Geochemical and Strontium Isotope Characterization of Produced Waters from Marcellus Shale Natural Gas Extraction

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Ⓢ *Supporting Information*

ABSTRACT: Extraction of natural gas by hydraulic fracturing of the Middle Devonian Marcellus Shale, a major gas-bearing unit in the Appalachian Basin, results in significant quantities of produced water containing high total dissolved solids (TDS). We carried out a strontium (Sr) isotope investigation to determine the utility of Sr isotopes in identifying and quantifying the interaction of Marcellus Formation produced waters with other waters in the Appalachian Basin in the event of an accidental release, and to provide information about the source of the dissolved solids. Strontium isotopic ratios of Marcellus produced waters collected over a geographic range of ∼375 km from southwestern to northeastern Pennsylvania define a relatively narrow set of values (ε_{Sr}^{SW} = +13.8 to +41.6, where ε_{Sr}^{SW} is the deviation of the $^{87}Sr/^{86}Sr$ ratio from that of seawater in parts per 10^4); this isotopic range falls above that of Middle Devonian seawater, and is distinct from most western Pennsylvania acid mine drainage and Upper Devonian Venango Group oil and gas brines. The uniformity of the isotope ratios suggests a basin-wide source of dissolved solids with a component that is more radiogenic than seawater. Mixing models indicate that Sr isotope ratios can be used to sensitively differentiate between Marcellus Formation produced water and other potential sources of TDS into ground or surface waters.
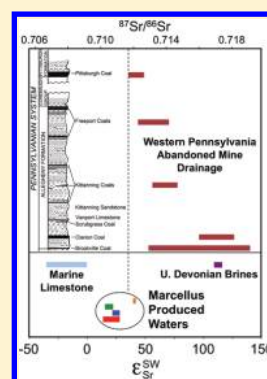
INTRODUCTION

Development of shale gas in the Appalachian Basin Marcellus Formation, one of the world's largest natural gas plays, has increased dramatically with the application of horizontal drilling and hydraulic fracturing techniques, a process that uses 8−15 million liters of water for each well.[1−3] Waters produced from the well comprise a portion of the fracturing fluid, an injected water solution including various chemicals used to facilitate the hydraulic fracturing, as well as possible formation brines. These produced waters have total dissolved solid (TDS) contents often exceeding 200 000 mg/L, with elevated levels of strontium (Sr), bromide (Br⁻), sodium (Na), calcium (Ca), barium (Ba), and chloride (Cl⁻), most likely from interaction with formation waters and/or salts in the producing formation.[4] Currently, TDS is considered an EPA secondary drinking water contaminant at levels above 500 mg/L.[5]

Deep injection is the least expensive method for disposing produced water, with most produced water in the U.S. being disposed in Class II injection wells that target formations with suitable porosity, permeability, and capacity.[6] However, only limited opportunities for deep injection exist in the areas of Pennsylvania where Marcellus Formation gas development is most intense. In these areas, increasingly greater volumes of produced water are being reused to hydraulically fracture subsequent wells. Where reuse is not practical, produced water

is either treated for surface discharge or transported to nearby states where deep injection capacity exists.[6] The storage and transportation of produced water prior to reuse, treatment, or deep injection provide some opportunity for these waters to become commingled with surface water or shallow groundwater through spills or releases. Deeper groundwater also could be affected if the integrity of the well is compromised.[7]

Recent stream contamination events and produced water releases have highlighted the need for methods to distinguish between multiple fossil fuel-related and other sources of TDS. For example, in 2008, high levels of sulfate, chloride, and bromide-dominated TDS were measured in the Monongahela River in western Pennsylvania; the source of this contamination was determined to be outflows from wastewater treatment plants which process both coal mine water and Marcellus Formation produced water.[8] Similarly, in 2009 a significant fish kill occurred in Dunkard Creek, a tributary of the Monongahela River that flows along the border between Greene County, PA, and Monongalia County, WV. This event was caused by a release of high-TDS water, the source of which is still under

debate.[9,10] Additionally, a number of fracturing fluid, produced water, and brine releases have occurred at Marcellus Formation well pads, including three releases at a single pad in Susquehanna County, PA, in which fracturing fluid reached a tributary of Towanda Creek.[11]

Although typical Marcellus Formation produced waters are chemically distinct from streams and uncontaminated groundwater, few geochemical parameters can unambiguously distinguish among all possible sources in the event of a spill or leakage. In Pennsylvania, such sources can include abandoned mine drainage, fly ash impoundments, brines from abandoned oil and gas wells from formations shallower than the Marcellus, road salt, wastewater outflows and septic systems, and industrial discharges. Here we explore the application of strontium (Sr) isotope ratios to address these issues.

The isotopic ratio of radiogenic strontium-87 (^{87}Sr, produced by the decay of ^{87}Rb over geologic time) to the stable Sr isotopes ^{84}Sr, ^{86}Sr, and ^{88}Sr has been shown to be an effective tracer of water−rock interactions and has been used to identify and quantify sources of groundwater constituents in areas impacted by human activity.[12−17] Unlike stable isotopes of oxygen, hydrogen, and carbon, the isotope composition of Sr is not affected by evaporation (e.g., from holding ponds) or biological activity. For the isotope ratio of Sr (expressed as $^{87}Sr/^{86}Sr$) to be used successfully as a natural tracer in ground and surface waters, the isotope ratios of the potential endmembers must be distinct. If potential endmembers have distinct Sr isotopic ratios, Sr isotopes can be used as sensitive indicators of even minute amounts of contamination from brines, and potentially to identify waters interacting with rocks from specific stratigraphic units.[18−20]

In addition, understanding the sources of these salts and metals can be useful in designing drilling strategies and understanding heterogeneities in the producing unit. Many formation brines, including those of the Appalachian Basin, have been found to have a significant component of evaporated seawater.[21−24] Conversely, the presence of lenticular salt deposits in a Marcellus core has led to the hypothesis that the high salinity originates from autochthonous salts.[4] Strontium isotopes can also be used to understand the origin of salts in produced waters, i.e., to determine if salts are from evaporated seawater and to identify additional sources of dissolved constituents (e.g., carbonates, exchangeable sites on clays). We carried out an isotope study of Marcellus produced waters to (1) identify unique isotope "fingerprints" of Marcellus waters to aid in verification of safe disposal; and (2) determine the source of dissolved solids that are abundant and ubiquitous in Marcellus waters.

