Origin of brines, salts and carbonate from shales of the Marcellus Formation: Evidence from geochemical and Sr isotope study of sequentially extracted fluids

Brian W. Stewart^{1*}, Elizabeth C. Chapman^{1†}, Rosemary C. Capo¹, Jason D. Johnson², Joseph R. Graney², Carl S. Kirby³, Karl T. Schroeder⁴

¹Department of Geology & Planetary Science, University of Pittsburgh, Pittsburgh, PA 15260

²Department of Geological Sciences, Binghamton University, Binghamton, NY 13850

³Department of Geology, Bucknell University, Lewisburg, PA 17837

⁴National Energy Technology Laboratory, U.S. Department of Energy, 626 Cochran Mill Rd., Pittsburgh, PA 15236

*Corresponding author: ph. 412-624-8883; fax 412-624-3914; bstewart@pitt.edu

†Current address: Echelon Applied Geoscience Consulting, 1229 Twelve Oaks Ct., Murrysville, PA 15668, USA

ABSTRACT

Fluids co-produced with methane from hydraulically fractured organic-rich shales of the Marcellus Formation (USA) are characterized by high total dissolved solids (TDS), including elevated levels of Ba, Sr and Br. To investigate the source and geologic history of these high-TDS fluids and their dissolved constituents, we carried out a series of sequential extraction experiments on dry-drilled cuttings extracted within, below and above the Marcellus Shale from a well in Tioga County, New York State. The experiments were designed to extract (1) water soluble components, (2) exchangeable cations, (3) carbonate minerals, and (4) hydrochloric acid-soluble constituents. The geochemistry of the resultant leachates highlights the different geochemical reservoirs for extractable elements within the shale; notably, Na and Br were largely water-soluble, while Ba was extracted primarily from exchangeable sites, and Ca and Sr were found both in exchangeable sites and carbonate. Strontium isotope ratios measured on the leachates indicate that each of the element reservoirs has a distinct value. Measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the water soluble component are similar to those of Marcellus produced water, while the ion exchange reservoir yields lower ratios, and carbonate Sr is lower still, approaching Devonian-Silurian seawater values. Despite the isotopic similarity of water leachates and produced water, the total water chemistry argues against generation of produced water by interaction of hydraulic fracturing fluid with “dry” shale. The high-TDS produced water is most likely trapped formation water (within and/or adjacent to the shale) that is released by hydraulic fracturing. The formation water was affected by multiple processes, possibly including basin scale, tectonically-driven fluid flow. Significant chemical and isotopic differences between Marcellus Shale produced water and overlying Upper Devonian/Lower Mississippian produced waters suggests a hydrologic barrier has been maintained in parts of the Appalachian Basin since the late Paleozoic.

1. Introduction

Recent improvements in natural gas drilling and extraction techniques have led to a boom in natural gas exploration from shale units previously considered too impermeable for methane production, including the Middle Devonian Marcellus Formation in the central-eastern United States (Fig. 1). The methane in these organic-rich shales, which serve as both the source and reservoir for hydrocarbons, is accessed through a combination of hydraulic fracturing to provide permeability for gas migration, and directional drilling to maximize the fractured volume of source rock sampled at each borehole. Hydraulic fracturing involves high-pressure injection of 11 to 26 million liters of fluid (Harper, 2008; King, 2012; Maloney and Yoxtheimer, 2013) in multiple stages. The injected fluid is primarily water (>99% by volume; Ground Water Protection Council and ALL Consulting, 2009), but additional additives are used in different stages, including hydrochloric acid to clean cement out of the well perforations, a proppant such as quartz sand to hold open fractures created during injection, biocides, friction reducers, scale

Figure 1. Map of the subsurface extent of the Marcellus Shale natural gas play (shaded) in the eastern USA. Blue lines indicate outcroppings of the shale. Tioga County, New York State, from which the cuttings for this study were obtained, is outlined in red. Modified after Milici and Swezey (2006) and Kolesar Kohl et al. (2014).

inhibitors, corrosion inhibitors, and other components depending on the particular needs and company practice (Soeder et al., 2014).

When gas-producing shales of the Marcellus Formation (here referred to collectively as the “Marcellus Shale”) are hydraulically fractured, 10-50% of the injected fluid is returned to the surface via the wellhead (Vidic et al., 2013). Most of this fluid returns in the first few days after pressure is released on the well, while smaller volumes of fluid continue to flow as methane is produced. The level of total dissolved solids (TDS) rises rapidly in the first few days of water return, reaching levels of $1\text{--}3 \times 10^5$ ppm after 7-30 days (Hayes, 2009). 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 (Hayes, 2009; Rowan et al., 2011; Chapman et al., 2012; Haluszczak et al., 2013; Barbot et al., 2013).

The origin of the dissolved solids in the high-TDS produced water is an unresolved issue, with suggestions including dissolution of water-soluble salts in the shale formation, extraction of pore-bound water, diffusion osmosis, and accessing of formation water in shale fractures or adjacent formations (Blauch et al., 2009; Warner et al., 2012a; 2012b; Haluszczak et al., 2013; Capo et al., 2014; Engle and Rowan, 2014; Engelder et al., 2014; Balashov et al., 2015; Rowan et al., 2015). The Marcellus Formation was deposited in the Appalachian Basin, a restricted foreland basin at near-equatorial latitudes that formed in response to tectonic loading to the east (Quinlan and Beaumont, 1984; Beaumont et al., 1988; Ettensohn, 1985; 1992; 2004; Kohl et al., 2014). It overlies the Lower Devonian Onondaga Limestone, and is overlain by silts and shales of the Hamilton Group, which is capped by the Tully Limestone. The section continues upward into Upper Devonian and Lower Mississippian shales and conventional hydrocarbon-bearing sandstones. Oil and gas in these units is thought to be sourced primarily from the underlying Marcellus Shale (Milici and Swezey, 2006; Zagorski et al., 2012). The units underlying the Marcellus Formation include the hydrocarbon-bearing Ordovician Utica Shale, as well as Silurian Salina Series evaporites in the north, which transition to limestones, shales and sandstones in the south-southwestern part of the play (Carter, 2007).

Strontium isotope studies of Marcellus Shale produced water (Chapman et al., 2012; Warner et al., 2012a; Capo et al., 2014; Kolesar Kohl et al., 2014) demonstrated that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of waters collected over a wide region (~375 km) fall within a relatively restricted range of values, from 0.7101 to 0.7121. This suggests that there may be a basin-wide source for the dissolved load of the produced water. Moreover, all $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for Marcellus produced water reported to date exceed those of Phanerozoic seawater, so any inferred evaporated seawater source must have been augmented by addition of a radiogenic (high $^{87}\text{Sr}/^{86}\text{Sr}$) component. Some studies suggest that stimulation of bacterial sulfate reduction and microbial dissolution of barite following hydraulic fracturing can vary the sulfate/alkalinity ratio (Engle and Rowan, 2014) and enhance Ba concentrations in produced water (Akob et al., 2015). Understanding the source of the co-produced fluid and its dissolved constituents can help to optimize extraction procedures, and can add constraints on some of the risks associated with shale gas extraction (Soeder et al., 2014; Vengosh et al., 2014). In addition, analysis of produced waters associated with hydraulic fracturing offers a unique opportunity to understand the origin of shale-derived fluids, and their relationship to produced water from “conventional” hydrocarbon extraction.

We report geochemical and Sr isotope data from a series of sequential leaching experiments carried out on drill cuttings from the Marcellus Shale and adjacent units. By selectively extracting different components of the shale (water-soluble, exchangeable, carbonate, and strong acid-soluble) we seek to understand (1) the geochemical trends exhibited by Marcellus produced water over time; (2) the origin of the high TDS levels in Marcellus produced water, and (3) the post-depositional fluid evolution history of the shale and its coexisting pore fluids and/or formation waters.

2. Methods

2.1. Samples

Dry-drilled cuttings from a vertical well extending through the Marcellus Shale in Tioga County, NY (Fig. 1) were collected in November 2009. Each sample represents a composite of excavated material; for units above and below the Marcellus Shale, the sampling interval was 9 m, while the sampling interval within the Marcellus Shale was 3 m (Johnson and Graney, 2015). For this study, we selected a subset of nine samples with median sampling depths ranging from 901 m to 1,434 m (Table 1). Based on a wireline log from a nearby well (<5 km away), the

Table 1

Sample information and results of semi-quantitative x-ray diffraction (XRD) and post-extraction mass loss.

