations and radium activities in produced waters have been shown to increase days after pumping has started, exceeding levels of 1,400 mg/L Ba and 5,000 to 16,000 pCi/L Ra (Chapman et al., 2012; Warner et al., 2012). These same waters can contain TDS exceeding 150,000 mg/L (Gregory et al., 2011) compared to a concentration of 35,000 mg/L TDS in seawater.

In addition to formation brines, solid-water interactions can also mobilize elements through a variety of pathways that depend on the formation composition and fracturing fluid chemistry (Wang et al., 2015). For example, the dissolution of acid-soluble minerals may be a release pathway since strong acids, such as hydrochloric or muriatic acid are used to initiate fractures, and they tend to be the single largest liquid additive in fracturing fluids (Gregory et al., 2011). Desorption of metals from host minerals can occur due to changes in pH and through the introduction of complexing agents (Wang et al., 2015). A complexing agent is a compound in

which independently existing molecules or ions of a nonmetal form coordinate bonds with a metal atom or ion. For iron control, EDTA and citrate form strong complexes with several metals and metalloids such as Pb (II), Cu (II), and Co (II), which can increase their mobility (Wang et al., 2015). Dissolved oxygen and other oxidative breakers, such as ammonium persulfate and magnesium peroxide are used to degrade the gel polymer chains by oxidative mechanisms (Fink, 2013; Vidic et al., 2013). These mechanisms may drive significant redox-sensitive geochemical reactions, e.g. increasing the solubility of reduced forms of uranium and chromium through oxidation (Wang et al., 2015).

Shale gas is natural gas produced from shale formations that typically function as both the low-permeable reservoir and the source rocks for the natural gas (Speight, 2013). Shale gas is distinct from gas in other reservoirs and from conventional gas. Figure 2 (Appendix) shows different types of onshore natural gas reserves (Gregory et al., 2011). The Middle Devonian Marcellus Shale formation is an organic-rich black shale formed from tectonic loading and sediments deposited in the oxygen-deficient sea of the Appalachian Basin (Lavergren et al., 2009; Curtis & Klemow, 2011). Black shales like the Marcellus Shale are known to be rich in sulfides and many potentially toxic elements, such as, Cd, Mo, U, Cr, Se, and V (Lavergren et al., 2009; Curtis & Klemow, 2011), and they are dominated by clay minerals (e.g. illite with some chlorite and smectite-illite mixed clays) with lesser quartz, silt, calcite, and pyrite (Roen, 1984; Engle and Rowan, 2014). Blauch et al. (2009) reported halite in Marcellus Shale cores within the bulk matrix and along the bedding planes. The Ordovician Utica Shale is a black shale as well, but with a high content of carbonates within the rock. The Marcellus Shale overlies the lower Devonian Onandaga Limestone and is overlain by sandstones, silts, and shales of the Hamilton Group and Mahantango Formation (Figure 3, Appendix). The section continues upward into the Upper Devonian and Lower Mississippian shales and conventional hydrocarbon-bearing sandstones where oil and gas in these units is thought to be sourced from the underlying Marcellus Shale (Carter, 2007). The units underlying the Marcellus Shale include the hydrocarbon-bearing Ordovician Utica Shale (Figure 3, Appendix) as well as the Silurian Salina Series evaporates, which transition to limestones, shales, and sandstones in the southwestern part of the play (Patchen & Carter, 2015).

Appalachian basinal brines are thought to permeate the Marcellus Shale and adjacent rock units. These brines are thought to be derived from residual Paleozoic seawater expelled from the Salina Series based on observed chloride and bromide relationships (Osborn & McIntosh, 2010). Heterogeneities in brine geochemistry in the Appalachian Basin suggest varying stages of alteration due to water-rock interactions, e.g. rock dissolution, sulfate reduction, and brine-aquifer rock interactions (Dresel & Rose, 2010; Osborn & McIntosh, 2010). As previously shown in paragraph three, brines in permeable host formations from Ordovician to Devonian eras can contain up to thousands ppm barium, which can possibly be explained by the sulfate-deficient brines reacting with Ba-containing minerals in the rock, e.g. silicates and carbonates (Dresel & Rose, 2010). Produced water from the Marcellus Shale is a Na-Ca-Cl brine with high levels of Sr, Ba, Br, and relatively high activities of ^{226}Ra and ^{228}Ra (Haluszczak et al., 2013; Engle & Rowan, 2014). Interestingly, Renock et al. (2016) suggests brine migration in the low-permeable black shale matrix to occur through horizontal and vertical fractures within the unit where brines can act as adsorbed water films on clays, capillary water, or free-flowing brine. Figure 4 (Appendix) shows the possible mechanisms contributing to the generation of produced water alkaline-earth (e.g. Ba, Ra, Sr) cation composition (Renock et al., 2016). This postulation

adds to the generally accepted hypothesis of subsurface mixing with deep formation brines as the source of high flowback TDS.

Studies have evaluated flowback chemistry and water-rock interactions between hydraulic fracturing fluids and corresponding shale formations. Dresel & Rose (2010) and Rowan et al. (2011) proposed there may be an alternative origin of high salinity in flowback water due to the release of *in situ* brines or formation water that they found from oil and gas wells in Pennsylvania. These saline brines in the Marcellus Shale formation are affecting the water quality of shallow drinking-water aquifers. However, the lack of a geological relationship to shale-gas wells shows that brine migration is occurring along natural pathways (Warner et al., 2012). Brines within shale formation likely contribute to the high Ra and TDS concentrations observed after well formation (Haluszczak et al., 2013). Chapman et al. (2012) suggested the modification of formation brines by radiogenic clays in the Marcellus Shale is required to explain Sr isotopic composition in flowback water. Studies have been conducted to mobilize metals and characterize metal association within specific solid phases as well as understand their origins in flowback fluid (Lavergren et al., 2009; Phan et al., 2015; Stewart et al., 2015; Wang et al., 2015). These studies used sequential extractions to characterize shale formation samples. Within the cation-exchangeable sites in the Marcellus Shale, nine to seventy-four percent of the total Ba was reported by Phan et al. (2015) and agreed upon by Stewart et al. (2015), although exchangeable Ba varies widely, and Ba availability and susceptibility to leaching is highly variable from different geographic locations and depths with the same well.

Many studies have researched hydraulic fracturing flowback brine, but there are limited published data focused on metals released from Marcellus Shale and Utica Shale drill cores. Some studies mentioned in the previous paragraph study outcrop samples rather than drill core samples in this research due to the difficulty in obtaining these materials. Drill cores are particularly important to study because they are collected from the deep “pay zone” where the hydraulic fracturing will occur. Also, there is little-to-no data on Utica Shale core samples and produced waters. The main objective of this research is to understand the intra- and inter-geologic unit metal composition of and contaminant release from Marcellus Shale and Utica Shale. Marcellus Shale and Utica Shale samples should experience similar elemental mobilization since they are thought to receive migrated formation brines from the same rock formation, the Salina Group. Rock dissolution and mixing with hydraulic fracking fluids may play a larger role in high elemental mobilization than formation brines. Interestingly enough, Utica Shale samples experienced more elemental mobilization than Marcellus Shale samples in anions and cations such as Br, Cl, and Na.

Materials and methods

1. Sample description

Rock samples were obtained from deep cores drilled in Ohio and northwestern Pennsylvania from the Pennsylvania Topographic and Geologic Survey. Table 2 (Appendix) enumerates all core samples used in the sequential extractions. Marcellus Shale and Utica Shale samples, along with their overlying and underlying confining units, were collected from multiple cores at multiple depths. Notable surrounding formations, i.e. Salina Series and Precambrian, were collected as well.