■ METHODS

Marcellus Produced Waters. Samples of hydraulic fracturing waters and waters produced during and after drilling from wellheads and impoundments from four counties across Pennsylvania (Figure 1) were obtained by DOE-NETL and Bucknell University. Some were collected as time series from the start of pumping, and others were collected from impoundments where they were being held prior to recycling or disposal. Samples BR-A1 through BR-A5 were produced waters collected from five wells in Bradford County; samples BR-A3, A4, and A5 had been recycled through several fracturing operations. Samples beginning with WE were collected from two closely spaced wells (<1 km apart; designated by "A" and "B" in sample name) in Westmoreland
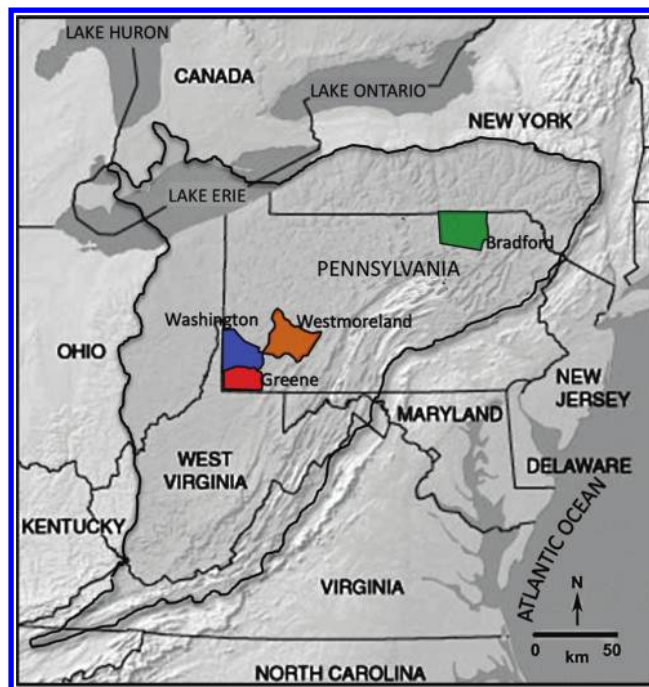

Figure 1. Map showing the extent of the Marcellus Formation (shaded), with the locations (indicated by county) of the samples reported in this study.

County, at the indicated number of days after the start of pumping. Samples labeled WA-B1-# through WA-B3-# were collected in Washington County from three different wastewater impoundments, at various depths (indicated by #) below the water surface (Table 1). Samples WA-A11 through WA-A30 were collected from a well in Washington County at the indicated number of days after the start of pumping. Samples beginning with GR were collected from a well in Greene County at the indicated number of days after the start of pumping; GR-AF is a sample of the water used to hydraulically fracture that well (fracturing fluid).

Coal Mine Drainage. Samples of coal mine drainage (acid, circumneutral, and net alkaline) from bituminous coals of the Pittsburgh Formation and Allegheny Group (Pittsburgh, Freeport, Kittanning, Clarion, and Brookville) were analyzed for Sr isotopes to compare with potential Marcellus produced water. Major element and Sr isotope geochemistry is presented in Supporting Information Table S1.

Analytical Methods. Samples were filtered to <0.45 μm and acidified with ultrapure concentrated nitric acid (HNO_3). Major and trace elements were analyzed by ICP-MS and ICP-OES at DOE-NETL and Bucknell University. Strontium isotope preparation and analysis was carried out under clean lab conditions at University of Pittsburgh. Using Sr concentrations determined by ICP-OES, aliquots containing between 2 and 10 μg of Sr were evaporated to dryness, redissolved in 6 N ultrapure HNO_3, and eluted through columns containing Eichrom Sr resin to separate Sr from all other constituents in the sample. The eluted Sr was evaporated to dryness and redissolved in 2 N ultrapure HNO_3. An aliquot containing approximately 500 ng of Sr was evaporated onto a Re filament preloaded with a Ta oxide carrier agent. Strontium isotopes of the samples as well as the Sr standard SRM 987 were measured using a multidynamic method on a Finnigan-MAT 262 thermal ionization mass spectrometer. The average

Table 1. Major Element and Strontium Isotope Data for Marcellus Produced Water Samples