Sample Name	Unit	Median Depth (m)	Quartz ^a	Calcite ^a	Pyrite ^a	Muscovite/Illite ^a	Chlorite Group ^a	% Sample Dissolved ^b
MDC-6	Tully Limestone	901	x	XX	—	X	X	60
MDC-22	Hamilton Group	1046	X	—	—	X	X	8
MDC-41	Hamilton Group	1221	X	—	—	X	X	8
MDC-54	Marcellus Shale	1337	X	—	X	X	X	6
MDC-61	Marcellus Shale	1358	X	—	X	X	X	3
MDC-65	Marcellus Shale	1370	X	X	XX	X	—	14
MDC-71	Marcellus Shale	1389	X	XX	X	X	—	26
MDC-78	Onondaga Limestone	1410	X	X	—	X	—	31
MDC-82	Oriskany Sandstone	1434	XX	XX	—	X	—	49

^aXRD abbreviations as follows: x = low intensity; X = high intensity; XX = highest intensity; — = not detected

^bWt. % sample dissolved after treatment with four leaching solutions (see text for details)

inferred units from which these samples were collected are the Tully Limestone (one sample); undifferentiated Hamilton Group (two samples); organic-rich Marcellus Shale (four samples); Onondaga Limestone (one sample); and Oriskany Sandstone (one sample). The Marcellus Shale samples were readily identifiable as dark, black powders, compared to the gray color of the rest of the samples. The unit directly below the Marcellus, inferred to be the Onondaga Limestone, was markedly harder than surrounding units. None of the units encountered during drilling contained significant amounts of formation waters; the Marcellus Shale samples came up slightly damp, and were air-dried before being placed in sample vials. All samples effervesced in 8% acetic acid, indicating that some carbonate was present.

2.2. Sequential extraction

A four-step aqueous sequential extraction procedure (Fig. 2) based on Stewart et al. (2001) and Spivak-Birndorf et al. (2012) was carried out on the samples as received. The procedure was designed to target different relatively accessible element reservoirs and mineral phases in the samples. The first leaching solution was water (ultrapure), added at a water:sample mass ratio of

Figure 2. Flow diagram for the sequential leaching procedure used in this study.

~60:1, to extract sample pore water and water-soluble salts, including chlorides and sulfates. The sample was shaken for 24 hours, centrifuged, and the H₂O solution removed and filtered to 0.45 µm for analysis. This was followed by an equal volume of ultrapure ammonium acetate (NH₄Ac) buffered to pH 8 added to the remaining sample to target exchangeable cations (displaced by the NH₄⁺ in the solution) at the surfaces of minerals and organic matter, as well as interlayer cations from low-charge clay structures (*e.g.*, smectite). This procedure was carried out in a similar fashion

to the H₂O leach, and was followed by equal volumes of 8% ultrapure acetic acid (HOAc)

to target carbonate minerals, and 0.1 M ultrapure HCl to target acid-soluble phases. The latter treatment could extract some interlayer cations from high-charge clay structures (*e.g.*, K in illite; DePaolo et al., 1983).

For the H₂O leachates, an aliquot was taken and immediately refrigerated for ion chromatography analysis, and the remaining aliquot was acidified with nitric acid (HNO₃). All

other leachate solutions were evaporated to dryness and redissolved in ultrapure HNO₃ for further analysis.

After final rinsing and removal of the HCl leachate, the residue left in each centrifuge tube was transferred using ultrapure water into an acid-washed, preweighed PMP beaker, dried at 100°C, and reweighed. This weight was used to calculate the total mass leached from all of the leaching solutions combined (Table 1). Two of the Marcellus Shale residues (MDC-61 and 71) were transferred to Teflon vials and dissolved completely using a combination of hydrofluoric, perchloric and nitric acids.

2.3. Mineralogical, geochemical and isotopic analysis

X-ray diffraction (XRD) analyses were performed at Bucknell University. To prepare the drill cuttings for analysis, a mortar and pestle were used to mill the samples to a fine powder. Samples were placed in a packed-powder mount for XRD analysis on a PANalytical X'Pert PRO MPD X-ray diffractometer with Cu K α radiation. Peak positions (d-spacings) were determined using the IdeCom software program. Search-match software was used to guide the visual inspection of XRD patterns against geologically reasonable mineral candidates in a reference library.

Leachates were analyzed for major and trace cations by ICP-MS and ICP-AES at Department of Energy's National Energy Technology Laboratory (DOE-NETL) in Pittsburgh. The water leachates were also analyzed for major anions by ion chromatography at DOE-NETL Pittsburgh.

Preparation for Sr isotope analysis was carried out under clean lab conditions at University of Pittsburgh. Aliquots containing between 0.8 and 5 μ g Sr were evaporated to dryness and redissolved in 6 N ultrapure nitric acid. Samples were then eluted through columns containing Eichrom® Sr resin in order to separate Sr from all other constituents in the sample. Column eluents were collected in acid-washed Teflon vials, evaporated to dryness, and redissolved in 2 N ultrapure nitric acid. For each sample, an aliquot containing ~500 ng Sr was evaporated onto a rhenium filament pre-loaded with a tantalum oxide carrier agent. ⁸⁷Sr/⁸⁶Sr isotope ratios were

measured using a multidynamic method on a Thermo Finnigan MAT 262 thermal ionization mass spectrometer, with an exponential mass fractionation correction to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. The average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of SRM 987 over the period of these analyses was 0.710244; to facilitate comparison with other data from this lab facility, we normalized all measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to a value for SRM 987 of 0.710240. The estimated external reproducibility of all sample $^{87}\text{Sr}/^{86}\text{Sr}$ measurements reported here is ± 0.000015 . Strontium isotope ratios are also reported as $\epsilon_{\text{Sr}}^{\text{SW}}$ (Andersson et al., 1994), defined as follows:

$$\epsilon_{\text{Sr}}^{\text{SW}} = 10^4 \left[\frac{^{87}\text{Sr}/^{86}\text{Sr}_{\text{sample}}}{^{87}\text{Sr}/^{86}\text{Sr}_{\text{seawater}}} - 1 \right]$$

where $^{87}\text{Sr}/^{86}\text{Sr}_{\text{seawater}}$ is the measured ratio in the present-day oceans (0.709166 at the University of Pittsburgh).

3. Results

3.1. Mineralogy and carbonate content

Table 1 shows the results of semi-quantitative x-ray diffraction (XRD) analysis and post-leaching mass loss. The mineralogical variations in these and additional samples from the same borehole are discussed in more detail by Johnson and Graney (2015). Quartz and illite were detected by XRD in all samples, while no halite or other water-soluble salts were detected in any of the samples. Pyrite was identified by XRD in all of the Marcellus Shale samples, but was not detected in units above and below the shale.

Most of the mass loss from the extractions (% sample dissolved, Table 1) is expected to result from dissolution of carbonate in the acetic and hydrochloric acid extractions. The bulk of the carbonate in these samples was likely extracted by acetic acid, because it was used prior to HCl in the extraction procedure. To evaluate whether a significant amount of clay could have also dissolved in the HOAc, we carried out a dissolution calculation using a rate law of $5.1 \times$

10^{-14} mol m⁻² s⁻¹ for illite (Köhler et al., 2003) and 5.9×10^{-14} mol m⁻² s⁻¹ for smectite (Rozalén et al., 2008) at pH = 2.4 and 20°C (our experimental conditions), and an assumed BET surface area of 130 m² g⁻¹ (Köhler et al., 2003). Based on these calculations, <0.02% of those clay minerals would dissolve during our HOAc extraction procedure.

A total of 60% of sample MDC-6 (Tully Limestone) was extracted by HOAc and HCl, while only 31% of more quartz-rich sample MDC-78 (Onondaga Limestone) dissolved, consistent with its locally siliceous character (Brett and Baird, 1996). The Oriskany Sandstone is calcareous in places and often calcite-cemented (Basan et al., 1980; Kostelnik and Carter, 2012), and calcite as well as quartz is abundant in sample MDC-82 (Table 1), which had a mass loss of 49%. Less than 10% dissolution was observed in the two Hamilton Group samples (MDC-22 and 41) and upper two Marcellus Shale samples (MDC-54 and 61), which also contained detectable chlorite group minerals. Higher mass loss was consistent with XRD-detectable calcite in the lower two Marcellus Shale samples MDC-65 (14%) and MDC-71 (26%). Some variability in carbonate vs. silicate fractions could also result from the presence of small carbonate or sand lenses within the cuttings sampling interval that were incorporated into the bulk sample.