2. Methods

2.1. Sample preparation

Sequential extractions were carried out in acid-washed Teflon and HDPE centrifuge tubes, using ultrapure reagents to extract metals and radionuclides from Marcellus Shale and Utica Shale samples as well as samples from surrounding formations. Samples used in the sequential extractions were prepared by crushing, and then they were pulverized in a SPEX ball mill, ground with a mortar and pestle (if necessary) and sieved to finer than 150 μm . Some samples were oven dried at 100 °C and 0.5 g of each sample was distributed into labelled Teflon centrifuge tubes. Acid-washed, polypropylene centrifuge tubes were labelled and weight as well to be used as appropriate extractant tubes after each fraction.

2.2. Sequential extractions

Samples were characterized by sequential extractions through four different operationally-defined fractions: (1) water soluble minerals, (2) exchangeable sites on clays, (3) carbonate minerals, and (4) reducible species. The extractant solutions for these four steps were: (1) MQW/ultrapure water, (2) 1 N ammonium acetate buffered to pH 8, (3) 8% acetic acid, and (4) 0.5 N hydroxylamine hydrochloride in 25% acetic acid. Each extractant solution was N_2 purged to mimic anoxic conditions. Using a 1:15 rock mass:fluid volume ratio for every extraction, samples were shaken twice for about three hours on a rotary mixer, then centrifuged at 4500 rcf for four to ten minutes after each shake. The supernatant was decanted into labelled extractant tubes. Samples were rinsed three times with 5 mL N_2 -purged ultrapure water to rid the previous extractant and centrifuged on the same settings. The supernatant was decanted into labelled extractant tubes. All supernatants from the same extraction were combined into the same labelled centrifuge tubes for each different sample. These extractants were syringe-filtered with a 0.45 μm membrane if necessary. After analyzing the anions, extractants were acidified with a few drops of 20% nitric acid for analysis of cations. Figure 5 (Appendix) summarizes these extraction processes. The soil pellet was used in the next extractant solution, and this rinsing-extraction procedure was conducted sequentially using the four extraction solutions. Two separate sets of sequential extractions were conducted. However, only anion data from the first fraction of the second sequential extraction has been recorded.

2.3. Analytical techniques

Extractant solutions from the sequential extractions were analyzed for anions by ion chromatography (IC) and cations by inductively coupled plasma mass spectrometry (ICP-MS). The first set of extractant solutions from the water soluble fraction were analyzed for their conductivities by a SevenExcellence conductivity meter. The second set of extractant solutions from the water soluble fraction were analyzed for their conductivities and redox.

Results and discussion

The cation and anion concentrations of different elements mobilized by the sequential extractions is shown in Table 3 and Table 4 (Appendix). The elements mobilized vary tremendously on their geochemical affinities and the fractions extracted by the different solutions. Of the cation concentrations, water-soluble, chloride-complexing cations, such as sodium are preferentially

released by ultrapure water. A range of 52% to 98% of the Na leached came from the water-soluble extraction. Calcium was only recorded in the water-soluble fraction.

Of the alkaline earth metals, such as strontium and barium, there was variation in their mobilization due to the sequential extractions. Figure 6 (Appendix) shows the fraction of Na, Ba, and Sr extracted from each leaching solution relative to the total amount extracted by all four leaches combined. Sr is extracted in either the exchangeable sites on clays (up to 81%) or carbonate minerals (up to 83%). Notably, Ba, which is highly concentrated in water produced from Marcellus Shale natural gas wells, is held mainly in the exchangeable sites on clays (73% to 91%) for most of the samples. One sample from the Salina Group and Middle Ordovician formations each had barium extracted from either both the exchangeable sites and carbonates fractions (MO6) or mainly the carbonate fraction (SG1). Although X-ray diffraction was not done on any of the rock samples, this trend may be because these samples do not have high clay content. The Salina Group sample may contain mainly evaporate while the Middle Ordovician sample was from the Black River Limestone, most likely containing mainly calcium carbonate. Excluding those samples, this suggests that Ba has a strong affinity for charged surfaces on clay minerals. Barite (BaSO_4) should not dissolve by the leaching solutions used in this study, which is consistent with its known dissolution behavior (Paytan et al., 1993).

Bromide, chloride, and sulfate were analyzed in the ultrapure water leaches only. Cl is present at levels roughly equivalent to Na (mass Na/Cl ratio average of all samples: 0.7; Marcellus Shale samples: 1.2; Utica Shale samples: 0.7). The high sulfate concentrations leached from the rock samples may have made it more difficult to leach Ba. The sulfate mass content in all rock samples averaged to about 2444 $\mu\text{g SO}_4/\text{g sample}$ (33.7 mg/L). The high sulfate leached from the rock samples may have been due to precipitation in the extractant centrifuge tubes while waiting in the refrigerator before analysis as well as the sequential extraction conditions not being anoxic enough. It may be better to complete these extractions in a glovebox and acidify samples as soon as possible to eliminate most pathways for sulfate to form. Under reducing, deep subsurface conditions, it may be possible to extract greater quantities of soluble and exchangeable Ba from the rock as long as sulfate levels remain low (i.e. by bacterial sulfate reduction), suppressing barite precipitation (Stewart et al., 2015).

Sodium, barium, bromide, and chloride released from the Marcellus Shale and Utica Shale samples are shown in Figure 7 (Appendix). Utica Shale samples released higher concentrations of Na, Br, and Cl than Marcellus Shale samples. Marcellus Shale sample, MS3, released an overwhelming amount of Ba (556 $\mu\text{g/g sample}$) compared to the other samples. This sample was the only Marcellus Shale sample from Pennsylvania while the other Marcellus sample was from Ohio along with the Utica samples.

The conductivities of rock samples were analyzed and plotted in Figure 8 (Appendix). The average conductivity among rock samples was 0.3 mS/cm, the highest being 2.7 mS/cm from a Salina Group rock sample (SG2). The average redox among rock samples was 176.1 mV, the highest being 244.2 mV from the Precambrian rock sample (P1). The Utica Shale samples averaged higher conductivities and redox than the Marcellus Shale samples.

It is possible Na, Br, and Cl may be leached from rock dissolution. Dilution and mixing of original formation brines with injected fracking fluid can be expressed in Figure 9 (Appendix). Researchers including Dresel and Rose (2010), Haluszczak et al. (2013), and Ziemkiewicz et al. (2015) use a Cl/Br plot to show the connection between conventional gas well brines and

seawater evaporation. The evaporation of seawater leads to increased Cl and Br during the initial evaporation and precipitation of calcite and gypsum. However, once halite precipitates out, the halite contains much lower Br than the associated brine (Haluszczak et al., 2013). This halite precipitation leads to a nearly horizontal path for the residual brine on the plot in Figure 9 (Appendix). Due to this effect, brines with high Br/Cl result from evaporation of seawater past the point of halite precipitation, and injected fracking fluid may then mix with these highly evaporated brines to produce brines plotting at Br values higher than that of seawater (Haluszczak et al., 2013). Figure 9 (Appendix) shows the Cl/Br ratio of produced water lies fairly below the seawater evaporation path, indicating dilution of original brine with injected fracking fluid. Produced water plots to the high-Br side of the seawater evaporation path, indicating that halite dissolution is not the major source of Cl in produced waters. If it were, produced waters would yield values with extremely high Cl/Br ratios (Haluszczak et al., 2013). In addition to the produced water data plotted against the seawater evaporation path, rock extraction data is also plotted, indicating a similar path as the produced water data. This trend shows that high brine in produced waters can instead result from injected fracking fluids dissolving salts from the rock formations.

Sodium and chloride released from the rock formations can be expressed in Figure 10 (Appendix). TDS in produced waters is not primarily due to simple congruent dissolution of halite. Congruent dissolution is the total dissolution of salt via basinal brines. It forms subsurface Na-Cl brines with high Cl contents and higher Br/Cl ratios compared to non-evaporite subsurface waters (Worden, 1996). Deviation from the 1:1 ratio line in Figure 10 (Appendix) indicates that either Na or Cl is sourced from rock dissolution of salts rather than formation brines. Most of the rock extracts fall below the 1:1 ratio line, indicating that more Cl is leached from the rock formation. The Utica Shale extracts leached slightly more Cl from the rock samples. However, Marcellus Shale extracts leached slightly more Na from the rock samples.