sample/location	description	mg/L							TDS g/L	$^{87}Sr/^{86}Sr^{a}$	$\varepsilon_{Sr}^{SW b}$
		Na	Ca	Mg	Fe	Sr	Ba	Cl			
Bradford Co., PA											
BR-A1	produced water	30,400	6,120	538	117	1,970	5,490	77,000	109.5	0.710653 ± 07	20.93 ± 0.10
BR-A2	produced water	49,400	20,800	1,750	123	5,230	12,000	159,000	211.4	0.710270 ± 10	15.53 ± 0.14
BR-A3	recycled prod. water	41,900	11,300	1,110	73.7	3,340	7,820	68,000	154.1	0.710742 ± 06	22.18 ± 0.08
BR-A4	recycled prod. water	34,000	7,930	840	50.5	2,870	6,470	77,000	136.6	0.710757 ± 08	22.39 ± 0.11
BR-A5	recycled prod. water	27,600	7,050	726	55.3	2,600	5,860	73,000	120.9	0.710733 ± 09	22.05 ± 0.13
Westmoreland Co., PA											
WE-A1.5	prod. water, day 1.5	NA^{c}	349	NA	NA	46.0	70.0	NA	14.8	0.711992 ± 06	39.81 ± 0.08
WE-A2	prod. water, day 2	2,792	624	43	NA	88.0	179	10,300	21.4	0.712013 ± 10	40.10 ± 0.14
WE-A4	prod. water, day 4	11,747	2,278	217	NA	381	740	29,000	44.8	0.712036 ± 10	40.43 ± 0.14
WE-A5	prod. water, day 5	14,216	2,880	254	NA	450	888	32,200	51.1	0.712027 ± 10	40.30 ± 0.14
WE-A7	prod. water, day 7	18,288	3,938	381	NA	651	1,405	42,000	65.7	0.712044 ± 06	40.54 ± 0.08
WE-A12	prod. water, day 12	23,928	5,603	518	NA	934	2,193	47,900	81.2	0.712013 ± 08	40.10 ± 0.11
WE-A15	prod. water, day 15	24,820	6,292	629	NA	1,127	2,687	53,500	89.5	0.712019 ± 10	40.19 ± 0.14
WE-A29	prod. water, day 29	26,297	6,236	671	NA	1,215	2,987	76,600	99.0	0.712091 ± 07	41.20 ± 0.10
WE-B3	prod. water, day 3	9,901	1,239	694	NA	214	333	19,000	33.3	0.712076 ± 11	40.99 ± 0.16
WE-B5	prod. water, day 5	16,704	2,782	376	NA	533	1,058	30,600	55.6	0.712108 ± 07	41.44 ± 0.10
WE-B7	prod. water, day 7	18,288	3,900	490	NA	738	1,490	40,700	69.4	0.712088 ± 08	41.16 ± 0.11
WE-B9	prod. water, day 9	18,510	4,627	559	NA	900	1,892	46,800	78.4	0.712108 ± 08	41.44 ± 0.11
WE-B13	prod. water, day 13	22,437	5,749	211	NA	1,063	2,306	71,100	89.3	0.712117 ± 09	41.57 ± 0.13
WE-B18	prod. water, day 18	NA	6,278	NA	NA	1,380	2,700	NA	98.1	0.712113 ± 09	41.51 ± 0.13
Washington Co., PA											
WA-A11	prod. water, day 11	32,500	12,278	1,267	38.6	1,393	151	88,500	136.2	0.711129 ± 08	27.64 ± 0.11
WA-A13	prod. water, day 13	35,070	14,028	1,478	41.8	1,694	194	102,100	146.7	0.710988 ± 10	25.65 ± 0.14
WA-A15	prod. water, day 15	37,100	15,269	1,632	17.3	1,832	253	107,300	153.4	NA	
WA-A17	prod. water, day 17	38,530	15,875	1,671	21.6	1,872	296	102,600	156.7	0.711056 ± 11	26.61 ± 0.16
WA-A20	prod. water, day 20	40,350	16,509	1,820	19.0	1,888	328	115,300	167.8	0.711088 ± 09	27.06 ± 0.13
WA-A25	prod. water, day 25	46,260	17,612	1,896	15.6	2,045	349	116,100	168.4	0.711021 ± 10	26.12 ± 0.14
WA-A30	prod. water, day 30	47,881	18,080	1,992	NA	2,151	379	NA	169.4	0.711076 ± 08	26.89 ± 0.11
WA-B1-8	impound#1, 8' depth	20,310	8,682	880	18.7	1,192	176	59,600	108.0	0.710880 ± 10	24.13 ± 0.14
WA-B1-4	impound#1, 4' depth	20,440	8,796	890	15.8	1,205	191	65,300	117.0	0.710905 ± 10	24.48 ± 0.14
WA-B2-9	impound#2, 9' depth	20,510	8,779	859	5.12	1,277	389	59,400	110.7	0.710969 ± 08	25.38 ± 0.11
WA-B2-6	impound#2, 6' depth	20,910	8,818	866	4.37	1,296	339	58,700	108.0	0.710954 ± 10	25.17 ± 0.14
WA-B3-10	impound#3, 10' depth	12,890	5,674	570	0.067	795	10.5	36,700	71.4	0.710737 ± 10	22.11 ± 0.14
WA-B3-5	impound#3, 5' depth	12,940	5,733	589	0.066	803	9.54	36,800	71.4	0.710722 ± 09	21.90 ± 0.13
Greene Co., PA											
GR-AF	frac water	20,923	4,377	567	16.0	1,389	393	41,900	88.7	0.710084 ± 08	12.90 ± 0.11
GR-A1	prod. water, day 1	26,020	6,532	776	43.7	1,397	1,108	63,700	127.2	0.710988 ± 08	25.65 ± 0.11
GR-A2	prod. water, day 2	30,100	7,903	828	44.9	1,823	1,560	65,000	138.8	0.710976 ± 10	25.48 ± 0.14
GR-A3	prod. water, day 3	26,840	7,372	866	49.2	1,721	1,487	67,300	137.8	0.710957 ± 07	25.21 ± 0.10
GR-A4	prod. water, day 4	30,910	8,874	755	38.1	2,009	1,756	70,200	146.2	0.710961 ± 09	25.27 ± 0.13
GR-A5	prod. water, day 5	28,270	7,952	762	1.10	1,868	1,638	71,200	143.1	0.710975 ± 08	25.47 ± 0.11
GR-A7	prod. water, day 7	32,800	8,786	841	26.6	2,415	962	81,900	157.0	0.710148 ± 08	13.80 ± 0.11
GR-A15	prod. water, day 15	32,380	9,634	953	28.1	2,275	2,273	86,500	161.5	0.711160 ± 09	28.08 ± 0.13
GR-A20	prod. water, day 20	34,520	10,390	976	36.1	2,484	2,525	87,700	188.2	0.711173 ± 09	28.26 ± 0.13
GR-A27	prod. water, day 27	NA	NA	NA	NA	NA	NA	NA	NA	0.711183 ± 41	28.40 ± 0.58

^{a}In-run uncertainty in last two decimal places of $^{87}Sr/^{86}Sr$ ratio. $^{b}\varepsilon_{Sr}^{SW} = 10^{4}(^{87}Sr/^{86}Sr_{sample}/^{87}Sr/^{86}Sr_{seawater} - 1)$; measured $^{87}Sr/^{86}Sr_{seawater} = 0.709169$. ^{c}NA = not analyzed.

$^{87}Sr/^{86}Sr$ ratio of SRM 987 over the period of these analyses was $0.710243 ± 0.000017$ ($n = 45$).

Strontium isotope ratios are presented using epsilon notation, where the $^{87}Sr/^{86}Sr$ ratio of the sample is normalized to the globally uniform $^{87}Sr/^{86}Sr$ ratio of present-day seawater:

$$\varepsilon_{Sr}^{SW} = 10^{4}\left(\frac{^{87}Sr/^{86}Sr_{sample}}{^{87}Sr/^{86}Sr_{seawater}} - 1\right)$$

Based on alternating measurements of SRM 987 and seawater ($n = 23$ for each), the offset between the two ($^{87}Sr/^{86}Sr_{SRM987} - {^{87}Sr/^{86}Sr_{seawater}}$) is 0.001074, leading to a corresponding seawater $^{87}Sr/^{86}Sr$ value of 0.709169.

RESULTS AND DISCUSSION

Produced Water Dissolved Load. Major element data from the Pennsylvania produced waters reported here (Table 1) indicate that these waters share many of the characteristics

previously reported for Marcellus Formation produced waters,[4] including variable but generally high TDS (20 000 to >200 000 mg/L), the predominance of Na and Cl in the dissolved load, and very high concentrations of Ba and Sr (up to 12 000 and 5200 mg/L, respectively). Chloride is largely balanced by Na^+, with Ca^{2+} providing most of the remaining charge balance (Figure 2a). The wells and impoundment waters from
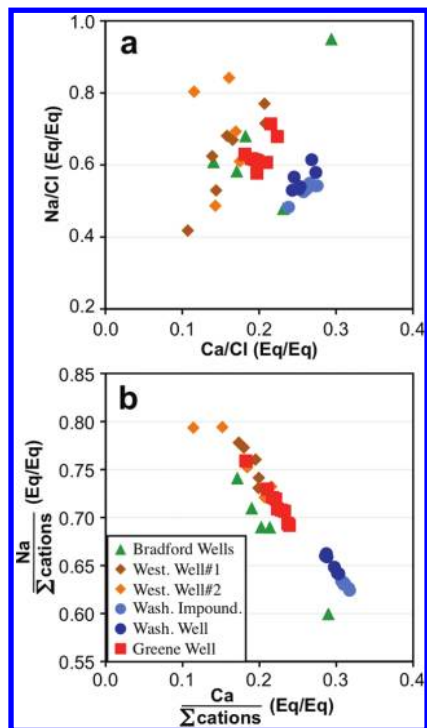

Figure 2. Variations in the chemical composition of Marcellus Formation produced water. (a) Na/Cl ratios plotted against Ca/Cl on an equivalent basis. Na and Ca are the dominant cations that together account for most of the Cl in produced waters, suggesting a source with both NaCl- and $CaCl_2$-type salts or brines. (b) Na and Ca normalized to the sum of all cations, on an equivalent basis. The offset of the Bradford County samples (green triangles) from the rest of the trend reflects the very high concentrations of Ba and Sr in these waters.