3.2. *Geochemistry of the sequential extractions*

The response of different elements to the sequential extraction solutions varies tremendously based on their geochemical affinities and the phase(s) extracted by the different solutions (Table 2). Of the cations, water-soluble, chloride-complexing cations such as Na are preferentially released by the H₂O leach. Other alkali elements (K, Rb) are leached by water, but in some cases significant amounts are also released to ammonium acetate (from exchange sites) and HCl (possibly from clay interlayer sites). The alkaline earth elements (Mg, Ca, Sr, Ba) also show variation in their response to the sequential leaches. Figure 3 shows the fraction of Na, Ca, Sr and Ba extracted from each leaching solution relative to the total amount extracted by all four leaches combined. While Na is almost entirely extracted by H₂O (Fig. 3a), Ca is held primarily in the carbonate phase (Fig. 3b), and Sr in either exchangeable sites or carbonate (Fig. 3c),

Table 2

Major and minor element concentrations in leachates of core cuttings. Concentrations reported as µg of element extracted per g of unleached starting material.

Sample & Unit	Leachate	Al	Si	P	Fe	Mg	Ca	Sr	Ba	Na	K	Rb	Mn	Co	Ni	Cu	Mo	S	Br	Cl	pH	
µg leached/g sample ^a																						
MDC-6 Tully Limestone	H ₂ O	84.8	174	<DL	25.2	45.0	632	12.1	22.5	346	153	0.351	0.456	<DL	<DL	0.408	<DL	<DL	75.1	3.87	356	8.0
	NH ₄ OAc	<DL	42.4	<DL	13.8	200	11,900	28.5	357	19.3	51.7	0.751	26.7	<DL	0.580	4.65	<DL	<DL	299	0.718	—	
	HOAc	216	187	92.2	4,880	4,670	183,000	261	31.1	101	28.0	0.128	689	0.764	1.52	<DL	<DL	<DL	2710	<DL	—	
	HCl	443	54.3	233	1,190	488	1,880	3.89	205	10.6	101	1.20	18.2	0.440	1.30	1.98	<DL	<DL	22.9	0.250	—	
MDC-22 Hamilton Group	H ₂ O	219	265	<DL	355	109	584	35.2	25.1	846	215	1.81	3.32	0.100	0.299	0.180	<DL	<DL	29.2	—	1,190	8.3
	NH ₄ OAc	8.06	33.2	<DL	32.6	224	4,360	40.0	113	21.4	75.0	0.989	69.6	0.353	1.18	4.21	<DL	<DL	70.7	0.832	—	
	HOAc	235	182	58.1	2,040	1,050	4,280	6.91	5.25	7.49	23.2	0.270	243	1.55	1.19	0.603	<DL	<DL	25.2	0.305	—	
	HCl	1,150	156	319	2,830	416	779	3.46	5.77	15.6	118	1.85	19.9	1.40	2.64	1.25	<DL	<DL	<DL	0.603	—	
MDC-41 Hamilton Group	H ₂ O	213	263	<DL	346	96.5	420	27.4	30.5	919	214	3.21	3.28	0.054	0.354	0.166	<DL	<DL	35.1	—	979	7.9
	NH ₄ OAc	13.6	55.8	<DL	31.4	317	5,600	61.1	193	26.7	113	1.57	85.2	0.276	0.801	4.14	<DL	<DL	93.1	3.76	—	
	HOAc	250	193	84.9	3,170	1,580	6,410	10.0	8.38	9.52	27.2	0.342	328	1.28	1.13	0.152	<DL	<DL	61.6	0.309	—	
	HCl	1,090	143	327	2,740	511	942	3.45	12.0	19.0	159	2.22	23.9	1.62	3.24	1.17	<DL	<DL	4.29	0.554	—	
MDC-54 Marcellus Shale	H ₂ O	102	131	<DL	184	71.6	369	19.5	45.0	647	140	0.782	1.88	<DL	0.415	0.217	2.55	304	7.58	662	8.0	
	NH ₄ OAc	7.29	27.7	<DL	24.2	295	1,460	43.3	628	21.9	98.8	1.42	22.8	<DL	2.32	4.06	<DL	<DL	196	0.661	—	
	HOAc	136	117	49.5	2,830	1,330	4,220	6.71	50.3	5.83	13.9	0.196	111	1.73	7.77	0.361	<DL	<DL	62.7	0.153	—	
	HCl	591	75.5	261	2,120	273	705	6.13	186	12.8	77.8	1.41	10.7	1.70	6.02	4.32	<DL	<DL	182	0.370	—	
MDC-61 Marcellus Shale	H ₂ O	9.65	29.1	<DL	24.8	87.5	700	24.4	33.4	780	80.1	0.406	1.06	<DL	0.382	<DL	26.9	410	8.81	665	7.5	
	NH ₄ OAc	3.56	29.2	<DL	12.4	388	2,250	39.3	798	27.2	123	2.09	10.9	0.072	8.27	9.89	12.8	414	<DL	—	—	
	HOAc	84.1	73.8	28.7	2,510	1,170	3,970	7.70	95.0	4.70	6.91	0.139	37.8	1.62	13.6	0.634	<DL	<DL	75.3	0.169	—	
	HCl	246	40.8	241	1,850	290	1,020	6.50	178	14.9	77.6	1.24	9.64	2.27	17.7	10.4	7.38	355	0.486	—		
	residue	—	—	—	—	—	—	80.9	—	—	—	161	—	—	—	—	—	—	—	—	—	
MDC-65 Marcellus Shale	H ₂ O	33.9	73.6	<DL	45.5	53.2	848	40.7	23.8	727	119	0.455	0.323	<DL	1.86	0.315	50.7	494	10.8	780	8.5	
	NH ₄ OAc	<DL	24.7	<DL	8.53	170	8,840	59.2	208	32.7	120	1.75	13.0	0.774	27.2	14.3	11.2	373	1.99	—	—	
	HOAc	71.8	67.7	49.9	2,840	1,940	26,800	70.6	14.9	23.2	10.6	0.148	80.2	1.68	23.6	0.757	<DL	383	0.308	—	—	
	HCl	142	57.0	272	1,430	637	2,400	9.39	37.1	16.1	73.2	1.16	14.0	2.90	30.9	9.79	3.01	451	0.482	—	—	
MDC-71 Marcellus Shale	H ₂ O	48.1	107	<DL	79.4	47.6	886	49.1	29.1	837	78.4	0.230	0.721	<DL	0.683	0.352	39.2	287	16.1	1,230	8.7	
	NH ₄ OAc	<DL	27.4	<DL	19.7	97.9	8,950	46.8	152	23.2	55.3	0.749	7.63	0.200	15.6	20.5	10.8	291	2.95	—	—	
	HOAc	46.1	60.6	26.9	683	3,570	69,800	136	15.0	46.6	6.07	0.068	74.7	0.628	14.4	0.765	<DL	870	0.449	—	—	
	HCl	174	86.8	350	1,570	2,070	4,920	12.7	42.5	15.2	40.2	0.743	17.0	1.27	18.6	8.82	1.66	296	0.604	—	—	
	residue	—	—	—	—	—	—	56.1	—	—	—	66.8	—	—	—	—	—	—	—	—	—	
MDC-78 Onondaga Limestone	H ₂ O	87.2	154	<DL	115	147	875	92.4	43.6	862	283	0.950	0.835	<DL	0.212	0.351	<DL	<DL	72.2	22.2	1,910	9.0
	NH ₄ OAc	<DL	35.6	<DL	15.8	312	13,100	86.9	200	27.1	110	1.37	17.0	0.040	1.57	4.96	<DL	<DL	235	0.552	—	—
	HOAc	171	137	29.5	4,810	4,840	54,700	111	17.2	53.7	25.1	0.339	129	0.346	2.25	<DL	<DL	<DL	835	0.416	—	—
	HCl	308	69.9	236	3,300	6,170	14,100	13.9	17.2	22.1	165	1.67	42.6	0.537	2.53	1.52	<DL	<DL	245	0.822	—	—
MDC-82 Oriskany Sandstone	H ₂ O	37.4	89.1	<DL	44.4	58.0	741	15.2	8.42	231	121	0.440	0.302	<DL	<DL	<DL	<DL	<DL	81.2	3.98	386	7.9
	NH ₄ OAc	<DL	38.5	<DL	16.7	124	14,400	26.3	58.8	14.7	39.0	0.431	9.69	5.34	0.440	3.18	<DL	<DL	242	0.450	—	—
	HOAc	113	111	108	2,990	2,190	145,000	154	6.20	60.0	17.3	0.094	105	5.86	1.05	<DL	<DL	<DL	1720	<DL	—	—
	HCl	339	33.6	720	1,540	212	1,750	5.49	3.46	14.3	63.9	0.702	9.70	4.94	0.821	1.50	<DL	<DL	12.8	0.353	—	—

^a <DL = below detection limit; "—" = not analyzed.

depending on the fraction of carbonate in the sample. Magnesium (not shown) behaves similarly to Ca.