One of the major concerns for flowback and produced water is TDS removal. Analogously, Na, Cl, and Br were among the highest contaminants leached from the Marcellus Shale and Utica Shale samples. Fortunately, industrial-grade wastewater treatment facilities are able to handle high TDS in shale produced waters, and their usage rate has remained fairly constant (Rodriguez and Soeder, 2015). Treated water from industrial facilities can be reused or discharged into surface waters. In Pennsylvania, the total rate of recycling increased from 13% to 72% as of 2011 (Rodriguez and Soeder, 2015).

Other wastewater treatment options, like deep underground injection, are ruled out frequently. Marcellus Shale gas development occurs in many areas where insufficient disposal wells are available, and the construction of new disposal wells is complex, time-consuming, and costly (Abualfaraj et al., 2014). Discharge and dilution of flowback and produced water into publicly owned municipal wastewater treatment plants (POTWs) has been utilized. However, the amount of TDS in these waters that can be accepted is limited (Gregory et al., 2011). For example, in Pennsylvania, the amount of oil and gas wastewater must not exceed one percent of the average daily volume of waste handled by the POTW (Gregory et al., 2011). Chemical precipitation processes, such as coagulation and flocculation, can be used to remove suspended solids and inorganic-scale-forming compounds, but are not effective for removing dissolved solids (Abualfaraj et al., 2014). A study of shale gas wastewater effluent from publicly owned treatment facilities found that even after treatment through filtration or flocculation, certain inorganic solids remained at unacceptable mean and maximum concentrations when compared

with various drinking water standards (Ferrar et al., 2013). While organic compounds may have been removed to acceptable levels, inorganics, such as magnesium, chloride, and TDS, were not reduced to drinking water MCLs after undergoing various physical treatment processes for 8–12 hours of residence time (Ferrar et al., 2013). Bromide concentrations in TDS can be concerning as well. While Br is not harmful as a diluted salt, it reacts with chlorine during the water treatment process to create trihalomethane, a known carcinogen (Rodriguez and Soeder, 2015).

Conclusions

There are two main proposed reaction mechanisms for mobilizing salts and metals in the Marcellus Shale, Utica Shale, and surrounding formations: (1) injected fracking fluids mixing with historic and migrated formation brines and salts, and, (2) injected fracking fluids mixing with the rock formation to dissolve associated salts and metals.

The main conclusions of this research are:

1. Multiple reaction mechanisms release and leach salts and metals from the target rock formation, e.g. dilution and mixing of formation brines (Dresel and Rose, 2010), rock dissolution of salts, dolomitization (Haluszczak et al., 2013), sulfate reduction (Haluszczak et al., 2013), and induced micro-fractures in rock (Renock et al., 2016).
2. Elements such as Na, Br, and Cl can be leached from rock dissolution of salts as indicated by graphical relationships and trends.
3. Utica Shale produced waters have the potential to be saltier and contain higher concentrations of elements such as Br and Cl than Marcellus Shale produced waters. Na, Br, and Cl leached from Utica Shale samples is higher than those leached from Marcellus Shale samples.

The characterization of more Pennsylvanian drill cores of Marcellus Shale and Utica Shale is needed. The analysis of these cores would aid in finding out more information on Utica Shale elemental release as well as explain the spike in barium extracted from the one Pennsylvanian Marcellus Shale sample (MS3).

Appendix

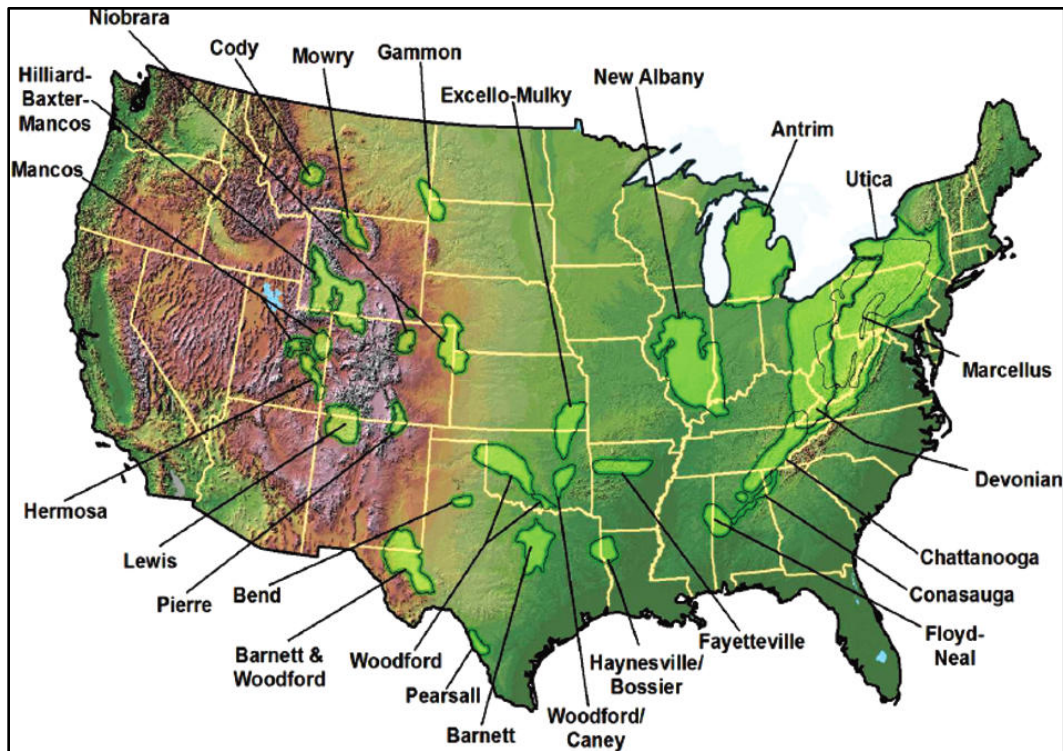


Figure 1: The locations of shale basins across the U.S. (Kargbo et al., 2010).

Constituent	Low (mg/L)	Medium (mg/L)	High (mg/L)
Total dissolved solids	66,000	150,000	261,000
Total suspended solids	27	380	3200
Hardness (as CaCO ₃)	9100	29,000	55,000
Alkalinity (as CaCO ₃)	200	200	1100
Chloride	32,000	76,000	148,000
Sulfate	No Data	7	500
Sodium	18,000	33,000	44,000
Calcium, total	3000	9800	31,000
Strontium, total	1400	2100	6800
Barium, total	2300	3300	4700
Bromide	720	1200	1600
Iron, total	25	48	55
Manganese, total	3	7	7
Oil and grease	10	18	260
Total radioactivity	No Data	No Data	No Data

Table 1: Typical range of common constituents in flowback water from natural gas development in the Marcellus shale formation (Gregory et al., 2011).