Washington County have more Ca-rich compositions compared to the other produced waters. Comparison of Na and Ca to the sum of all cations (Figure 2b) indicates the importance of Na and Ca to the overall dissolved load. The offset of the Bradford County samples from this trend reflects the extremely high concentrations of Sr and Ba in these waters, which contribute significantly to the overall dissolved load. There are no clear geographic trends in concentration from the southwestern-most to the northeastern-most produced waters, although the Bradford County produced waters tend to have the highest concentrations of dissolved constituents, and the Westmoreland County waters tend to have the lowest.

Marcellus produced waters are known for their high Ba and Sr concentrations.[4] Both of these are alkaline earth elements, with geochemical characteristics similar to those of Ca and magnesium (Mg). When normalized to Ca to account for the large variations in TDS, Ba and Sr show a positive correlation across the region, with only the Greene County well data diverging significantly from the trend (Figure 3a). However, data from each well or region fall within unique, non-
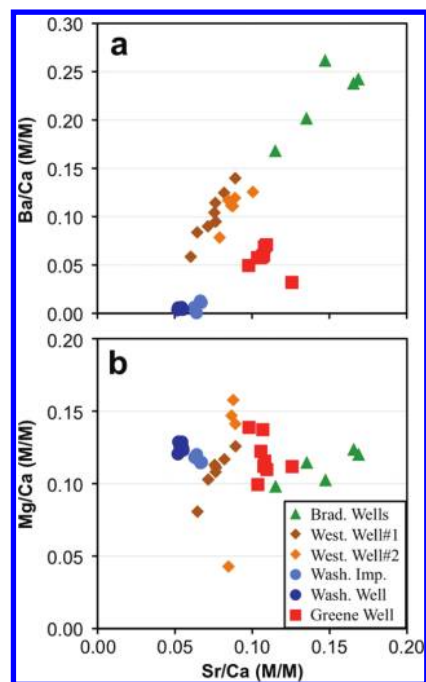

Figure 3. Variations in Sr, Ba, and Mg with Ca in Marcellus Formation produced waters. (a) Ca-normalized Ba concentrations show a generally coherent positive trend across Pennsylvania when plotted against Ca-normalized Sr, with the well waters from Greene County showing the most significant deviation from the trend. (b) Ca-normalized Mg concentrations do not exhibit a regional-scale trend, and are only weakly correlated within each well or region.

overlapping parts of this plot. In contrast, the Mg/Ca ratio shows no systematic correlation with Sr/Ca in the Marcellus Basin as a whole, although individual wells or regions sometimes have a weak correlation (Figure 3b). In addition, the Mg/Ca ratio varies over a much smaller range of values (most within the molar ratio of 0.10−0.15) compared to the range of Ba/Ca and Sr/Ca ratios. Thus Mg and Ca are relatively coherent across the basin, whereas Ba, and to a lesser extent Sr, may be affected more strongly by local variations.

The shifts in Ba and Sr across the basin are unlikely to result solely from variations in the shale barite ($BaSO_4$) content (and dissolution in hydraulic fracturing fluid), as the Sr/Ba ratios in the produced waters are significantly higher than those expected for marine barite (0.03−0.08).[25] The positive correlations of Ba with Sr at high Sr/Ba ratios within individual wells argues against either introduction of Ba from drilling muds or removal of Ba by scaling (e.g., precipitation of $BaSO_4$ in pipes and pore spaces) prior to extraction of the brine, as both of these should affect Ba much more strongly than Sr. The range of Ba and Sr concentrations in produced waters is most likely controlled by the combined dissolution of Ba- and Sr-rich minerals such as barite, witherite ($BaCO_3$), celestite ($SrSO_4$), and strontianite ($SrCO_3$), with the large differences in Ba/Ca and Sr/Ca among different regions reflecting the co-occurrence of these minerals at different abundances within shales of the Marcellus Formation.[26]

Sr Isotope Composition of Produced Waters. Strontium isotope ratios for Marcellus Formation produced waters are reported in Table 1. Most produced waters fall within an ε_{Sr}^{SW} range of +13.8 to +28.4; only the Westmoreland County wells deviate significantly, with an ε_{Sr}^{SW} range of +39.8 to +41.6. The total range of values for Marcellus produced waters,

including the Westmoreland County samples, is quite restricted compared to possible water and rock with which they might interact. For example, Phanerozoic marine limestone falls within a range of −35 to 0,[27] and abandoned coal mine drainage outflows in western Pennsylvania can range from +35 to +140 (Table S1). Assuming that this wide range reflects typical ground and surface waters in the area, the ε_{Sr}^{SW} values of Marcellus produced waters will likely be a distinguishing characteristic compared to local shallow groundwater or surface waters, or to other high-TDS waters.

In those sites where produced water was collected as it came out of the well, Sr (as well as other major elements not plotted) shows a clear trend of increasing concentration over time (Figure 4a). This apparently reflects progressive incorporation
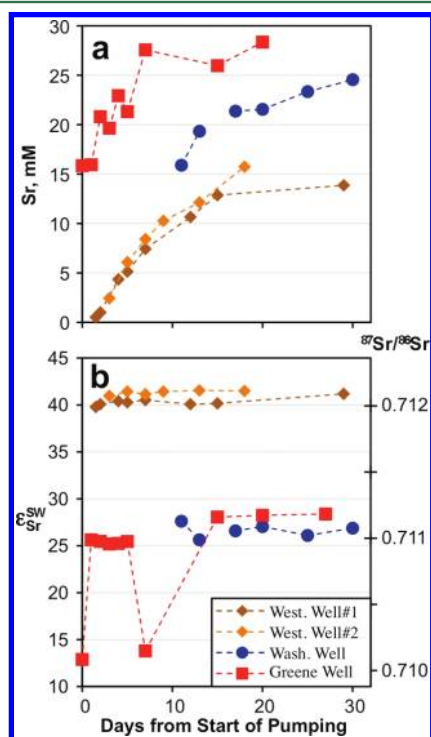

Figure 4. Variations in (a) Sr concentration and (b) ε_{Sr}^{SW} (or $^{87}Sr/^{86}Sr$) plotted against the day of sample collection from the start of pumping. For the Greene County well (red squares) the point at day 0 is fracturing fluid. In all cases, the Sr concentration starts out lower and builds gradually to near a steady state value by 30 days. In contrast, the ε_{Sr}^{SW} values appear to hit a steady state value within 5−10 days after initiation of pumping, reflecting the domination of Marcellus Formation salt or brine Sr to the overall Sr budget.

of salts or connate brines into the hydraulic fracturing fluid. In contrast, the produced waters reached a relatively constant ε_{Sr}^{SW} value within the first two days of pumping (Figure 4b). It appears that in most cases, individual wells will produce waters with a very narrow range of ε_{Sr}^{SW} values, most likely reaching a steady state value within the first few days after commencement of pumping.