Notably, barium, which is highly concentrated in water produced from Marcellus Shale natural gas wells, is held primarily in exchangeable sites for all samples (Fig. 3d). This suggests

Figure 3. Fractions of Na, Ca, Sr and Ba leached from all samples in this study relative to the total amount extracted by the four leaching solutions. Sequential extractions took place in the order shown (left to right)

that Ba has a strong affinity for charged surfaces on clay minerals, and that it is not held appreciably in carbonate minerals. Barite (BaSO_4), if present, was not significantly dissolved by the leaching solutions used in this study, which is consistent with its known dissolution behavior (Paytan et al., 1993).

Assuming that Ca, Mg and Fe extracted by HOAc were in carbonate minerals, Ca-carbonate minerals are predominant in samples with high total carbonate content (Fig. 4), while as much as half of the carbonate in less calcareous samples is Mg-Fe-rich, presumably in the form of dolomite-ankerite, or as magnesite-siderite combined with calcite. Leachates extracted by HCl had higher $(\text{Mg}+\text{Fe})/(\text{Ca}+\text{Mg}+\text{Fe})$ ratios than the

acetic acid fraction. This suggests dissolution by HCl of residual refractory Fe-Mg carbonates and/or partial dissolution of other Mg- and Fe-rich phases such as chlorite.

Figure 4. Molar (Mg+Fe)/(Ca+Mg+Fe) in the acetic acid leachates for all samples in this study plotted against the calculated total weight percent carbonate content (based on acetic acid leachate chemistry). Marcellus Shale leachates are filled blue triangles, Hamilton Group leachates are open triangles, and open circles are overlying and underlying sandstones and limestones.

Phosphorus was strongly enriched in the HCl leachate, suggesting dissolution of a phosphate mineral such as apatite. Aluminum was extracted to the greatest extent by the HCl leachate in all samples, indicating partial dissolution of an aluminosilicate mineral phase. However, Si was not consistently high in the HCl extraction, and instead tended to peak in the H₂O or HOAc extractions. Because none of the pH values reached levels necessary for high Si solubility (>9; Krauskopf,

1956), the released silica could have been in colloidal form, possibly representing biogenic Si in the sample (Schieber, 1996).

Chloride was analyzed in the H₂O leachates only, and total elemental sulfur (S_{total}) was determined on all samples without speciation. In the water leachates, Cl is present at levels roughly equivalent to Na (molar Na/Cl from 0.7 to 1.8, mean 1.3). Bromide, where analyzed, was highest in the H₂O leachate. Sulfur showed no clear release pattern, although it tended to be enriched in the HOAc leachate fraction in samples with the highest amount of carbonate. The organic-rich shales (MDC-54, 61, 65, 71) tended to release greater amounts of S to water and ammonium acetate solutions than did other samples, probably reflecting higher amounts of pyrite. In each of these samples, however, the S_{total}/Fe ratio in the water leachates was in excess of that of pyrite, possibly due to Fe resorption or precipitation of Fe oxyhydroxides during the leaching process; speciation modeling of the water leachates (Geochemist's Workbench[®] v10.1) indicates that pyrite is undersaturated and hematite and goethite are oversaturated. These conditions most likely reflect the benchtop (oxic) leaching conditions, and are not necessarily

going to be obtained during hydraulic fracturing in the deep subsurface, where conditions are likely to be much more reducing. These models also indicate that barite is only slightly above saturation in the Marcellus Shale water leachates ($Q/K_{sp} = 1.2-2.6$, where Q is the reaction quotient and K_{sp} the solubility product constant), and suggest that Ba levels in our leaching experiments are controlled by barite solubility. 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 (e.g., by bacterial sulfate reduction; Engle and Rowan, 2014), suppressing barite precipitation.

3.3. Sr isotopes in the sequential extractions

Measurement of isotope ratios of leachates from all samples and residues from two of the organic-rich shales (Table 3) indicate significantly different ϵ_{Sr}^{SW} values in different mineral and ion exchange sites within individual samples. All samples follow a trend with the sequential extractions in which the H_2O leachate falls within a relatively narrow ϵ_{Sr}^{SW} range of +6 to +28 ($^{87}Sr/^{86}Sr = 0.7096$ to 0.7112) that also largely overlaps with the range of Marcellus produced water values (Fig. 5), followed by a decrease in ϵ_{Sr}^{SW} in the NH_4Ac (exchangeable) leachate, and a further decrease in the $HOAc$

Table 3
Strontium isotope ratios of leachates and residues

Sample Name/ Unit	Leachate	$^{87}Sr/^{86}Sr^a$	ϵ_{Sr}^{SWb}
MDC-6	H ₂ O	0.710852 ± 0.000011	23.77 ± 0.16
Tully	NH ₄ OAc	0.709868 ± 0.000011	9.90 ± 0.16
Limestone	HOAc	0.708187 ± 0.000010	-13.80 ± 0.14
MDC-22	H ₂ O	0.711181 ± 0.000010	28.41 ± 0.14
Hamilton	NH ₄ OAc	0.710452 ± 0.000011	18.13 ± 0.16
Group	HOAc	0.709449 ± 0.000011	3.99 ± 0.16
MDC-41	H ₂ O	0.711102 ± 0.000009	27.30 ± 0.13
Hamilton	NH ₄ OAc	0.710449 ± 0.000011	18.09 ± 0.16
Group	HOAc	0.709328 ± 0.000012	2.28 ± 0.17
MDC-54	H ₂ O	0.710867 ± 0.000012	23.99 ± 0.17
Marcellus	NH ₄ OAc	0.710551 ± 0.000010	19.53 ± 0.14
Shale	HOAc	0.709771 ± 0.000009	8.53 ± 0.13
	HCl	0.711274 ± 0.000008	29.73 ± 0.11
MDC-61	H ₂ O	0.710412 ± 0.000011	17.57 ± 0.16
Marcellus	NH ₄ OAc	0.710132 ± 0.000010	13.62 ± 0.14
Shale	HOAc	0.709267 ± 0.000009	1.42 ± 0.13
	HCl	0.710514 ± 0.000010	19.01 ± 0.14
	residue	0.731007 ± 0.000010	307.98 ± 0.14
MDC-65	H ₂ O	0.710129 ± 0.000010	13.58 ± 0.14
Marcellus	NH ₄ OAc	0.709396 ± 0.000011	3.24 ± 0.16
Shale	HOAc	0.708276 ± 0.000008	-12.55 ± 0.11
	HCl	0.709833 ± 0.000010	9.41 ± 0.14
MDC-71	H ₂ O	0.710126 ± 0.000010	13.54 ± 0.14
Marcellus	NH ₄ OAc	0.709380 ± 0.000009	3.02 ± 0.13
Shale	HOAc	0.708248 ± 0.000010	-12.94 ± 0.14
	HCl	0.708915 ± 0.000009	-3.54 ± 0.13
	residue	0.731322 ± 0.000011	312.42 ± 0.16
MDC-78	H ₂ O	0.709594 ± 0.000009	6.04 ± 0.13
Onondaga	NH ₄ OAc	0.709302 ± 0.000011	1.92 ± 0.16
Limestone	HOAc	0.708583 ± 0.000012	-8.22 ± 0.17
	HCl	0.710421 ± 0.000010	17.70 ± 0.14
MDC-82	H ₂ O	0.709990 ± 0.000011	11.62 ± 0.16
Oriskany	NH ₄ OAc	0.709418 ± 0.000009	3.55 ± 0.13
Sandstone	HOAc	0.708766 ± 0.000010	-5.64 ± 0.14

^aSRM 987 Sr standard = 0.710240; 2 σ uncertainty based on in-run statistics.

^b $\epsilon_{Sr}^{SW} = (^{87}Sr/^{86}Sr_{sample}/^{87}Sr/^{86}Sr_{seawater} - 1)10^4$ where $^{87}Sr/^{86}Sr_{seawater} = 0.709166$.

Figure 5. Strontium isotope ratio of sequential leachates of Marcellus Shale (filled symbols, colored lines) and adjacent units. Measured ϵ_{Sr}^{SW} values of Marcellus Shale produced water are plotted for comparison (data from Chapman et al., 2012; Capo et al., 2014). The indicated range of Devonian seawater (= unaltered Devonian marine carbonate) is from Deiner et al. (1996). Error bars on the ϵ_{Sr}^{SW} values are smaller than the size of the symbols. Leachate symbols are the same as in Figure 3.