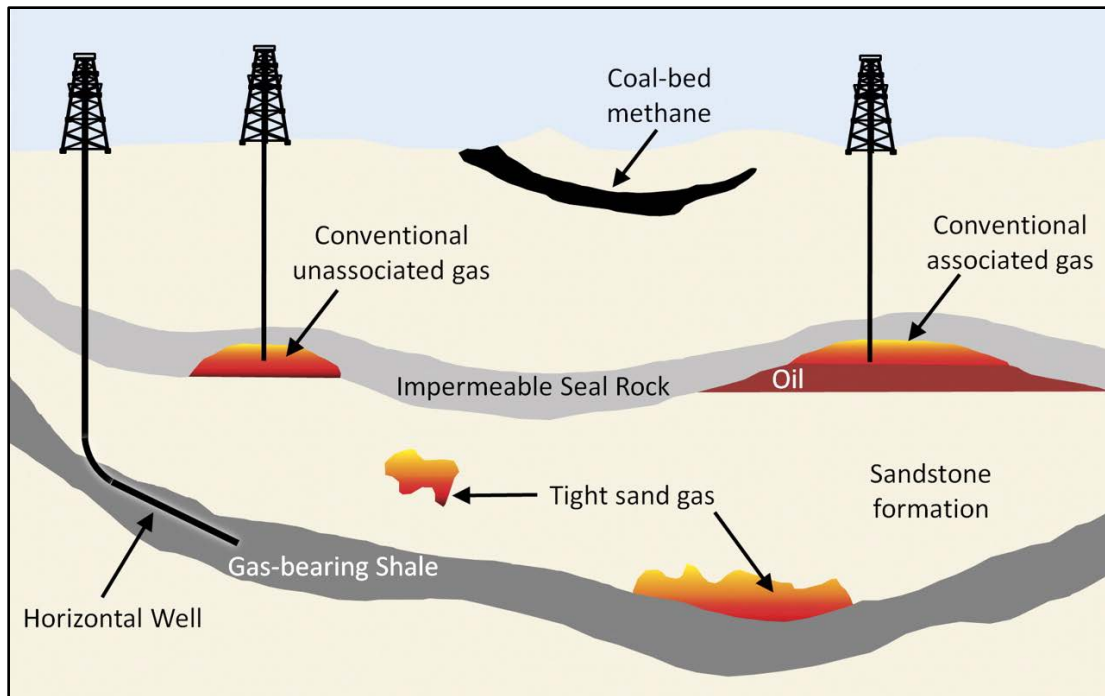


Figure 2: The types and common orientations of onshore natural gas resources (Gregory et al., 2011).

359 MYA	Devonian	Ohio Shale	Key
		Genesee/Sonyea/West Falls/Java Fms	
		Tully Limestone	
		Hamilton Grp/Mahantango Sandstone	
		Marcellus Shale Formation	
		Onondaga Limestone	
		Bois Blanc Fm/Huntersville Chert	
		Ridgeley Sandstone	
		Helderberg Group	
		416 MYA	
	Salina Group		
	Lockport Dolomite/McKenzie Fm		
	Clinton Group		
443 MYA	Ordovician	Medina Grp/Tuscarora Fm	Cap rocks Pay zone Basement
		Queenston Shale	
		Reedsville Shale	
		Utica Shale Formation	
		Trenton/Black River/Point Pleasant Fms	
	Loysburg		
448 MYA		Beekmantown Group	

Figure 3: The generalized stratigraphic nomenclature representing Devonian, Silurian, and Ordovician rocks. The key highlights which formations overlie (cap rock) and underlie (basement) the Marcellus Shale and Utica Shale formations (pay zone). The key also highlights the suggested source of brines in the Marcellus Shale.

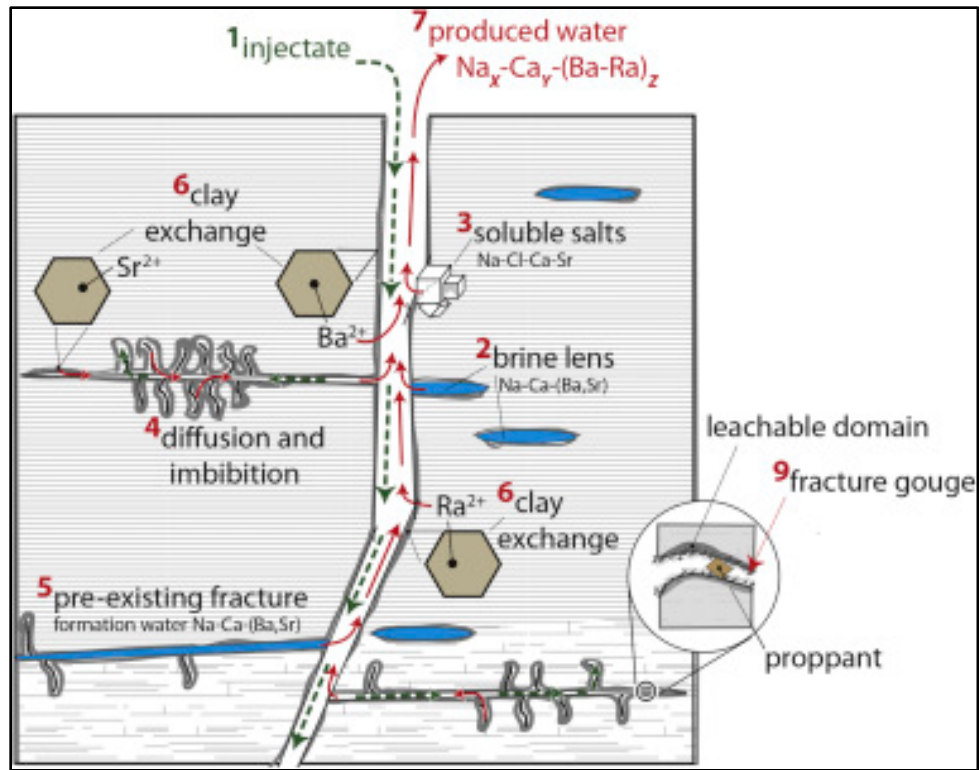


Figure 4: The possible mechanisms contributing to the generation of produced water alkaline-earth (i.e. Ca, Sr, Ba, Ra) cation composition (Renock et al., 2016).

Sample ID	Formation	Age	Depth (ft)	Location	GPS	Core #	Core ID
M 1	Big Lime	M	4148	Ohio	39.7137 -81.4619	2936	4
M 2	Berea Sandstone	M	808	Ohio	40.7710 -81.4098	991	6
SG 1	Salina Group	UD	1645	Ohio	38.5943 -82.8220	3409	2
UD 1	Kope Formation	UD	943	Ohio	40.5873 -83.2407	3372	3
UD 2	Angola Shale	UD	3618	Ohio	39.7137 -81.4619	2936	4
UD 3	Rhinestreet Shale Mahantango	UD	3838	Ohio	39.7137 -81.4619	2936	4
MD 1	Sandstone	MD	5108	PA	41.8688 -78.6124	EGSP #1	
MS 1	Marcellus Shale	MD	4131	Ohio	39.7137 -81.4619	2936	4
MS 2	Marcellus Shale	MD	4135	Ohio	39.7137 -81.4619	2936	4

MS 3	Marcellus Shale	MD	5162.5	PA	41.8688	EGSP		
	Onondaga				-78.6124	#1		
MD 2	Limestone	MD	4138	Ohio	39.7137		2936	4
	Onondaga				41.8688	EGSP		
MD 3	Limestone	MD	5211.3	PA	-78.6124	#1		
					40.7710			
SG 2	Salina Group	S	3557	Ohio	-81.4098		991	6
					40.5873			
UO 1	Queenston	UO	672	Ohio	-83.2407		3372	3
					40.5873			
UO 2	Queenston	UO	428	Ohio	-83.2407		3372	3
					39.5659			
US 1	Utica Shale	MO	839	Ohio	-84.1160		2627	1
					39.5659			
US 2	Utica Shale	MO	849	Ohio	-84.1160		2627	1
					39.5659			
US 3	Utica Shale	MO	859	Ohio	-84.1160		2627	1
					39.5659			
US 4	Utica Shale	MO	893	Ohio	-84.1160		2627	1
					40.5873			
US 5	Utica Shale	MO	1144	Ohio	-83.2407		3372	3
					39.5659			
MO 1	Point Pleasant	MO	819	Ohio	-84.1160		2627	1
					39.5659			
MO 2	Point Pleasant	MO	829	Ohio	-84.1160		2627	1
					40.5873			
MO 3	Point Pleasant	MO	1344	Ohio	-83.2407		3372	3
					39.5659			
MO 4	Trenton	MO	927	Ohio	-84.1160		2627	1
	Black River				39.5659			
MO 5	Limestone	MO	1090	Ohio	-84.1160		2627	1
	Black River				40.5873			
MO 6	Limestone	MO	1546	Ohio	-83.2407		3372	3
					39.5659			
P 1	Precambrian	P	3458	Ohio	-84.1160		2627	1

Table 2: A list of all core samples and their corresponding formation names, depths, and locations used in the sequential extractions. Organized by geologic period. SG: Salina Group. UD: Upper Devonian. MD: Middle Devonian. MS: Marcellus Shale. UO: Upper Devonian. US: Utica Shale. MO: Middle Ordovician. P: Precambrian.