Origin of TDS in Marcellus Produced Waters. The relatively narrow range of ε_{Sr}^{SW} values of Marcellus Formation produced waters appears to be a distinguishing characteristic of these waters. Even when corrected for ^{87}Rb decay using available Rb concentration data, these values fall above the range of Middle Devonian seawater values,[28] and in fact above any Phanerozoic seawater.[27] If the salts or brines that are

accessed by hydraulic fracturing are of marine origin, there must have been addition of radiogenic Sr (^{87}Sr) prior or subsequent to incorporation into shales of the Marcellus Formation. Possible sources include the silicate portion of the shale itself (primarily clays), which should be relatively enriched in ^{87}Sr, or basinal fluids that interacted with adjacent units before being incorporated (as brine or salt) in the Marcellus Formation. Given the relative homogeneity of the Sr isotope ratios over the ~375 km distance represented by our sampling, large-scale fluid flow is a more likely source of the radiogenic Sr than localized incorporation of Sr from the shale. Evans[29] documented multiple episodes of fluid migration in the Marcellus Formation based on fluid inclusion analysis. The somewhat bimodal distribution of values between the Westmoreland County waters and all of the others could reflect lithological variations within the Marcellus Formation, or variations in ε_{Sr}^{SW} across the depositional basin. Additional produced water data combined with stratigraphic correlations will be required to characterize specific geographic trends in the Sr isotope ratios.

An important question in hydraulic fracturing is the extent to which the induced fractures remain in the target formation. If the fractures and hydraulic fracturing fluid come into contact with underlying or overlying formations, then additional solids could be introduced into the fluid. The Marcellus Formation in the sampling area is underlain by the Onondaga or Selinsgrove Limestone, and is overlain by shale and limestone members of the Hamilton Group. The Cherry Valley Limestone also divides upper and lower shale members of the Marcellus Formation. Unaltered marine limestones would normally have low ε_{Sr}^{SW} values (−35 to 0), while other shale units are likely to have variable ε_{Sr}^{SW} values reflecting different sedimentary sources and histories. The narrow range of ε_{Sr}^{SW} values from Marcellus Formation produced waters argues against significant incursions of hydraulic fracturing fluid into adjacent units. If the fluids did interact with adjacent units, the produced water would inherit the isotope signatures of brines or salts from those units, and it is highly unlikely that these would have isotopic compositions in the same narrow range as the ε_{Sr}^{SW} values measured here. The argument against incursions into adjacent units is further bolstered by the apparently rapid attainment of steady state in ε_{Sr}^{SW} achieved by produced waters. Interaction with units outside of the Marcellus gas production zones would likely cause greater variation than what is seen in the time series data (Figure 4b). The drop in ε_{Sr}^{SW} on day 7 of the Greene County well production could reflect incorporation of solids from another source, either within or outside of the Marcellus Formation, but this isotope excursion was relatively short-lived. On the whole, the isotope variations in the Marcellus produced waters analyzed in this study are best explained by interactions with salts or brines within the shale itself.

Signatures of Marcellus Produced Waters. Elevated TDS alone is not always an effective tracer of produced water contributions,[30] nor are variations in concentrations of dissolved chemical species, even those that are present at unusually high levels. Due to the low solubility of barite ($K_{sp} = 10^{-10}$), Ba cannot be considered a conservative element in aqueous systems, especially in cases where sulfate could be introduced from abandoned coal mine drainage (AMD). The very high concentrations of Ba in produced water may be stabilized by organic matter, excess Cl⁻, or the addition of antiscalants to hydraulic fracturing fluids, but dilution by

freshwater is likely to cause significant precipitation of barite, which may be enhanced by further oxidation of S^- to SO_4^{2-}[31] and the interaction of produced water with AMD. High Na and Cl concentrations are also characteristic of Marcellus produced waters. However, streams and rivers in populated areas often already contain significant concentrations of Na and Cl due to the use of road salt, leakage of septic systems, and wastewater outflows.[32,33] In some cases, alkaline abandoned mine drainage can have Na/Ca ratios equal to or higher than those of produced water (Table S1). A modest inflow of produced water would not be easily distinguishable or quantifiable under these circumstances. Moreover, brines from abandoned and leaking oil and gas wells from shallower formations commonly contain Na, Cl, Ba, and Sr at concentrations comparable to those of Marcellus produced waters.[34]

Similarly, carbon isotopes alone are not always sufficient in distinguishing sources of high TDS. Isotopic fingerprinting using carbon isotopes can distinguish microbial from thermogenic methane.[35−42] However, in some cases this method may not be able to distinguish between different stratigraphic sources of natural gas, such as between shallower natural gas sources tapped decades ago vs. a deep shale source in the Marcellus Formation, or between pipeline and storage gases and native thermogenic gas. Thermogenic methane from different units and ages can have similar methane isotopic signatures, resulting in ambiguous determination of the provenance of the carrier fluid.[37,41−43]

Because Marcellus produced waters have a restricted range of Sr isotope compositions, ε_{Sr}^{SW} values could be a powerful tool for identifying possible sources of TDS introduced into streams or shallow aquifers. In the Appalachian region of the U.S., increases in dissolved solids to waterways can have several vectors, including road salt, drainage from inactive coal mines, leaching of coal fly ash disposal sites, and leakage of produced water from Marcellus Formation natural gas production. If the Sr concentration and isotope composition of two waters are known, then their mixing ratio can be precisely calculated, provided they have different ε_{Sr}^{SW} values. The isotope ratio of the mixture is given by:

$$R_m = \frac{J_1 C_1 R_1 + J_2 C_2 R_2}{J_1 C_1 + J_2 C_2} \tag{1}$$

where R_m is the isotope ratio of the final mixture (expressed as ε_{Sr}^{SW}), J_1 and J_2 are the fluxes of the two endmember liquids prior to mixing, C_1 and C_2 are the Sr concentrations of the endmembers, and R_1 and R_2 are the Sr isotope compositions of the endmembers. This can be rearranged to give the flux ratio:

$$\frac{J_1}{J_2} = \frac{C_2 R_2 + C_2 R_m}{C_1 R_m + C_1 R_1} \tag{2}$$

As can be seen from eq 1, the isotope ratio of the mixture will be very sensitive to a component with a high Sr concentration, such as Marcellus produced waters. In a hypothetical case of produced water with 1000 mg/L Sr and $\varepsilon_{Sr}^{SW} = +25$ mixing into a stream containing 0.5 mg/L Sr with $\varepsilon_{Sr}^{SW} = +50$, an addition of only 0.05% of the produced water would shift the stream ratio from +50 to +37.5, well outside of measurement precision ($< \pm 0.2$).