(carbonate) leachate, and finally an increase in ϵ_{Sr}^{SW} with the HCl leach. In the two shale samples in which the residual solid was completely dissolved and analyzed, the residue yields ϵ_{Sr}^{SW} values significantly higher than any of the leachates (+308 and +312 for MDC-61 and 71, respectively). Recombining the leachate Sr concentrations and isotope compositions to calculate a

whole-rock ϵ_{Sr}^{SW} value yields +164 and +55 ($^{87}Sr/^{86}Sr = 0.7208$ and 0.7131) for MDC-61 and 71, respectively. The lower value for MCD-71 reflects the

greater amount of low- ϵ_{Sr}^{SW} carbonate in that sample.

The low ϵ_{Sr}^{SW} of the carbonate fraction may provide an explanation for the trend of increasing ϵ_{Sr}^{SW} commonly observed during the first few days of flowback (Chapman et al., 2012; Capo et al., 2014). The earliest injected hydraulic fracturing fluid contains HCl to clean well perforations and improve permeability (Vidic et al., 2013). This acidic water is likely to dissolve carbonate cement and small limestone lenses within the shale, as well as portions of the well casing, lowering its ϵ_{Sr}^{SW} until the acid is neutralized. Based on time series analysis (Chapman et al., 2012; Capo et al., 2014), this low- ϵ_{Sr}^{SW} component is replaced within the first 3-10 days of flowback by Sr from preexisting formation fluids within the shale or adjacent units that are accessed through hydraulic fracturing. This is consistent with data from multiple Marcellus Shale wells reported by Hayes (2009), which showed that total alkalinity generally decreased in flowback and produced water from day 1 to day 90. Thus the mixing relationship for Sr

observed between early and late returned fluids from hydraulically fractured Marcellus Shale wells (Capo et al., 2014) represents mixing between early fluids with dissolved carbonate and preexisting brines within or near the target formation.

4. Discussion

4.1. Comparison of shale leachates to produced water

An important issue for understanding and controlling produced water characteristics is the origin of the high TDS levels commonly observed in flowback just hours to days after hydraulic fracturing. Blauch et al. (2009) suggested that they result from dissolution of salt minerals in the shale by the injected fluid, while others have argued that the high TDS represent leakage of formation water back into the well via hydraulic fractures (e.g., Warner et al., 2012a; 2012b; Capo et al., 2014; Rowan et al., 2015), or extraction of pore fluids (Balashov et al., 2015). One approach is to examine the chemistry of shale leachates to determine whether available cations in soluble minerals and on surface sites can reproduce the observed chemistry (concentrations and element ratios) of produced waters. Although hydrochloric acid is added to the injected fluid during the initial stages of hydraulic fracturing (see discussion in Section 3.3, above), the acid appears to be neutralized early on, based on the pH of the earliest returned water (Hayes, 2009), and subsequent stages are carried out without added HCl (FracFocus, 2014). Therefore, for the bulk of the hydraulic fracturing process, the water leachate can be considered a reasonable approximation of hydraulic fracturing fluid interacting with shale. As indicated in Figure 6a, all of the water leachates have a higher Na/Cl and Ca/Na than the Marcellus produced waters. In addition, they contain a higher proportion of K than the produced waters, possibly from interaction with illite (Fig. 6b).

Largely conservative behavior would be expected from Na, Ca and Sr in the aqueous environment as long as carbonate, sulfate or chloride salts are not precipitating. Therefore, ratios of these elements can be used to compare the leachates to produced waters. In produced waters from the Marcellus (Chapman et al., 2012; Haluszczak et al., 2014), both Na/Ca and Sr/Ca are significantly higher, in some cases by more than an order of magnitude, than in any leachates from this study, including water, ammonium acetate, acetic acid, hydrochloric acid (Fig. 7a, b). In contrast, Ba/Ca ratios in produced waters (Fig. 7c) show a large variation that overlaps those of the H₂O and NH₄Ac shale leachates. However, Ba is known to vary significantly in Marcellus produced

waters, possibly due to precipitation of barite (scaling) in rock fractures or the borehole, or to geographic variations in sulfate levels (Engle and Rowan, 2014). Even the NH₄Ac (exchangeable cation) leachates, which contain >60% of the extractable Ba, do not reach Ba/Ca ratios as high as the highest produced waters. On the whole, the offset in major cations and anions between Marcellus produced water and all leachates indicates that the dominant source of

Figure 6. Ternary diagrams comparing molar concentrations of Ca²⁺, Na⁺, K⁺ and Cl⁻ in water leachates from this study to those in Marcellus produced water (filled red squares) from Haluszczak et al. (2013). Marcellus Shale leachates are filled blue triangles, Hamilton Group leachates are open triangles, and open circles are overlying and underlying sandstones and limestones..

TDS in Marcellus Shale produced water is not from dissolution of soluble components of shale during hydraulic fracture stimulation. Nonetheless, longer-term leaching studies under the P-T-X conditions of hydraulic fracturing are needed to better replicate the downhole environment and to evaluate the resulting chemistry of fluid-shale interaction.

4.2. Origin of high-TDS Marcellus Shale produced water

If dissolution of water-soluble components of the shale cannot explain the chemistry of Marcellus produced waters, other possibilities include extraction of tightly bound pore water (Balashov et al., 2015) or migration of stratabound

formation waters due to hydraulic fracturing (Capo et al., 2014; Rowan et al., 2015). Nearly all of the sodium was stripped by the water extraction (Fig. 3a), so the total amount of Na extracted can be used to estimate the volume of pore-bound water in the Marcellus Shale samples, assuming that this leaching step would extract any available pore-bound water. Based on these leachate data, a rock:water ratio of about 50:1 (w/w) would be required to reach Na levels typical of late-stage Marcellus produced water. This is commensurate with the porosity range observed in the Marcellus Shale (Milliken et al., 2013), but it is unlikely that such a high rock:water interaction ratio could be achieved during hydraulic fracturing, because finely crushed drill

Figure 7. Molar ratios of Na/Ca, Sr/Ca and Ba/Ca of the Marcellus Shale sequential leachates. Data from Marcellus Shale produced water are shown for comparison (from Chapman et al., 2012; Haluszczak et al., 2013; Capo et al., 2014). Symbols are the same as in Figure 3.

cuttings likely expose a much greater surface area per unit mass than the hydraulic fracturing process. Given the probable high capillary pressures in the shale (Engelder, 2012), the net flow of water into the target formation during hydraulic fracturing (Vidic et al., 2013), and the differences in major element chemistry between the water leachates and Marcellus produced water (Section 4.1), we consider it unlikely that the observed volume of high-TDS waters (even during the low-flow production phase) represents solely pore-bound water that was immobile until being released by hydraulic fracturing.

We suggest that the high-TDS water produced during Marcellus Shale gas extraction represents long-lived, *in situ* formation water that is tapped or mobilized by hydraulic fracturing. This fluid could be present in pores, fractures and sandy lenses within the shale (Rowan et al., 2015), or in permeable units above or below the target zone. In this scenario, a portion of the injected fluid is removed during the flowback and early production phase of the well, with the remainder imbibed by the shale itself. During the main gas production phase, the relatively low pressure of the wellbore creates a hydraulic head gradient, inducing the formerly trapped fluids to flow along pathways created or intercepted by hydraulic fracturing. In the Marcellus Shale, the great depth to the producing region combined with the relative impermeability of the shale (even with fractures) generally minimizes the flow of *in situ* water to the wellbore. After cessation of hydraulic fracturing, the pressure differential is toward the wellbore itself; therefore, the primary vector for produced water to interact with shallower units or surface waters is likely to be via the wellbore, rather than upward migration along fractures (Soeder et al., 2014; Vengosh et al., 2014; Kolesar Kohl et al., 2014).

Limited Sr isotope data from water producing units below the Marcellus Shale (e.g., Medina Sandstone, Utica Shale) yield $\epsilon_{\text{Sr}}^{\text{SW}}$ values within the range of those of Marcellus produced waters (Osborn et al., 2012; Warner et al., 2012a), and the imprint of Marcellus-like waters in the H₂O leachates extends up to the Tully Limestone (Fig. 5). However, highly saline produced water from Upper Devonian and Lower Mississippian units overlying the Tully Limestone (Dresel and Rose, 2010) typically have much more radiogenic $\epsilon_{\text{Sr}}^{\text{SW}}$ values (+98 to +169; Osborn et al., 2012;

Chapman et al., 2012; 2013; Kolesar Kohl et al., 2014) than those from the Marcellus. This suggests that a long-lived hydrologic barrier exists between the Marcellus Shale and Upper Devonian gas-producing units, at least in portions of the Appalachian Basin. This barrier must have developed (or sealed) subsequent to hydrocarbon generation and expulsion, as Upper Devonian/Lower Mississippian gas- and oil-bearing units are thought to be sourced in part by the Marcellus Shale (Zagorski et al., 2012). In this scenario, tectonically driven basin-scale flow in the late Paleozoic (Garven et al., 1993; Evans and Battles, 1997; Osborn et al., 2012) served to homogenize the isotopic composition of fluids at or below the Tully Limestone, and in parts of the Appalachian Basin they have remained largely isolated from overlying units since that time. A barrier preventing upward movement of aqueous fluids could also serve to stop or slow gas migration, preserving the observed “reversals” of normal $\delta^{13}\text{C}$ trends for methane, ethane and propane (Burruss and Laughrey, 2010) in Marcellus and deeper units. In the northeastern section of the Marcellus play closer to the Appalachian structural front, faulting and folding could have provided pathways for deeper fluids (aqueous and gas) to migrate upward and mix with the shallower formation waters, in some cases approaching the near surface environment (e.g., at Salt Springs State Park, Pennsylvania; Warner et al., 2012a; Johnson et al., 2015).