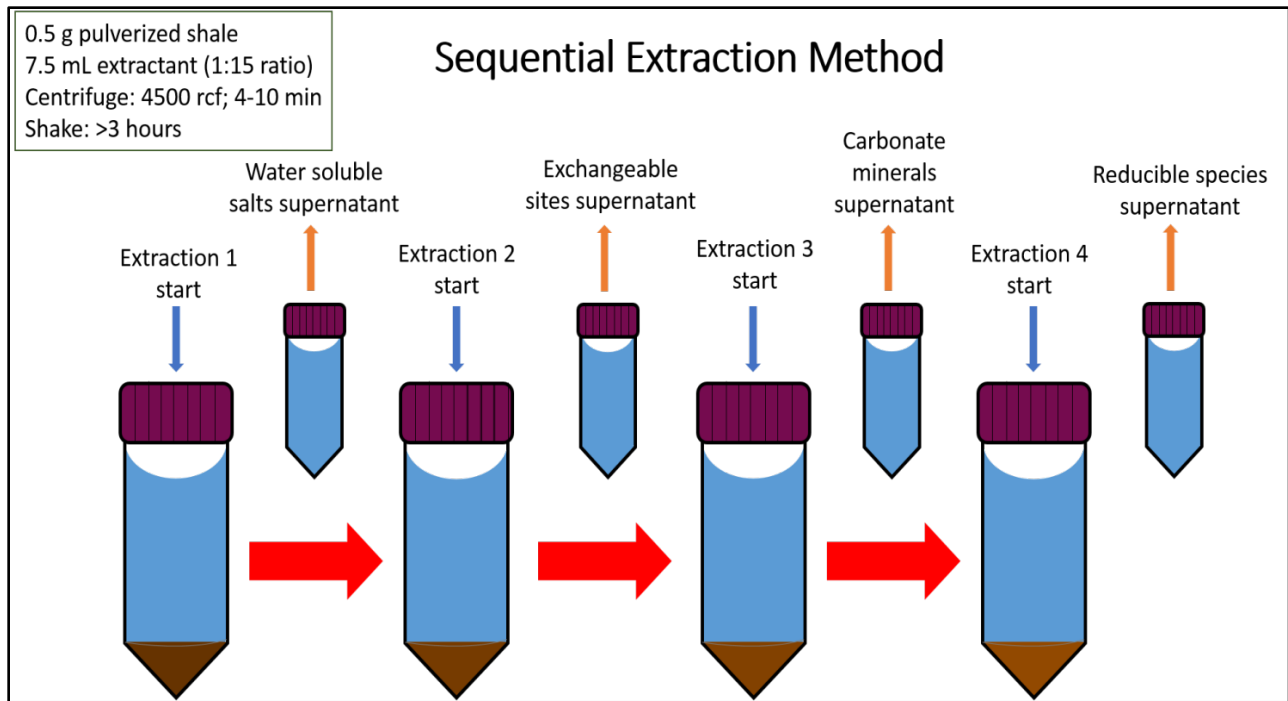


Figure 5 Legend

Extraction 1	N ₂ purged MQW
Extraction 2	N ₂ purged 1 N ammonium acetate buffered to pH 8
Extraction 3	N ₂ purged 8% acetic acid
Extraction 4	N ₂ purged 0.5 N hydroxylamine hydrochloride in 25% acetic acid
Analysis on Extractions	IC: analyzes anions in water soluble fraction ICP-MS: analyzes cations in all fractions
Extraction 1 Only Analysis	Conductivity and redox measurements

Figure 5: This diagram and corresponding legend show a simplified version of the sequential extraction method.

Sample	Target Matrix	μg / g sample	Na	Al	Ca	Mn	Fe	Co	Sr	Ba	U	Depth (ft)
SG 1	Salts	124.44	1.11	184.71	0.02	-	0.12	4.46	-	0	1645	
	Exchange	20.85	5.66	-	0.34	-	0.04	7.24	0.34	0.02	-	
	Carbonates	55.86	30.94	-	33.41	264.20	0.05	20.85	23.46	0.27	-	
	Reducible	21.39	6.85	-	4.50	47.19	0.01	3.57	0.07	0.06	-	
	Σ	222.55	44.56	-	38.26	311.40	0.22	36.11	23.86	0.35		
UD 3	Salts	1077.83	18.47	144.15	0.10	-	-	4.64	0.05	0	3838	
	Exchange	43.00	3.74	-	40.36	0.12	0.07	30.12	15.02	0.03	-	
	Carbonates	10.24	179.98	-	74.22	587.57	0.53	1.80	0.41	0.02	-	
	Reducible	56.40	222.38	-	4.20	533.52	0.39	0.41	0.97	0.01	-	
	Σ	1187.47	424.56	-	118.89	1121.22	0.99	36.97	16.45	0.06		
MD 1	Salts	551.81	35.04	483.66	0.24	3.43	-	29.40	2.24	0.011	5108	
	Exchange	155.84	8.14	-	5.28	0.68	0.06	39.59	161.91	0.06	-	
	Carbonates	39.02	251.96	-	51.49	597.80	0.46	44.44	4.38	0.13	-	
	Reducible	41.68	181.42	-	2.25	526.94	0.51	1.51	10.92	0.02	-	
	Σ	788.35	476.56	-	59.26	1128.86	1.04	114.93	179.46	0.22		
MS 2	Salts	917.18	19.28	256.91	0.09	0.47	0.01	25.95	0.18	0.004	4131	
	Exchange	24.07	5.36	-	8.75	0.14	0.14	51.91	16.24	0.09	-	
	Carbonates	18.26	149.89	-	30.43	441.27	0.69	14.67	0.29	0.09	-	
	Reducible	13.25	125.70	-	1.90	463.21	1.48	1.06	1.76	0.02	-	
	Σ	972.76	300.22	-	41.18	905.09	2.33	93.59	18.46	0.21		
MS 3	Salts	690.95	13.71	988.54	0.55	8.33	0.03	47.79	8.76	0.749	5162.5	
	Exchange	24.71	4.36	-	4.28	-	0.10	49.25	475.21	0.96	-	
	Carbonates	6.50	69.10	-	4.02	129.89	0.31	2.53	16.17	0.17	-	
	Reducible	21.00	107.93	-	2.22	956.78	1.46	2.43	55.50	0.40	-	
	Σ	743.17	195.10	-	11.07	1095.01	1.91	102.01	555.64	2.28		
MD 2	Salts	773.15	19.13	257.06	0.13	0.36	-	27.57	0.06	0.003	4138	
	Exchange	20.35	5.98	-	8.19	0.36	0.10	44.12	9.12	0.06	-	
	Carbonates	47.22	150.39	-	78.49	736.19	0.48	48.10	1.45	0.19	-	
	Reducible	11.77	79.63	-	1.41	335.39	0.73	1.16	2.17	0.02	-	
	Σ	852.49	255.13	-	88.23	1072.31	1.31	120.95	12.80	0.27		
MD 3	Salts	116.88	20.98	367.88	0.18	2.27	0.002	13.52	0.07	0.037	5211.3	
	Exchange	14.55	4.51	-	0.64	-	0.08	15.25	2.61	0.28	-	
	Carbonates	20.63	13.97	-	11.22	67.54	0.07	27.21	0.32	0.25	-	
	Reducible	10.27	19.24	-	0.24	141.08	0.18	0.99	0.67	0.10	-	
	Σ	162.33	58.69	-	12.28	210.89	0.34	56.98	3.67	0.66		
UO 1	Salts	680.19	10.90	185.80	0.04	-	-	4.09	-	0.002	428	
	Exchange	9.59	2.07	-	4.75	0.11	0.07	12.15	2.59	0.05	-	
	Carbonates	23.87	141.44	-	100.72	467.81	0.66	21.74	0.30	0.06	-	