In western Pennsylvania, AMD has long been a source of pollution to local waterways. In several recent cases, an increase in TDS in local waterways has been attributed both to AMD and to leakage of produced waters.[8−10] Cases such as these can

potentially be resolved using Sr isotopes to identify the source of TDS. The Sr isotope composition of AMD from a variety of localities (Table S1) tends to be higher than that of produced water, and it also varies somewhat systematically with stratigraphic position of the mined coal (Figure 5). Although
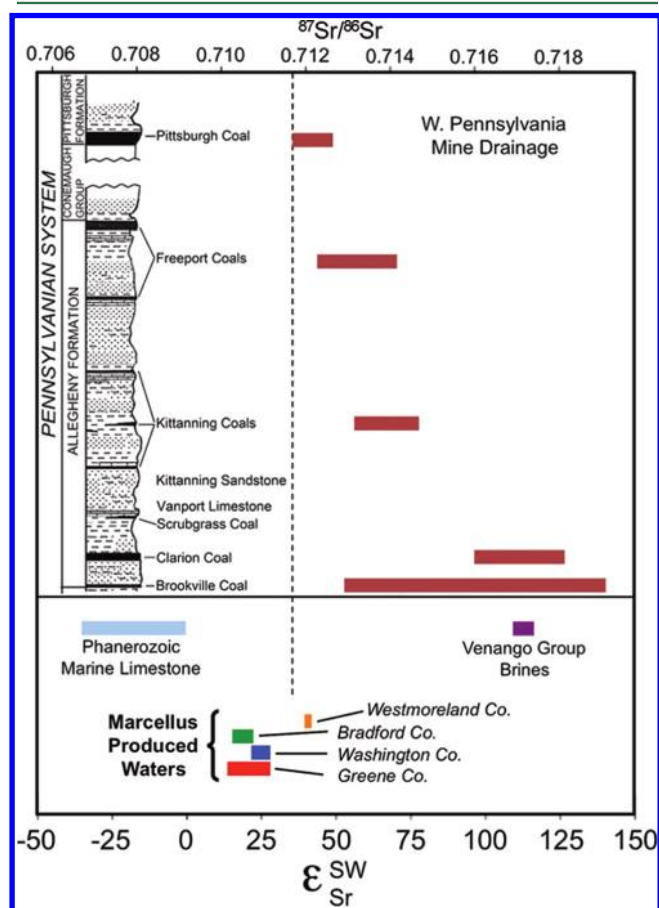

Figure 5. Strontium isotopic variations of Marcellus Formation produced waters compared to western Pennsylvania AMD, Phanerozoic limestone,[27] and brines from the Venango Group, Pennsylvania.[20] The Marcellus produced waters define a relatively tight field compared to other possible sources of Sr in the Marcellus natural gas production region. The isotopic composition of AMD waters appears to vary systematically with stratigraphic height, with the only overlap between AMD and produced waters coming from Pittsburgh coal AMD and produced waters from Westmoreland County. The tight clustering of Marcellus produced water values and large difference between these and other possible TDS sources indicate that Sr isotopes can be an effective tracer for produced water.

there is a limited degree of overlap in ε_{Sr}^{SW} values, in most cases a clear distinction would be expected between produced water and AMD sources. The same is true of leakage from fly ash impoundments, which could have a range of ε_{Sr}^{SW} values from −8 to +80,[44,45] as well as very high Ba and Sr concentrations.[46]

The utility of Sr isotopes in identifying and quantifying sources of TDS to waterways can be further enhanced by combining ε_{Sr}^{SW} with a distinguishing chemical parameter. This study indicates that Sr/Ca ratios of produced water, while forming a basin wide trend, tend to vary from well to well (Figure 3a). Because both Sr and Ca are expected to be conservative tracers in these aqueous systems, combining Sr/Ca ratios with ε_{Sr}^{SW} values is likely to allow us to distinguish between sources in nearly all cases. To demonstrate, we

calculated mixing equations for a hypothetical stream with an isotope ratio ($\varepsilon_{Sr}^{SW} = +35$) between those of the Westmoreland County produced waters and all other produced waters, but with Sr/Ca ratios typical of natural streams. Mixing curves were generated for this stream interacting with Marcellus produced waters, acid mine drainage from the Pittsburgh Coal Seam, and brines drawn from abandoned oil wells tapping the Venango Group (Figure 6).[20] Produced waters from each well or region
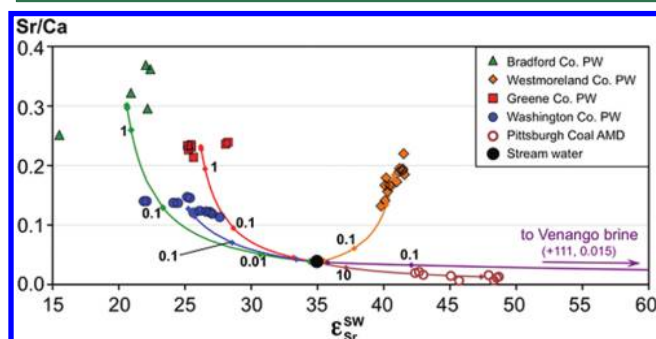
Figure 6. Mixing curves for a hypothetical stream being impacted by Marcellus Formation produced waters (all filled symbols indicated as "PW"), acid mine drainage (open circles), and Venango Group oil well brines (off scale). The produced waters are separated in Sr/Ca- ε_{Sr}^{SW} space by geographic location. For each endmember, a weighted mean value is used to calculate the mixing curve, and individual samples are shown for comparison (except for Venango Group brines, which plot off scale to the right). The labeled tick marks on the curve indicate the percent flux of each endmember added to the hypothetical streamwater. A very small amount of produced water (0.01–0.1%) added to the stream can produce large shifts in ε_{Sr}^{SW} of 5–15 epsilon units (note that typical measurement uncertainty is <0.2 epsilon units). A 1% addition of produced water will shift the stream isotopic composition to the ε_{Sr}^{SW} of the produced water. Conversely, much larger amounts of AMD are required to shift the isotopic composition of the stream toward that endmember.