4.3. Post-depositional fluid evolution

For the samples processed in this study, each leaching solution extracted Sr with a distinct $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, indicating cation reservoirs within individual samples that remained mutually isolated for possibly hundreds of millions of years. The lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were in the carbonate mineral fraction dissolved by acetic acid. Unaltered calcium carbonate that precipitated from Middle Devonian seawater would have an $\epsilon_{\text{Sr}}^{\text{SW}}$ value in the range of -22 to -17 ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7076\text{-}0.7079$; Diener et al., 1996). The lowest value measured in the carbonate fraction of Marcellus Shale samples from this study was -12.9, which approaches the expected Devonian carbonate ratio (Fig. 5). To evaluate the possibility of introducing non-carbonate Sr to

Figure 8. Rb/Sr- $^{87}\text{Sr}/^{86}\text{Sr}$ mixing diagram for the acetic acid leachates ($\approx$ carbonate). The linear trends suggest mixing between “pristine” carbonate and a high $^{87}\text{Sr}/^{86}\text{Sr}$ and Rb/Sr endmember. Open squares are the values for the carbonate corrected back to the ~ 390 Ma age of deposition of the Marcellus Shale, which also display a high level of correlation (dashed line). The thick gray arrow shows the trajectory for mixing with the HCl leachate endmember; given that the carbonate does not follow this trajectory, the observed trend is unlikely to be a leaching artifact.

carbonate Sr during the HOAc leaching process, we plot $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Rb/Sr for the HOAc leaches in Figure 8. The measured values have a strong linear correlation ($R^2 = 0.995$), suggesting mixing of a low $^{87}\text{Sr}/^{86}\text{Sr}$, low Rb/Sr component with a component high in both. When the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are corrected for ^{87}Rb decay to the likely time of deposition (~ 390 Ma), the values shift slightly downward, but the correlation remains. The apparent mixing relationship could reflect deposition of carbonate cement from an evolving

diagenetic fluid receiving high Rb, high $\epsilon_{\text{Sr}}^{\text{SW}}$ inputs. A portion of the trend could also represent a small input from the shale clastic component during leaching, which would have a relatively greater influence on

the shale samples with low carbonate content. However, based on the component extracted with the stronger HCl leachate, leaching of more resilient Rb and Sr would move values toward a much higher Rb/Sr endmember than is observed (gray arrow, Fig. 8). Moreover, the observation that the stratigraphically separated (by ~ 50 m) samples of Marcellus Shale fall along a well-defined trend implies a petrogenetic relationship rather than localized leaching artifacts.

If the carbonate cement in the shale represents an early diagenetic component, the exchangeable and water-soluble reservoirs reflect overprinting by later fluid flow processes. A possible geochemical fluid evolution pathway is demonstrated in Figure 9. The initial

Figure 9. Leachate Sr/Ca ratios and $^{87}\text{Sr}/^{86}\text{Sr}$ values corrected for ^{87}Rb decay to 390 Ma. Also shown are published produced water data (yellow triangles) that are not corrected to 390 Ma because Rb concentrations were not available; however, unpublished data indicate that Marcellus produced waters have very low Rb/Sr ratios, leading to age corrections of <0.0001 (maximum correction of 0.0001 indicated with error bar). The dashed line indicates an inferred fluid evolution line for diagenetic/catagenetic fluids following deposition of the Marcellus Shale. The arrows indicate approximate vectors for aragonite recrystallization to calcite and dissolution of celestite/strontianite (movement toward high Sr/Ca with seawater $^{87}\text{Sr}/^{86}\text{Sr}$ signatures), and for transformation of smectite-illite interlayered clays to illite and dissolution of K-feldspar and mica (movement toward higher $^{87}\text{Sr}/^{86}\text{Sr}$ with negligible effect on Sr/Ca). The light blue shaded region represents the calculated Sr/Ca of pore fluid that would be in equilibrium with coexisting calcite cement (dark blue diamonds) extracted with HOAc. Note that the shale water leachates (filled green circles), when corrected to 390 Ma, fall almost entirely below the produced water values.

diagenetic/pore fluid after deposition would have had a Middle Devonian or older seawater $^{87}\text{Sr}/^{86}\text{Sr}$ signature, as it likely consisted of evaporated paleo-seawater (Rowan et al., 2015). This fluid could have originated from within the Marcellus or from deeper evaporites sources (*e.g.*, the Silurian Salina Group). Clay transformations within and below the Marcellus Shale from smectite-illite interlayers to primarily illite would expel radiogenic Sr into the pore fluid, moving

the fluid to higher $^{87}\text{Sr}/^{86}\text{Sr}$ values (Chaudhuri and Clauer, 1993; Osborn et al., 2012), while minimally affecting the Sr/Ca ratio of the fluid. In addition, dissolution of radiogenic minerals such as K-feldspar and mica could also drive the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio upward; Chaudhuri and Clauer (1993) suggest that this is an important process for modifying the Sr isotope composition of oilfield produced waters. The Sr/Ca ratio would increase as aragonite-calcite transformations released Sr into the diagenetic fluid (McGregor and Gagan, 2003). Strontium could also be contributed by dissolution of celestite (observed in the underlying Oriskany Sandstone; Stowe, 1928) or strontianite (observed in septarian concretions in the Marcellus Shale; Chamberlain et al., 1986; Siegel et al., 1987), although Siegel et al. (1987) suggest that the strontianite formed during the Pleistocene.

We suggest that a combination of these processes operated both below and within the Marcellus shale to move the diagenetic fluid along the pathway shown in Figure 9. Early-formed carbonate cement (with Sr/Ca lower than its coexisting fluid) preserves the early fluid composition, while later fluid compositions were imprinted on the exchange sites (with variable Sr/Ca depending on the sites) and finally trapped within pores in the shale when compaction restricted further fluid migration. This trapped component became the water-leachable portion (either as trapped fluid or salt residues from its evaporation after the cuttings were brought to the surface). The observation that leachates from sandstone and limestone samples adjacent to the Marcellus Shale have similar Sr isotope characteristics as the shale (Fig. 5) indicates that the isotopic signatures of these reservoirs were not imparted by the host rock. The highly saline produced water from Marcellus gas wells could represent a continuation of these processes (as indicated in Figure 9) or they could result from basin-scale fluid flow (primarily at or below the level of the Hamilton Group), with their final composition reflecting an amalgamation of all of these processes on a basin-wide scale. In either case, a portion of this fluid became trapped in fractures or permeable units within, below, and possibly above the Marcellus Shale, to be tapped by induced fractures.

5. Conclusions

Dry-drilled cuttings extracted within, below and above the Marcellus Shale from a well in Tioga County, New York State, USA, were subjected to a sequential leaching procedure in order to determine geochemical reservoirs, element mobility, fluid flow history, and the origin of dissolved solids in Marcellus Shale produced water. Major findings include:

1. The four leaching solutions (water, ammonium acetate, acetic acid, and hydrochloric acid) extracted geochemically and isotopically distinct element suites from the shale and surrounding units. Of the total amount extracted, nearly all of the Ba was located in exchangeable sites, the Na was primarily water-soluble, and most of the Ca was in carbonate. Other elements exhibited more complex extraction patterns depending on the lithology. In all cases the $^{87}\text{Sr}/^{86}\text{Sr}$ of the leachate decreased progressively with sequential leaches of water, ammonium acetate, and acetic acid (carbonate), and increased in the HCl leachate.
2. Extracted water-soluble and exchangeable components of the Marcellus Shale yielded $^{87}\text{Sr}/^{86}\text{Sr}$ ratios generally within the range of Marcellus produced waters, but the major element geochemistry was not consistent with the derivation of produced water dissolved solids from water-rock interaction during hydraulic fracturing. Total dissolved solids in the 60:1 water:rock leachates were lower than those in produced water by a factor of at least 10^3 . High-TDS produced waters from the Marcellus Shale more likely represent formation waters in sandy lenses, fractures or adjacent units that are tapped by hydraulic fracturing.
3. The generally observed trend in hydraulic fracturing flowback water of rapidly climbing $^{87}\text{Sr}/^{86}\text{Sr}$ ratios over the first few days followed by stabilization or very slow increases in subsequent produced water can be explained by initial dissolution of shale carbonate and well casing cement followed by gradual mixing in of high-TDS formation waters.
4. Marcellus Shale produced waters, water leachates from the Middle Devonian samples in this study, and the few deeper brines that have been analyzed for Sr isotopes all exhibit similar $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. In contrast, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of overlying Upper Devonian/Lower

Mississippian produced waters in many parts of the Appalachian Basin are significantly higher, suggesting that Middle Devonian and older produced waters were prevented from migrating upward into overlying units over much of their history.