	Reducible	12.57	116.31	-	2.31	299.47	0.54	0.87	0.66	0.02	-
	Σ	726.21	270.71	-	107.81	767.38	1.28	38.85	3.55	0.13	
US 2	Salts	2468.57	20.36	329.30	0.61	2.91	0.11	18.24	0.34	0.003	849
	Exchange	25.86	2.45	-	11.49	0.10	0.09	55.23	12.24	0.04	-
	Carbonates	21.21	249.97	-	83.80	766.25	0.91	64.26	0.46	0.05	-
	Reducible	12.09	179.18	-	3.71	433.24	0.50	2.77	1.08	0.03	-
	Σ	2527.72	451.97	-	99.61	1202.50	1.61	140.50	14.12	0.13	
US 5	Salts	1608.96	5.86	598.12	0.80	-	-	14.34	0.23	0.010	1144
	Exchange	23.15	1.65	-	23.53	0.07	0.18	33.83	9.01	0.11	-
	Carbonates	20.89	119.27	-	54.92	466.16	0.81	10.98	0.28	0.12	-
	Reducible	12.93	140.07	-	7.63	810.49	1.25	1.78	0.91	0.07	-
	Σ	1665.94	266.85	-	86.88	1276.72	2.25	60.92	10.42	0.31	
MO 4	Salts	1482.42	22.25	325.99	0.06	-	-	13.49	0.15	0.003	927
	Exchange	32.51	4.87	-	5.55	0.15	0.05	57.52	13.98	0.04	-
	Carbonates	23.79	468.09	-	75.58	1039.14	0.86	64.65	0.64	0.06	-
	Reducible	23.25	395.53	-	5.49	724.53	0.64	4.05	2.53	0.05	-
	Σ	1561.97	890.74	-	86.67	1763.82	1.55	139.72	17.30	0.16	
MO 6	Salts	84.04	24.04	195.49	0.06	-	-	7.07	-	0.002	1546
	Exchange	18.06	7.51	-	0.52	0.04	0.11	23.17	0.90	0.02	-
	Carbonates	37.56	66.69	-	55.71	220.84	0.16	149.14	0.73	0.04	-
	Reducible	23.46	20.98	-	0.18	35.93	0.03	0.17	0.17	0.01	-
	Σ	163.11	119.22	-	56.46	256.81	0.30	179.55	1.80	0.07	

Table 3: Metal concentrations extracted from Marcellus Shale, Utica Shale, and corresponding surrounding formations for targeted fractions. Dash signifies below detection level. na: Not Analyzed. SG: Salina Group. UD: Upper Devonian. MD: Middle Devonian. MS: Marcellus Shale. UO: Upper Devonian. US: Utica Shale. MO: Middle Ordovician.

Sample	Conductivity (mS/cm)	Redox (mV)	Cl (ug/g)	Br (ug/g)	SO ₄ ⁻ (ug/g)	Depth (ft)
M 1	0.113	156.8	495.06	1.92	344.75	4148
M 2	0.134	213.2	1278.07	3.85	105.77	808
SG 1	0.125	113.60	437.62	25.2	103.72	1645
UD 1	0.203	165.3	1729.8	11.2	368.29	943
UD 2	0.195	159.6	1357.92	14.59	720.75	3618
UD 3	0.166	164.20	1765.02	36.93	524.28	3838
MD 1	0.176	nd	616.68	25.73	3643.94	5108
MS 1	0.205	164.5	736.02	6.18	1938.4	4135
MS 2	0.220	158.60	798.92	27.46	2068.98	4131
MS 3	0.289	nd	584.88	24.14	7888.18	5162.5
MD 2	0.129	nd	884.98	26.15	1551.72	4138
MD 3	0.091	nd	307.24	23.97	1214.67	5211.3
SG 2	2.716	203.8	6069.22	nd	86083.7	3557
UO 1	0.140	227.50	936.16	26.62	754.41	428
UO 2	0.677	211.3	3400.8	21.62	10281.6	672
US 1	0.346	171.4	2147.42	18.43	3548.28	839
US 2	0.343	164.40	3393.13	67.99	2837.07	849
US 3	0.344	157.8	2168.21	17.27	3241.4	859
US 4	0.313	172.6	2326.33	18.07	2258.79	893
US 5	0.470	178.00	2763.92	37.31	5388.73	1144
MO 1	0.247	187.3	2176.12	17.71	1117.10	819
MO 2	0.351	161.8	2466.14	17.68	2113.43	829
MO 3	0.210	159.1	1206.61	8.09	1351.07	1344
MO 4	0.232	nd	1944.09	35.25	3251.43	927
MO 5	0.076	163.8	231.05	0.38	185.81	1090
MO 6	0.061	nd	160.69	nd	101.78	1546
P 1	0.145	244.2	1727.09	12.39	81.47	3458

Table 4: Conductivities, redox, and anion concentrations extracted from Marcellus Shale, Utica Shale, and corresponding surrounding formations for targeted fractions. nd: No Data. SG: Salina Group. UD: Upper Devonian. MD: Middle Devonian. MS: Marcellus Shale. UO: Upper Devonian. US: Utica Shale. MO: Middle Ordovician.