fall in a unique portion of Sr/Ca-ε_{Sr}^{SW} space. Using the mean values as mixing endmembers, we can calculate the shift in Sr/Ca and ε_{Sr}^{SW} resulting from addition of the produced waters or AMD to a stream; the labeled tick marks on the curves indicate the percentage of produced water or AMD required to generate the observed shift. In some cases, a flux equivalent to only 0.01% of the streamflow results in significant shifts of the streamwater isotope ratios, and a 0.1% addition can move the Sr/Ca and ε_{Sr}^{SW} of the stream up to halfway toward the produced water endmember values. In all cases, the stream ε_{Sr}^{SW} value is completely dominated by produced water when the produced water flux reaches 1% of the streamflow. In contrast, much more AMD (>10%) would be required to shift stream waters significantly toward AMD ε_{Sr}^{SW} values. Because the AMD inflows in any given location are likely to be significantly different in ε_{Sr}^{SW} from Marcellus produced waters, this method is likely to yield definitive evidence for the source of TDS contamination. In the event of a produced water spill, the amount of produced water or other contaminant entering the stream can be quantified. We note that the example shown in Figure 6 is for a stream with an isotopic composition not very different from Marcellus produced waters. Streams with ε_{Sr}^{SW} values greater than about +50, which are likely to be common in the Appalachian Basin, will be even more sensitive to influxes of Marcellus produced waters. Influxes of more than one contaminant into a stream would define a mixing field (rather than line) in a mixing diagram and could still be usefully quantified. Addition of other conservative tracers would allow extension of this simple mixing model to more complex cases of multiple contaminant sources.

An approach that integrates geochemistry, hydrogeology, and knowledge of historical background is critical to the successful remediation of existing water quality problems and the protection of water resources in the Appalachian Basin and other geologically and hydrochemically complex areas. These data suggest that the Sr isotope ratios constitute an extremely sensitive tracer with strong potential as a tool for verification of safe water disposal, and can be used to determine the origin of TDS in surface and ground waters affected by multiple sources as well as quantify mixing between them.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Table S1, containing major element chemistry, pH, alkalinity, and Sr isotope ratios for coal mine drainage outflows in western Pennsylvania. This information is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

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■ REFERENCES

(1) *Modern Shale Gas Development in the United States: A Primer*; United States Department of Energy Office of Fossil Energy: Oklahoma City, OK, 2009; http://www.netl.doe.gov/technologies/oil-gas/publications/epreports/shale_gas_primer_2009.pdf.
(2) Kerr, R. A. Natural gas from shale bursts onto the scene. *Science* **2010**, *328* (5986), 1624–1626.
(3) *2009 Year End Workload Reports*; Pennsylvania Department of Environmental Protection: Harrisburg, PA, 2010; http://files.dep.state.pa.us/OilGas/BOGM/BOGMPortalFiles/OilGasReports/2009/2009_Year_End_Reports.pdf.
(4) Blauch, M. E.; Myers, R. R.; Moore, T. R.; Lipinski, B. A., Marcellus Shale post-frac flowback waters - Where is all the salt coming from and what are the implications? 2009 Society of Petroleum Engineers Eastern Regional Meeting, SPE 125740, Charleston, WV, 2009; pp 1–20.
(5) *National Primary Drinking Water Regulations*; EPA 816-F-09-004; United States Environmental Protection Agency: Washington, DC, 2009; http://water.epa.gov/drink/contaminants/upload/mcl-2.pdf.
(6) *Final Report: Water Management Technologies Used by Marcellus Shale Gas Producers*; United States Department of Energy-NETL-

Argonne National Lab: Argonne, IL, 2010; http://www.evs.anl.gov/pub/dsp_detail.cfm?PubID=2537.

(7) Kargbo, D. M.; Wilhelm, R. G.; Campbell, D. J. Natural gas plays in the Marcellus Shale: Challenges and potential opportunities. *Environ. Sci. Technol.* **2010**, *44* (15), 5679−5684.

(8) *Pennsylvania Nonpoint Source Management Program FFY2008 Annual Report*; Pennsylvania Department of Environmental Protection: Harrisburg, PA, 2009; http://www.epa.gov/reg3wapd/pdf/pdf_nps/nps_annualreports/2008/FY2008_PA-Final-Annual-Report.pdf.

(9) Renner, R. Spate of gas drilling leaks raises Marcellus concerns. *Environ. Sci. Technol.* **2009**, *43* (20), 7599.

(10) *Press Release: PA Fish and Boat Commission sues Consol Energy over Dunkard Creek environmental disaster*; Pennsylvania Fish and Boat Commission: Harrisburg, PA, 2011; http://www.fish.state.pa.us/newsreleases/2011press/dunkard-sue.htm.

(11) *Supplemental Generic Environmental Impact Statement on the Oil, Gas and Solution Mining Regulatory Program*; New York State Department of Environmental Conservation: Albany, NY, 2011; http://www.dec.ny.gov/energy/47554.html.

(12) Bayless, E. R.; Bullen, T. D.; Fitzpatrick, J. A. Use of ^{87}Sr/^{86}Sr and δ^{11}B to identify slag-affected sediment in southern Lake Michigan. *Environ. Sci. Technol.* **2004**, *38* (5), 1330−1337.

(13) Leung, C.-M.; Jiao, J. J. Use of strontium isotopes to identify buried water main leakage into groundwater in a highly urbanized coastal area. *Environ. Sci. Technol.* **2006**, *40* (21), 6575−6579.

(14) Brinck, E. L.; Frost, C. D. Detecting infiltration and impacts of introduced water using strontium isotopes. *Ground Water* **2007**, *45* (5), 554−568.

(15) Jiang, Y.; Wu, Y.; Yuan, D. Human impacts on karst groundwater contamination deduced by coupled nitrogen with strontium isotopes in the Nandong Underground River System in Yunan, China. *Environ. Sci. Technol.* **2009**, *43* (20), 7676−7683.

(16) Hamel, B. L.; Stewart, B. W.; Kim, A. G. Tracing the interaction of acid mine drainage with coal utilization byproducts in a grouted mine: Strontium isotope study of the inactive Omega Coal Mine, West Virginia (USA). *Appl. Geochem.* **2010**, *25* (2), 212−223.

(17) Christian, L. N.; Banner, J. L.; Mack, L. E. Sr isotopes as tracers of anthropogenic influences on stream water in the Austin, Texas, area. *Chem. Geol.* **2011**, *282* (3/4), 84−97.

(18) Barnaby, R. J.; Oetting, G. C.; Gao, G. Strontium isotopic signatures of oil-field waters: Applications for reservoir characterization. *Am. Assoc. Pet. Geol. Bull.* **2004**, *88* (12), 1677−1704.

(19) Peterman, Z. E.; Thamke, J. N.; Futa, K.; Oliver, T. A. Strontium isotope detection of brine contamination in the East Poplar oil field, Montana. *U.S.G.S. Open-File Rep.* **2010**, *2010−1326*, 1−20.

(20) Chapman, E. C.; Capo, R. C.; Stewart, B. W.; Hedin, R. S.; Weaver, T. J.; Edenborn, H. M. Strontium isotope quantification of siderite, brine, and acid mine drainage contributions to abandoned gas well discharges in the Appalachian Plateau. *Appl. Geochem.* **2012**, submitted.

