Trace metal distribution and mobility in drill cuttings and produced waters from Marcellus Shale gas extraction: Uranium, arsenic, barium

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ABSTRACT

Development of unconventional shale gas wells can generate significant quantities of drilling waste, including trace metal-rich black shale from the lateral portion of the drillhole. We carried out sequential extractions on 15 samples of dry-drilled cuttings and core material from the gas-producing Middle Devonian Marcellus Shale and surrounding units to identify the host phases and evaluate the mobility of selected trace elements during cuttings disposal. Maximum whole rock concentrations of uranium (U), arsenic (As), and barium (Ba) were 47, 90, and 3333 mg kg^{-1}, respectively. Sequential chemical extractions suggest that although silicate minerals are the primary host for U, as much as 20% can be present in carbonate minerals. Up to 74% of the Ba in shale was extracted from exchangeable sites in the shale, while As is primarily associated with organic matter and sulfide minerals that could be mobilized by oxidation. For comparison, U and As concentrations were also measured in 43 produced water samples returned from Marcellus Shale gas wells. Low U concentrations in produced water (<0.084–3.26 µg L^{-1}) are consistent with low-oxygen conditions in the wellbore, in which U would be in its reduced, immobile form. Arsenic was below detection in all produced water samples, which is also consistent with reducing conditions in the wellbore minimizing oxidation of As-bearing sulfide minerals.

Geochemical modeling to determine mobility under surface storage and disposal conditions indicates that oxidation and/or dissolution of U-bearing minerals in drill cuttings would likely be followed by immobilization of U in secondary minerals such as schoepite, uranophane, and soddyite, or uraninite as conditions become more reducing. Oxidative dissolution of arsenic containing sulfides could release soluble As in arsenate form under oxic acidic conditions. The degree to which the As is subsequently immobilized depends on the redox conditions along the landfill flow path. The results suggest that proper management of drill cuttings can minimize mobilization of these metals by monitoring and controlling Eh, pH and dissolved constituents in landfill leachates.

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1. Introduction

Unconventional oil and gas production using directional drilling and hydraulic fracturing techniques has transformed the future energy outlook of not only the USA but also the rest of the world (Engelder and Lash, 2008; Kargbo et al., 2010). Although a number of studies discuss the potential economic and environmental benefits of increased production of unconventional fossil fuels (e.g., Cathles, 2012; Dale et al., 2013; Howarth et al., 2011), more

scientific research is needed to develop best practices and address public concerns related to its expansion (Gregory et al., 2011; Howarth et al., 2011; Souther, 2013; Vidic et al., 2013; Soeder et al., 2014; Vengosh et al., 2014).

The Middle Devonian Marcellus Formation in the Appalachian Basin is a major unconventional natural gas play that spans much of the northeastern USA, comprising black shale and discontinuous limestone and marls (Soeder, 2012; Wang and Carr, 2013; Kohl et al., 2014). To date, much of the research on the environmental impacts of Marcellus Shale drilling relates to the origin of stray gas (e.g., Osborn et al., 2011; Molofsky et al., 2013), the potential for brine migration into aquifers (e.g., Chapman et al., 2012; Warner et al., 2012; Kolesar Kohl et al., 2014), and the disposal and treatment of wastewater returned from the wells (e.g.,

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Schmidt, 2013; Shaffer et al., 2013; States et al., 2013; Wilson and VanBriesen, 2013). Waters returned from Marcellus Shale unconventional wells can have high total dissolved solids (median TDS ~160,000 mg L^{-1}; maximum >325,000 mg L^{-1}; Hayes, 2009; Chapman et al., 2012; Barbot et al., 2013; Haluszczak et al., 2013), with Ba concentrations that can exceed 22,000 mg L^{-1} and Sr content exceeding 10,000 mg L^{-1} (Blauch et al., 2009; Chapman et al., 2012; Barbot et al., 2013; Rowan et al., 2015). Although the amount of water produced per unit of natural gas for unconventional wells is ~35% less than that of conventional gas wells (Lutz et al., 2013), treatment of these brines introduces unique challenges (Ferrar et al., 2013; Shaffer et al., 2013), including efficient removal of the elevated levels of radium (73–6540 pCi L^{-1}, Rowan et al., 2011), a decay product of uranium.

Less attention has been paid to drill cutting waste from unconventional shale wells in the Appalachian Basin (Barry and Klima, 2013; Johnson and Graney, 2011). These wells are often deeper (>2000 m) than existing oil and gas wells in the region, and a single well pad can have multiple subsurface lateral extensions that range from 400 to over 2000 m in length (Dale et al., 2013). These laterals primarily drill through the hydrocarbon-rich black shale of the target formation. Black shales can be enriched in potentially toxic trace elements including arsenic (As), barium (Ba), and uranium (U) compared to other sedimentary rocks (Lavergren et al., 2009; Leventhal, 1991; Leventhal et al., 1981; Swanson, 1961; Vine, 1969).