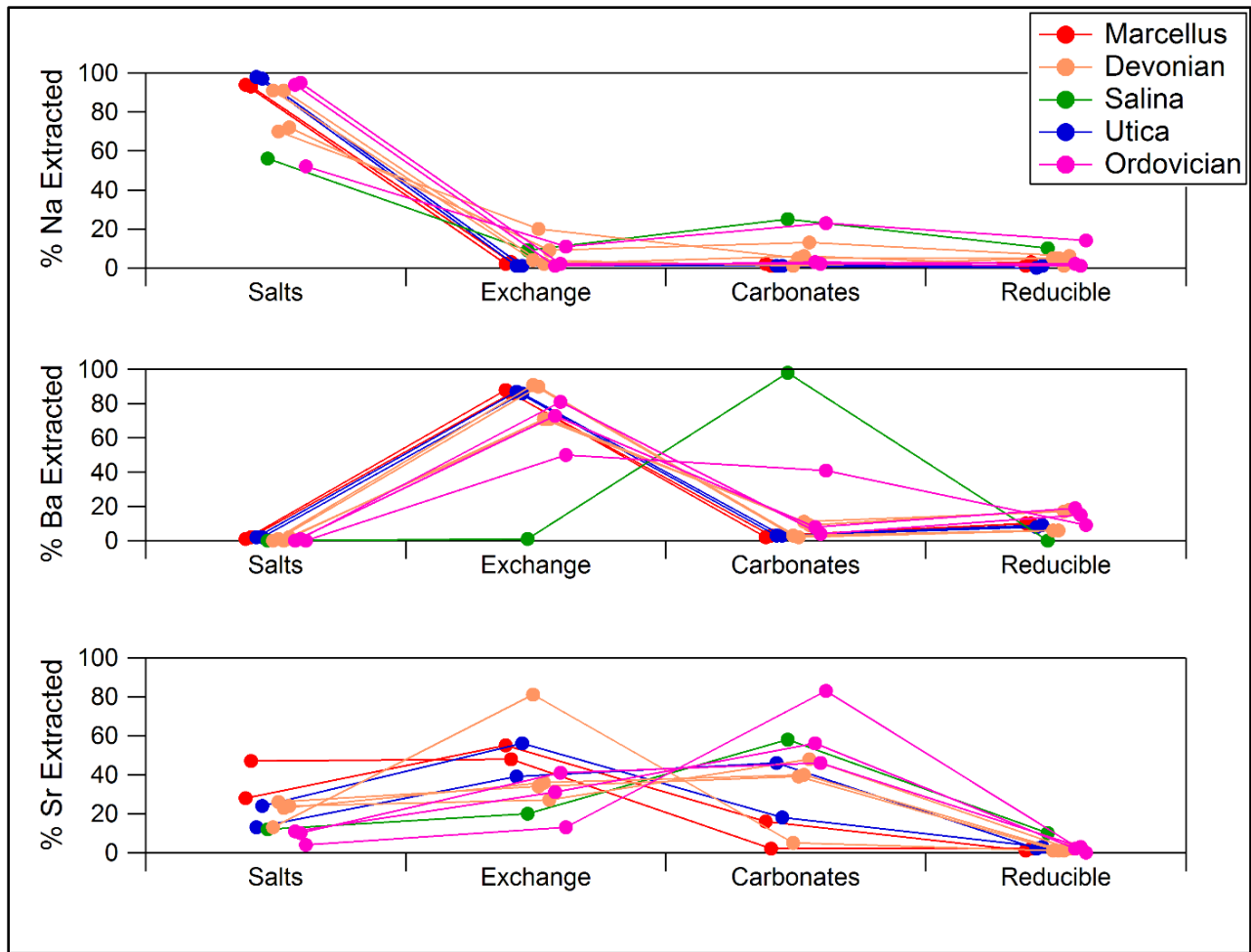


Figure 6: Na, Ba, and Sr extracted from each leaching fraction relative to the total amount extracted by all four leaches combined. Na is mainly leached from water-soluble salts. Ba is mainly leached from exchangeable sites on clays. Sr is mainly leached from both exchangeable sites and carbonates.

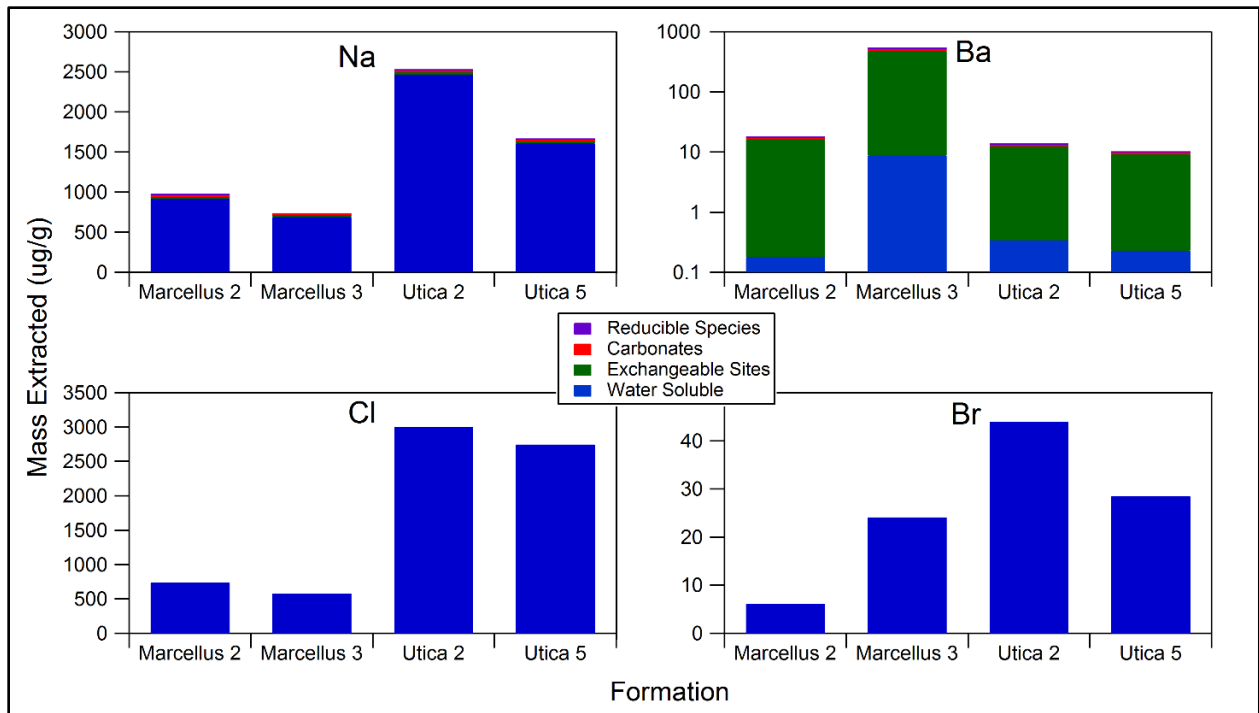


Figure 7: Mass content of Na, Ba, Cl, and Br released from sequential extractions. Na and Ba were analyzed in all four fractions. Cl and Br were analyzed in the water soluble fraction. Ba is plotted on a log scale to show lower values. Marcellus 2 and Marcellus 3 correspond to sample IDs MS2 and MS3. Utica 2 and Utica 5 correspond to sample IDs US2 and US5.

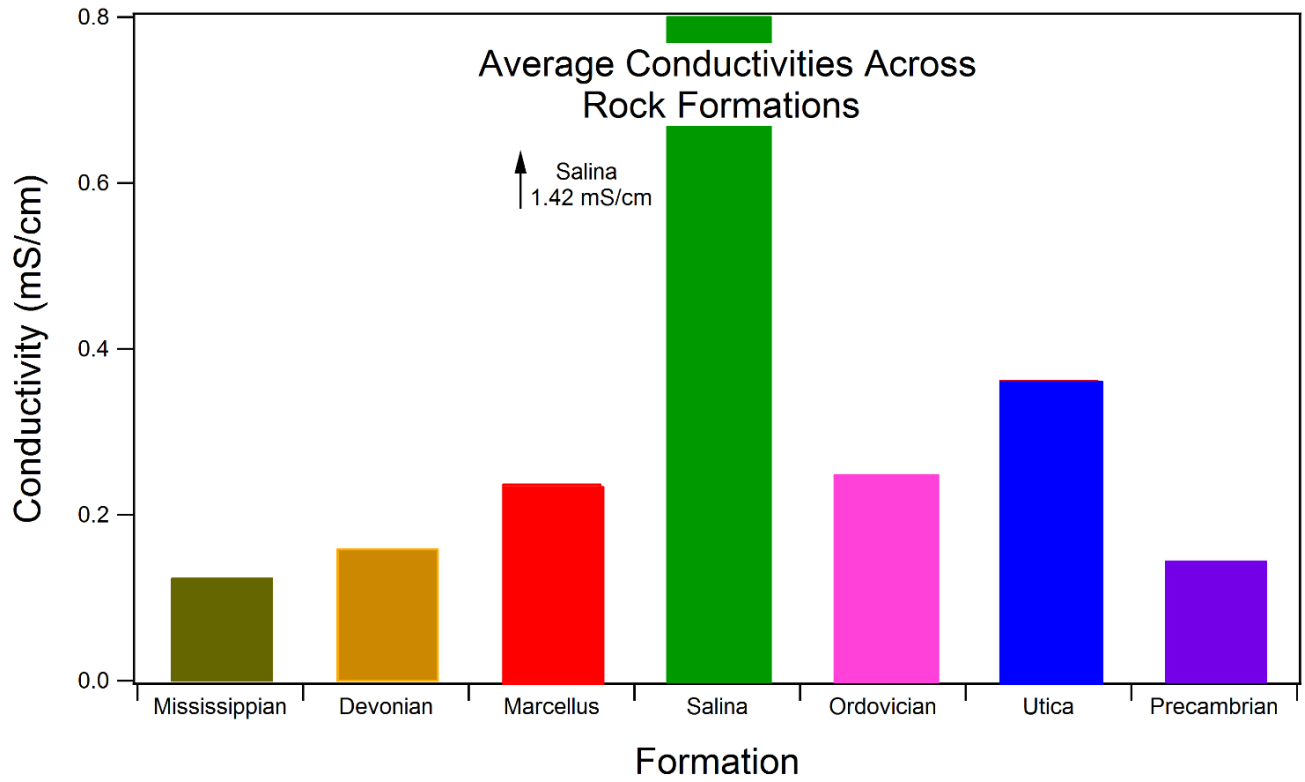


Figure 8: The average conductivities of the rock samples from the water-soluble fraction. The Salina Group samples (SG1 and SG2) had the highest average conductivity.