(21) Steuber, A. M.; Walter, L. M. Origin and chemical evolution of formation waters from Silurian-Devonian strata in the Illinois basin, USA. *Geochim. Cosmochim. Acta* **1991**, *55* (1), 309−325.

(22) Rowan, E. L.; de Marsily, G. Infiltration of Late Palaeozoic evaporative brines in the Reelfoot rift: a possible salt source for Illinois basin formation waters and MVT mineralizing fluids. *Pet. Geosci.* **2001**, *7* (3), 269−279.

(23) McIntosh, J. C.; Walter, L. M.; Martini, A. M. Extensive microbial modification of formation water geochemistry: Case study from a Midcontinent sedimentary basin, United States. *Geol. Soc. Am. Bull.* **2004**, *116* (5/6), 743−759.

(24) Rowan, E. L. Inorganic chemistry of produced water in the Appalachian Basin. In *EPA Technical Workshop for the Hydraulic Fracturing Study*; Arlington, VA, 2011; pp 10−13.

(25) Paytan, A.; Averyt, K.; Faul, K.; Gray, E.; Thomas, E. Barite accumulation, ocean productivity, and Sr/Ba in Barite across the Paleocene−Eocene Thermal Maximum. *Geology* **2007**, *35* (12), 1139−1142.

(26) Siegel, D. I.; Chamberlain, S. C.; Dossert, W. P. The isotopic and chemical evolution of mineralization in septarian concretions: Evidence for episodic paleohydrogeologic methanogenesis. *Geol. Soc. Am. Bull.* **1987**, *99* (3), 385−394.

(27) Burke, W. H.; Denison, R. E.; Hetherington, E. A.; Koepnick, R. B.; Nelson, H. F.; Otto, J. B. Variation of seawater ^{87}Sr/^{86}Sr throughout Phanerozoic time. *Geology* **1982**, *10* (10), 516−519.

(28) Diener, A.; Ebneth, S.; Veizer, J.; Buhl, D. Strontium isotope stratigraphy of the Middle Devonian: Brachiopods and conodonts. *Geochim. Cosmochim. Acta* **1996**, *60* (4), 639−652.

(29) Evans, M. A. Fluid inclusions in veins from the Middle Devonian shales: A record of deformation conditions and fluid evolution in the Appalachian Plateau. *Geol. Soc. Am. Bull.* **1995**, *107* (3), 327−339.

(30) Frost, C. D.; Brinck, E. L.; Mailloux, J.; Sharma, S.; Campbell, C. E.; Carter, S. A.; Pearson, B. N. Innovative approaches for tracing water co-produced with coalbed natural gas: Applications of strontium and carbon isotopes of produced water in the Powder River Basin, Wyoming and Montana. In *Coalbed Natural Gas: Energy and Environment*; Reddy, K. J., Ed.; Nova Publishers: Hauppauge, NY, 2010; pp 59−80.

(31) Blount, C. W. Barites solubilities and thermodynamic quantities up to 300°C and 1400 bar. *Am. Miner.* **1977**, *62* (9/10), 942−957.

(32) Berner, E. K.; Berner, R. A. *Global Environment: Water, Air, and Geochemical Cycles*; Prentice Hall: Upper Saddle River, NJ, 1996.

(33) Mullaney, J. R.; Lorenz, D. L.; Arntson, A. D. Chloride in groundwater and surface water in areas underlain by the glacial aquifer system, northern United States. *USGS Sci. Invest. Rep.* **2009**, *5086*, 1−41.

(34) Dresel, P. E.; Rose, A. W. Chemistry and origin of oil and gas well brines in western Pennsylvania. *Pennsylvania Geol. Surv. Open-File Rep.* **2010**, *10−01.0*, 1−48.

(35) Schoell, M. The hydrogen and carbon isotopic composition of methane from natural gases of various origins. *Geochim. Cosmochim. Acta* **1980**, *44* (5), 649−661.

(36) Schoell, M. Genetic characterization of natural gases. *Am. Assoc. Pet. Geol. Bull.* **1983**, *67* (12), 2225−2238.

(37) Baldassare, F. J.; Laughrey, C. D. Identifying the sources of stray methane by using geochemical and isotopic fingerprinting. *Environ. Geosci.* **1997**, *4* (2), 85−94.

(38) Kaplan, I. R.; Galperin, Y.; Lu, S.-T.; Lee, R.-P. Forensic environmental geochemistry: differentiation of fuel-types, their sources and release time. *Org. Geochem.* **1997**, *27* (5/6), 289−317.

(39) Martini, A. M.; Walter, L. M.; McIntosh, J. C. Identification of microbial and thermogenic gas components from Upper Devonian black shale cores, Illinois and Michigan basins. *Am. Assoc. Pet. Geol. Bull.* **2008**, *92* (3), 327−339.

(40) Osborn, S. G.; McIntosh, J. C. Chemical and isotopic tracers of the contribution of microbial gas in Devonian organic-rich shales and reservoir sandstones, northern Appalachian Basin. *Appl. Geochem.* **2010**, *25* (3), 456−471.

(41) Révész, K. M.; Breen, K. J.; Baldassare, F. J.; Burruss, R. C. Carbon and hydrogen isotopic evidence for the origin of combustible gases in water-supply wells in north-central Pennsylvania. *Appl. Geochem.* **2010**, *25* (12), 1845−1859.

(42) Osborn, S. G.; Vengosh, A.; Warner, N. R.; Jackson, R. B. Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proc. Nat. Acad. Sci.* **2011**, *108* (20), 8172−8176.

(43) Saba, T.; Orzechowski, M. Letter: Lack of data to support a relationship between methane contamination of drinking water wells and hydraulic fracturing. *Proc. Nat. Acad. Sci.* **2011**, *108* (37), E663.

(44) Spivak-Birndorf, L.; Stewart, B. W.; Capo, R. C.; Chapman, E. C.; Schroeder, K. T.; Brubaker, T. M. Strontium isotope study of coal utilization by-products interacting with environmental waters. *J. Environ. Qual.* **2012**, *41* (1), 144−154.

(45) Brubaker, T. M.; Stewart, B. W.; Capo, R. C.; Schroeder, K. T.; Chapman, E. C.; Spivak-Birndorf, L. J.; Vesper, D. J.; Cardone, C. R.; Rohar, P. C. Coal fly ash interaction with environmental fluids:

Geochemical and strontium isotope results from combined column and batch leaching experiments. *Appl. Geochem.* **2012**, submitted.

(46) Querol, X.; Umaña, J. C.; Alastuey, A.; Ayora, C.; Lopez-Soler, A.; Plana, F. Extraction of soluble major and trace elements from fly ash in open and closed leaching systems. *Fuel* **2001**, *80* (6), 801−813.

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