A typical unconventional Marcellus gas well (2100 m vertical with a 1200 m lateral extension) would generate over 150 m^3 of drill cutting material from both vertical and lateral sections (United States Department of Environmental Conservation New York State, 2011), which is equivalent to about 375 tons by weight (assuming a bulk density of 2.5 ton/m^3). During 2011, almost 725 thousand tons of drill cuttings were generated in Pennsylvania alone; a small portion was reused but most were disposed of in landfills (Maloney and Yoxtheimer, 2012). From January of 2012 to September of 2014, an additional 3578 unconventional gas wells were drilled in Pennsylvania (Pennsylvania DEP, 2014). Landfills in Pennsylvania, New York, Ohio, West Virginia, and New Jersey have reported increases in the volume of Marcellus Shale related waste (Maloney and Yoxtheimer, 2012; Ohio DNR, 2012; Pennsylvania DEP, 2011). In Pennsylvania, more than 1.2 million tons of drill cutting waste was disposed at landfills in 2013 which did not include loads rejected due to exceeding radiation limit (Pennsylvania DEP, 2014).

Landfill disposal of drilling waste involves separation of solids (e.g. shale, sand, and clay) from drilling mud to reduce liquid content as well as salinity (Ball et al., 2012). Barite is commonly used as weighting agent and is known to incorporate Ra into its structure (Ball et al., 2012). The solid material may be further processed prior to reuse as abandoned mine fill, roadside base, construction material, or in wetland restoration (Ball et al., 2012; Barry and Klima, 2013; Kargbo et al., 2010). Ball et al. (2012) reviewed the advantages and drawbacks of both bioremediation technologies and non-biological technologies for treatment of contaminated drilling waste. They also note that drilling waste disposal is subject to a range of local environmental and safety regulations not always optimized to the nature of unconventional wells. In the USA, drill cuttings related to oil and gas exploration and production are exempt from federal hazardous waste management standards (US DEP, 2002); however, reports of radiation levels in drilling waste exceeding Pennsylvania regulatory standards have led to initiation of a study to examine radioactivity in byproducts associated with oil and gas development and the procedures involved in its transportation, storage and disposal (Pennsylvania DEP, 2012).

Marcellus well drill cuttings are generally fine-grained (~85% by weight of the particles range between 0.025 and 6.3 mm in dia-

meter; Barry and Klima, 2013) and have high clay content, which results in a high surface area for potential reactions and metal release. Subaerial weathering of the Marcellus Shale can result in the loss of major and trace elements via oxidation of organic matter and pyrite, and plagioclase and clay dissolution (Jin et al., 2013). Therefore the use of core samples and drill cuttings in experimental studies can provide a more accurate picture of element mobility relevant to drill cutting disposal. Although uranium concentrations in excess of 80 ppm have been reported from Marcellus core samples (Leventhal et al., 1981; Wang and Carr, 2012; Chermak and Schreiber, 2014), limited published data exist on the distribution of U, As and Ba among minerals in the Marcellus Shale, and on the mobility of these elements in drill cutting waste from unconventional gas well production.

We report here the results of selective sequential extraction experiments and multi-acid dissolution of unweathered rock samples of the Marcellus Formation and adjacent units from core and drill cuttings to determine the content and distribution of uranium, arsenic, and barium in different host phases of the shale and adjacent units. Geochemical simulations are presented to investigate the potential stability of these minerals in the storage environment. To investigate the relationship between interaction of injected water with reservoirs of U, As, and Ba in the rock, we also report U, As, and Ba concentrations of 43 samples of returned waters from 10 unconventional Marcellus Shale gas wells throughout Pennsylvania. The objectives of this study were to aid in the assessment of the retention and mobility of U, As and Ba in drill cuttings under typical storage conditions, and to provide insight into the source of these elements in produced waters.

2. Materials and methods

2.1. Sample description

Fifteen rock samples from two wells that penetrated the Marcellus Formation and associated units were analyzed: eight samples (G1–G8) ranging from 2374 to 2407 m depth from a core from Greene County, Pennsylvania, and seven (T1–T7), ranging in depth from 901 to 1434 m, of dry-drilled cuttings from Tioga County, New York (Fig. 1). Because the latter well was drilled with air, samples were not contaminated with drilling mud that commonly contains significant amounts of barite (Johnson and Graney, 2015). Dry-drilled cutting samples T1–T7 (<2 mm diameter) were divided into representative splits using a fluted sample splitter; core samples G1–G8 were first pulverized in a mixer mill and then divided with the splitter to the appropriate sample masses.