5. Geochemically and isotopically distinct reservoirs record different stages of fluid evolution of the Marcellus Shale. Carbonate cement appears to reflect precipitation from an early fluid with near-seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, while later overprints on exchange sites and ultimately pore water indicate a more radiogenic fluid, possibly due to expulsion of Sr from clays during smectite-illite transformation or K-spar and mica dissolution within and below the Marcellus Shale.

Acknowledgements

We thank M. Engle and E. Rowan for detailed and insightful reviews that greatly improved the manuscript. This work was supported by the Colcom Foundation (CSK, RCC, JRG), with additional funding from the U.S. Department of Energy, Office of Fossil Energy, as performed through the National Energy Technology Laboratory's ongoing research under the RES contract DE-FE0004000 (RCC, BWS).

References

- Akob, D.M., Cozzarelli, I.M., Dunlap, D.S., Rowan, E.L., Lorah, M.M., 2015. Organic and inorganic composition and microbiology of produced waters from Pennsylvania shale gas Wells. *Appl. Geochem.* this volume.
- Andersson, P.S., Wasserburg, G.J., Ingri, J., Stordal, M.C., 1994. Strontium, dissolved and particulate loads in fresh and brackish waters: the Baltic Sea and Mississippi Delta. *Earth Planet. Sci. Lett.* 124, 195-210.
- Balashov, V.N., Engelder, T., Gu, X., Fantle, M.S., Brantley, S.L., 2015. A model describing flowback chemistry changes with time after Marcellus Shale hydraulic fracturing. *Am. Assoc. Petroleum Geol. Bull.* DOI:10.1306/06041413119.
- Barbot, E., Vidic, N.S., Gregory, K.B., Vidic, R.D., 2013. Spatial and temporal correlation of water quality parameters of produced waters from Devonian-age shale following hydraulic fracturing. *Environ. Sci. Technol.* 47, 2562-2569.
- Basan, P.B., Kissling, D.L., Hemsley, K.D., Kersey, D.G., Dow, W.G., Chaiffetz, M.S., Isaacson, P., Barrett, S., Carne, L., 1980. Geological Study and Reservoir Evaluation of Early Devonian Formations of the Appalachians, Robertson Research Inc., Houston, TX.
- Beaumont, C., Quinlan, G., Hamilton, J., 1988. Orogeny and stratigraphy: Numerical models of the Paleozoic in the eastern interior of North America. *Tectonics* 7, 389-416.
- Blauch, M.E., Myers, R.R., Moore, T.R., Lipinski, B.A., 2009. Marcellus Shale post-frac flowback waters - Where is all the salt coming from and what are the implications? Society of Petroleum Engineers Eastern Regional Meeting, Charleston, WV, pp. SPE 125740, pp. 1-20.
- Brett, C.E., Baird, G.C., 1996. Middle Devonian sedimentary cycles and sequences in the northern Appalachian Basin. In: Witzke, B.J., Ludvigson, G.A., Day, J. (Eds.), *Paleozoic Sequence Stratigraphy; Views from the North American Craton*, GSA Special Papers, v. 306. Geological Society of America, Boulder, CO, pp. 213-241.
- Burruss, R.C., Laughrey, C.D., 2010. Carbon and hydrogen isotopic reversals in deep basin gas: Evidence for limits to the stability of hydrocarbons. *Org. Geochem.* 41, 1285-1294.

- Capo, R.C., Stewart, B.W., Rowan, E.L., Kolesar, C.A., Wall, A.J., Chapman, E.C., Hammack, R.W., Schroeder, K.T., 2014. The strontium isotopic evolution of Marcellus Formation produced waters, southwestern Pennsylvania. *Int. J. Coal Geol.* 126, 57-63.
- Carter, K.M., 2007. Subsurface rock correlation diagram, oil and gas producing regions of Pennsylvania. Pennsylvania Geological Survey Open-File Report OFOG 07-01.1, 4th ser., <http://www.dcnr.state.pa.us/topogeo/publications/pgspub/openfile/drc/index.htm>.
- Chamberlain, S.C., Dossert, W.P., Siegel, D.I., 1986. A new paragenesis and new localities for witherite. *Canadian Mineralogist* 24, 79-90.
- Chapman, E.C., Capo, R.C., Stewart, B.W., Hedin, R.S., Weaver, T.J., Edenborn, H.M., 2013. Strontium isotope quantification of siderite, brine, and acid mine drainage contributions to abandoned gas well discharges in the Appalachian Plateau. *Appl. Geochem.* 31, 109-118.
- Chapman, E.C., Capo, R.C., Stewart, B.W., Kirby, C.S., Hammack, R.W., Schroeder, K.T., Edenborn, H.M., 2012. Geochemical and strontium isotope characterization of produced waters from Marcellus Shale natural gas extraction. *Environ. Sci. Technol.* 46, 3545-3553.
- Chaudhuri, S., Clauer, N., 1993. Strontium isotopic compositions and potassium and rubidium contents of formation waters in sedimentary basins: Clues to the origin of the solutes. *Geochim. Cosmochim. Acta* 57, 429-437.
- DePaolo, D.J., Kyte, F.T., Marshall, B.D., O'Neill, J.R., Smit, J., 1983. Rb-Sr, Sm-Nd, K-Ca, O, and H isotopic study of Cretaceous-Tertiary boundary sediments, Caravaca, Spain: Evidence for an oceanic impact site. *Earth Planet. Sci. Lett.* 64, 356-373.
- Diener, A., Ebner, S., Veizer, J., Buhl, D., 1996. Strontium isotope stratigraphy of the Middle Devonian: Brachiopods and conodonts. *Geochim. Cosmochim. Acta* 60, 639-652.
- Dresel, P.E., Rose, A.W., 2010. Chemistry and Origin of Oil and Gas Well Brines in Western Pennsylvania. Open-File Report OFOG, v. 10-01.0, Pennsylvania Geological Survey, Harrisburg, PA.
- Engelder, T., 2012. Capillary tension and imbibition sequester frack fluid in Marcellus gas shale. *Proc. Nat. Acad. Sci.* 109, E3625.

- Engelder, T., Cathles, L.M., Bryndzia, L.T., 2014. The fate of residual treatment water in gas shale. *J. Unconven. Oil Gas Resour.* 7, 33-48.
- Engle, M.A., Rowan, E.L., 2014. Geochemical evolution of produced waters from hydraulic fracturing of the Marcellus Shale, northern Appalachian Basin: A multivariate compositional data analysis approach. *Int. J. Coal Geol.* 126, 45-56.
- Ettensohn, F.R., 1985. Controls on development of Catskill delta complex basis facies. In: Woodrow, D.W., Sevon, W.D. (Eds.), *The Catskill Delta*, Geological Society of America Special Paper 201, pp. 65-77.
- Ettensohn, F.R., 1992. Controls on the origin of the Devonian-Mississippian oil and gas shales, east-central United States. *Fuel* 71, 1487-1492.
- Ettensohn, F.R., 2004. Modeling the nature and development of major paleozoic clastic wedges in the Appalachian Basin, USA. *J. Geodynam.* 37, 657-681.
- Evans, M.A., Battles, D.A., 1997. Regional syn-orogenic fluid migration in the central Appalachians: Fluid geochemistry and fluid migration pathways. In: Hendry, J.P., Carey, P.F., Parnell, J., Ruffell, A.H., Worden, R.H. (Eds.), *Contributions to the Second International Conference on Fluid Evolution, Migration and Interaction in Sedimentary Basins and Orogenic Belts*, pp. 87-92.
- FracFocus, 2014. Hydraulic Fracturing: The Process. <http://fracfocus.org/hydraulic-fracturing-how-it-works/hydraulic-fracturing-process>
- Garven, G., Ge, S., Person, M.A., Sverjensky, D.A., 1993. Genesis of stratabound ore deposits in the Midcontinent basins of North America. 1. The role of regional groundwater flow. *Am. J. Sci.* 293, 487-568.
- Ground Water Protection Council and ALL Consulting, 2009. *Modern Shale Gas Development in the United States: A Primer*, Oklahoma City, OK, http://www.netl.doe.gov/technologies/oil-gas/publications/epreports/shale_gas_primer_2009.pdf.
- Haluszczak, L.O., Rose, A.W., Kump, L.R., 2013. Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA. *Appl. Geochem.* 28, 55-61.
- Harper, J.A., 2008. The Marcellus Shale—An old “new” gas reservoir in Pennsylvania. *Penn. Geol.* 38, 2-13.