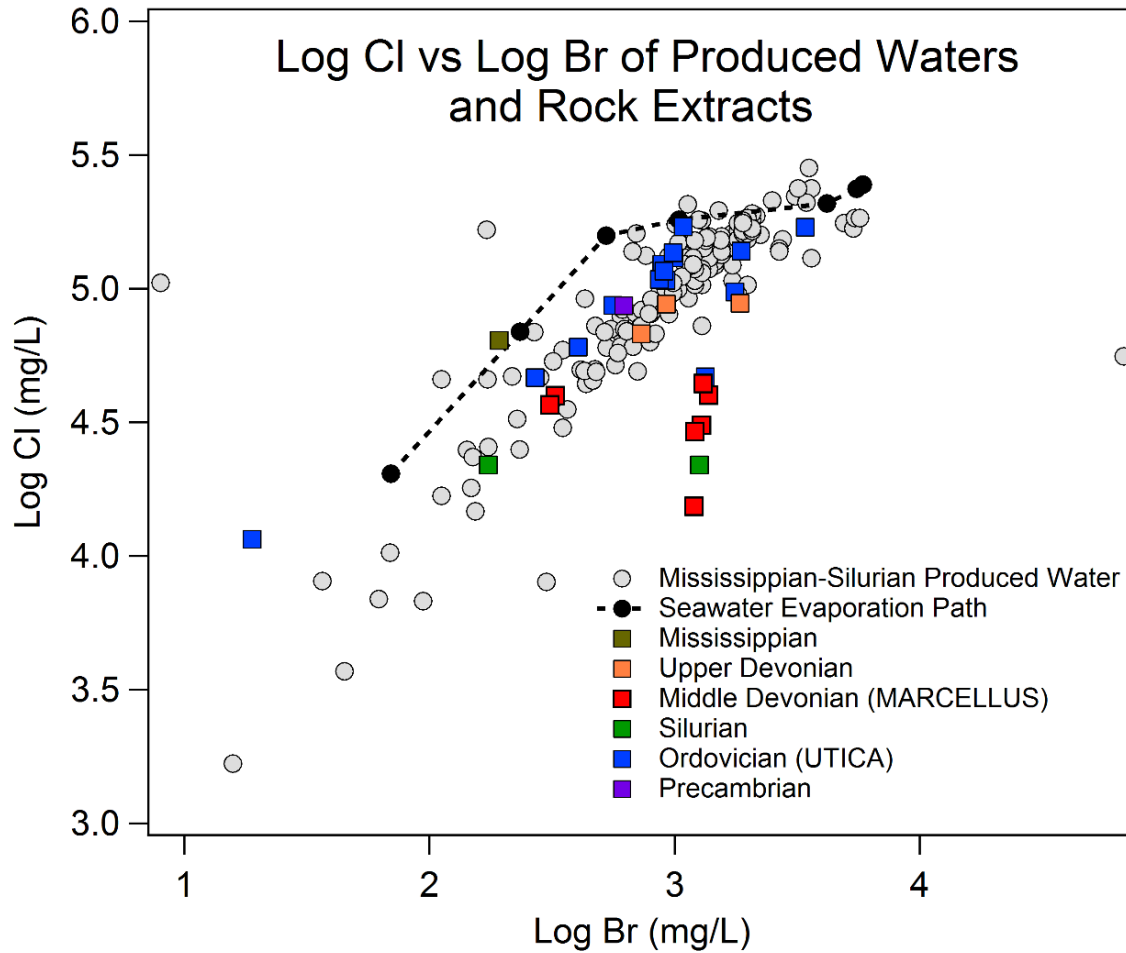


Figure 9: Plot of Log Cl vs Log Br, indicating the path of the evaporation of seawater (dashed line). Produced water data (grey dots) and rock extracts (colored squares) are plotted as well. Utica Shale rock samples follow the trend the best. Rock extracts are plotted as a 50:1 rock:fluid ratio.

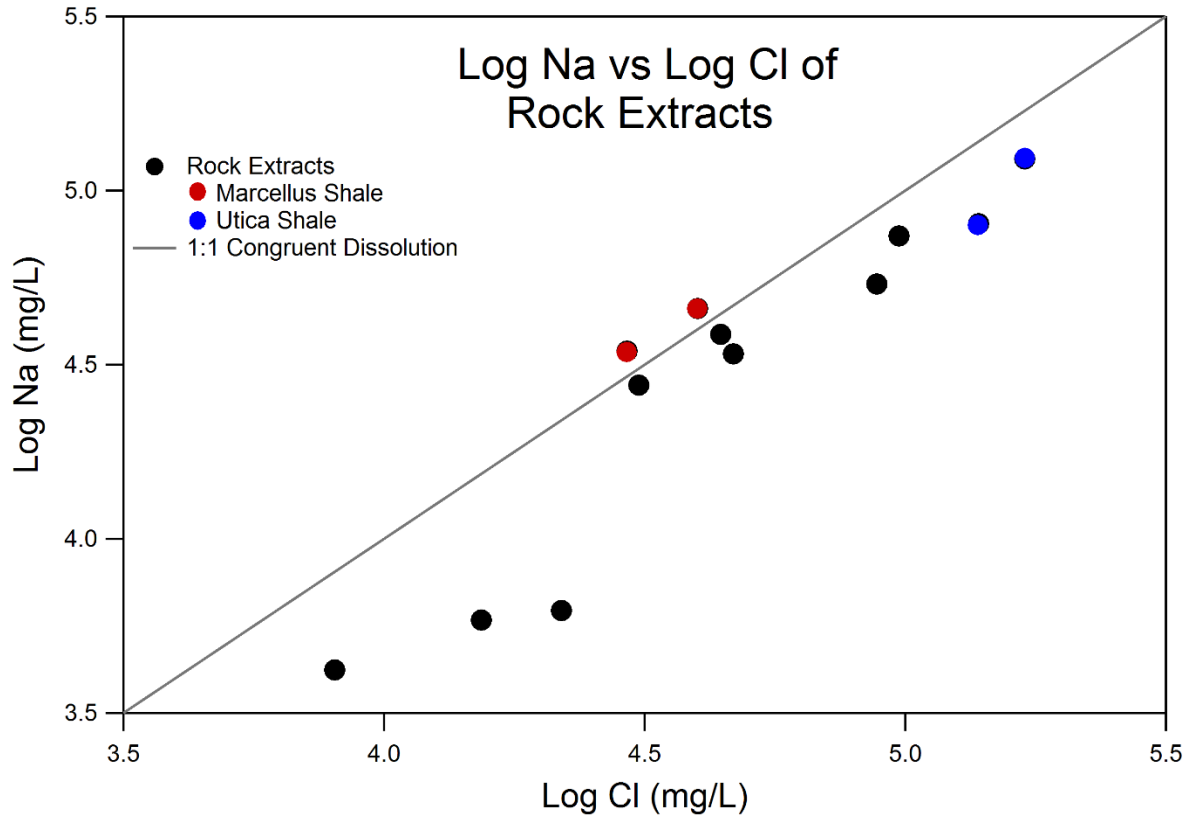


Figure 10: Plot of Log Na vs Log Cl, indicating the role rock dissolution plays in leaching these elements from the rock samples in the sequential extractions. Na may be leached from Marcellus Shale rock while Cl may be leached from Utica Shale rock. Deviation from the 1:1 line indicates that either Na or Cl is being sourced from a reaction mechanism different from historic formation brines. Rock extracts are plotted as a 50:1 rock:fluid ratio.

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