- Hayes, T., 2009. Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas. Report by the Gas Technology Institute, Des Plaines, IL. Marcellus Shale Coalition.
- Johnson, J.D., Graney, J.R., 2015. Fingerprinting Marcellus Shale waste products from Pb isotope and trace metal perspectives. *Appl. Geochem.* this issue.
- Johnson, J.D., Graney, J.R., Capo, R.C., Stewart, B.W., 2015. Identification and quantification of regional brine and road salt sources in watersheds along the New York / Pennsylvania border, USA. *Appl. Geochem.* this issue.
- King, G.E., 2012. Hydraulic Fracturing 101: What every representative, environmentalist, regulator, reporter, investor, university researcher, neighbor and engineer should know about estimating frac risk and improving frac performance in unconventional oil and gas wells. SPE Hydraulic Fracturing Conference, The Woodland, Texas, USA, SPE-152596-MS, pp. 1-80.
- Kohl, D., Slingerland, R., Arthur, M., Bract, R., Engelder, T., 2014. Sequence stratigraphy and depositional environments of the Shamokin (Union Springs) Member, Marcellus Formation, and associated strata in the middle Appalachian Basin. *Am. Assoc. Petroleum Geol. Bull.* 98, 483-513.
- Köhler, S.J., Dufaud, F., Oelkers, E.H., 2003. An experimental study of illite dissolution kinetics as a function of pH from 1.4 to 12.4 and temperature from 5 to 50°C. *Geochim. Cosmochim. Acta* 67, 3583-3594.
- Kolesar Kohl, C.A., Capo, R.C., Stewart, B.W., Wall, A.J., Schroeder, K.T., Hammack, R.W., Guthrie, G.D., 2014. Strontium isotopes test long-term zonal isolation of injected and Marcellus Formation water after hydraulic fracturing. *Environ. Sci. Technol.* 48, 9867-9873.
- Kostelnik, J., Carter, K.M., 2012. Unraveling the stratigraphy of the Oriskany Sandstone: A necessity in assessing its site-specific carbon sequestration potential. *Environ. Geosci.* 16, 187-200.
- Krauskopf, K.B., 1956. Dissolution and precipitation of silica at low temperatures. *Geochim. Cosmochim. Acta* 10, 1-26.

- Maloney, K.O., Yoxtheimer, D.A., 2013. Production and disposal of waste materials from gas and oil extraction from the Marcellus Shale play in Pennsylvania. *Environ. Pract.* 14, 278-287.
- McGregor, H.V., Gagan, M.K., 2003. Diagenesis and geochemistry of *Porites* corals from Papua New Guinea: Implications for paleoclimate reconstruction. *Geochim. Cosmochim. Acta* 67, 2147-2156.
- Milici, R.C., Swezey, C.S., 2006. Assessment of Appalachian Basin oil and gas resources: Devonian shale–Middle and Upper Paleozoic total petroleum system. U.S.G.S. Open-File Report 2006-1237, 1-70.
- Milliken, K.L., Rudnicki, M., Awwiller, D.N., Zhang, T., 2013. Organic matter–hosted pore system, Marcellus Formation (Devonian), Pennsylvania. *Am. Assoc. Petroleum Geol. Bull.* 97, 177-200.
- Osborn, S.G., McIntosh, J.C., Hanor, J.S., Biddulph, D., 2012. Iodine-129, $^{87}\text{Sr}/^{86}\text{Sr}$, and trace elemental geochemistry of northern Appalachian Basin brines: Evidence for basinal-scale fluid migration and clay mineral diagenesis. *Am. J. Sci.* 312, 263-287.
- Paytan, A., Kastner, M., Martin, E.E., Macdougall, J.D., Herbert, T., 1993. Marine barite as a monitor of seawater strontium isotope composition. *Nature* 366, 445-449.
- Quinlan, G.M., Beaumont, C., 1984. Appalachian thrusting, lithospheric flexure, and the Paleozoic stratigraphy of the Eastern Interior of North America. *Can. J. Earth Sci.* 21, 973-996.
- Rowan, E.L., Engle, M.A., Kirby, C.S., Kraemer, T.F., 2011. Radium content of oil- and gas-field produced waters in the northern Appalachian Basin (USA): Summary and discussion of data. U.S. Geol. Surv. Sci. Invest. Rep. 2011-5135, 1-31.
- Rowan, E.L., Engle, M.A., Kraemer, T.F., Schroeder, K.T., Hammack, R.W., Doughten, M.W., 2015. Geochemical and isotopic evolution of water produced from Middle Devonian Marcellus Shale gas wells, Appalachian Basin, Pennsylvania. *Am. Assoc. Petroleum Geol. Bull.* DOI:10.1306/07071413146.
- Rozalén, M.L., Huertas, F.J., Brady, P.V., Cama, J., García-Palma, S., Linares, J., 2008. Experimental study of the effect of pH on the kinetics of montmorillonite dissolution at 25°C. *Geochim. Cosmochim. Acta* 72, 4224-4253.

- Schieber, J., 1996. Early diagenetic silica deposition in algal cysts and spores: a source of sand in black shales? *J. Sed. Res.* 66, 175-183.
- Siegel, D.I., Chamberlain, S.C., Dossert, W.P., 1987. The isotopic and chemical evolution of mineralization in septarian concretions: Evidence for episodic paleohydrogeologic methanogenesis. *Geol. Soc. Am. Bull.* 99, 385-394.
- Soeder, D.J., Sharma, S., Pekney, N., Hopkinson, L., Dillmore, R., Kutchko, B., Stewart, B., Carter, C., Hakala, A., Capo, R., 2014. An approach for assessing engineering risk from shale gas wells in the United States. *Int. J. Coal Geol.* 126, 4-19.
- Spivak-Birndorf, L., Stewart, B.W., Capo, R.C., Chapman, E.C., Schroeder, K.T., Brubaker, T.M., 2012. Strontium isotope study of coal utilization by-products interacting with environmental waters. *J. Environ. Qual.* 41, 144-154.
- Stewart, B.W., Capo, R.C., Chadwick, O.A., 2001. Effects of rainfall on weathering rate, base cation provenance, and Sr isotope composition of Hawaiian soils. *Geochim. Cosmochim. Acta* 65, 1087-1099.
- Stowe, M.H., 1928. An occurrence of Oriskany sandstone with celestite cement. *Am. J. Sci.* 16, 446-450.
- Vengosh, A., Jackson, R.B., Warner, N.R., Darrah, T.H., Kondash, A., 2014. A critical review of the risks to water resources from unconventional shale gas development and hydraulic fracturing in the United States. *Environ. Sci. Technol.* 48, 8334-8348.
- Vidic, R.D., Brantley, S.L., Vandenbossche, J.M., Yoxtheimer, D., Abad, J.D., 2013. Impact of shale gas development on regional water quality. *Science* 340.
- Warner, N.R., Jackson, R.B., Darrah, T.H., Osborn, S.G., Down, A., Zhao, K., White, A., Vengosh, A., 2012a. Geochemical evidence for possible natural migration of Marcellus Formation brine to shallow aquifers in Pennsylvania. *Proc. Nat. Acad. Sci.* 109, 11961-11966.
- Warner, N.R., Jackson, R.B., Darrah, T.H., Osborn, S.G., Down, A., Zhao, K., White, A., Vengosh, A., 2012b. Reply to Engelder: Potential for fluid migration from the Marcellus Formation remains possible. *Proc. Nat. Acad. Sci.* 109, E3626.
- Zagorski, W.A., Wrightstone, G.R., Bowman, D.C., 2012. The Appalachian Basin Marcellus gas play: Its history of development, geologic controls on production, and future potential as

a world-class reservoir. In: Breyer, J.A. (Ed.), Shale Reservoirs - Giant Resources for the 21st Century, AAPG Memoir, v. 97, pp. 172-200.