A total of 43 produced water samples from 10 wells were analyzed (Fig. 1): five wells in Bradford County (Wells 1–5); and produced waters from two closely spaced wells (<1 km) in Westmoreland County (Wells 6 and 7), one well in Washington County (Well 8) and two wells in Greene County (Wells 9 and 10). The Bradford County samples were collected as individual "grab" samples from waste impoundments of each well, which had been recycled through several fracturing operations; thus, the time after the start of water flow from the well is undefined. The first fluids returned from a producing well are often referred to as "flowback" and later fluids as "produced waters." Because the determination of the transition between the two can vary with local regulatory definitions, in this paper we follow the convention of Rowan et al. (2015) and refer to all waters returned from the well post-hydraulic fracturing as "produced water." Sample days refer to the number of days following the initiation of returned water flow (beginning with Day 0). Time-series samples from Wells 6–9 span from day 1 to day 30. Concentrations of As and U are reported for additional samples from Well 9 (days 27, 67,
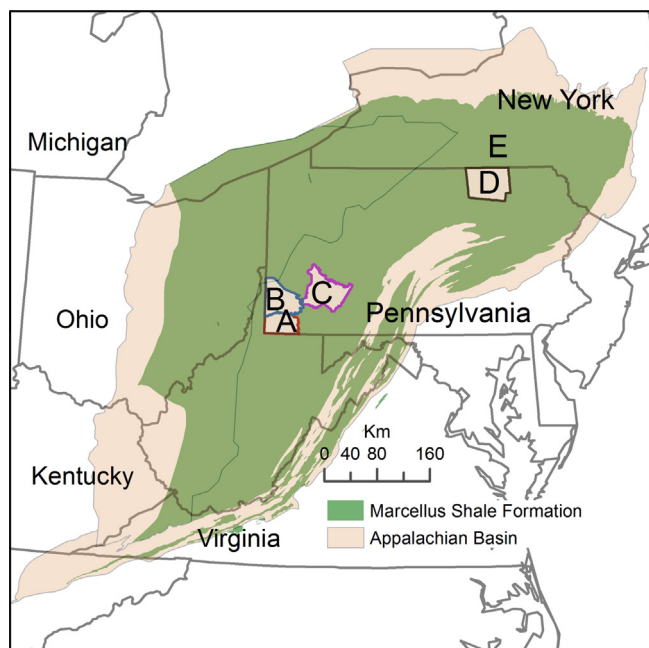
Fig. 1. Location of Marcellus Formation samples analyzed in this study: core from Greene County, Pennsylvania (location A) and dry-drilled well cuttings from Tioga County, New York, USA (location E). Produced water samples from unconventional Marcellus Shale gas wells from four counties in Pennsylvania: 5 wells in Bradford Co. (location D), 2 wells in Westmoreland Co. (location C), 1 well in Washington Co. (location B), and 2 wells in Greene Co. Map is modified after Whitacre (2014).

438, and 813 after hydraulic fracturing; water started flowing back in December 2010) and Well 10 (days 1, 4, 47, 80, and 320). Produced water samples were collected by personnel from DOE-NETL, USGS and Bucknell University. Aqueous samples were separated from oil, if present, and immediately syringe-filtered through a 0.45 μm membrane and acidified on-site to pH <2 using ultra-pure HNO_3. Limited geochemical data from some of these samples were previously reported in Chapman et al. (2012).

2.2. Methods

2.2.1. Whole rock digestions

For whole rock elemental concentrations, approximately 150–200 mg of powder were digested with concentrated HNO_3, HF, HCl, and $HClO_4$, based on the procedure of Spivak-Birndorf et al. (2012), modified after Yokoyama et al. (1999) and Duan et al. (2010). Details of the digestion procedure can be found in the Supplementary Information. Certified USGS reference materials SGR-1 (shale) and AGV-1 (andesite) were simultaneously digested and measured for U, Ba, and Ca. Procedural blanks for the multi-acid dissolution ($n = 2$) were estimated to be ⩽0.1 ng for U, 0.6 ng for Ba, and 0.3 ng for As, which would result in a maximum contribution of ⩽0.004%, 0.001%, and 0.02%, respectively.

2.2.2. Sequential extractions

To quantify distribution of U, As, and Ba in (1) water soluble minerals, (2) exchangeable sites on clays and organic matter, (3) carbonate minerals, and (4) sulfides and organic matter, splits of approximately two grams of rock were subjected to a multi-step sequential extraction procedure (water, ammonium acetate buffered at pH 8, acetic acid, and hydrogen peroxide), modified from Spivak-Birndorf et al. (2012), after Tessier et al. (1979) and Willis and Johannesson (2011). Details of the sequential extraction are presented in Supplementary Information and shown in Fig. S1. The Marcellus Shale samples prior to leaching were black, and residues after the oxidizable extraction step were light gray. The resi-

due primarily contains silicate minerals; residue composition was estimated from the difference between the whole-rock dissolution and the sum of the sequential fractions. Carbonate content was calculated from the calcium and magnesium concentrations of the acetic acid extraction, which was designed to target carbonate minerals (primarily calcite and dolomite) without disturbing other mineral phases. For the sequential extraction procedure, maximum blank contributions of U, Ba, and As in each fraction were 0.08%, 0.1%, and 0.04%, respectively.

2.2.3. Analytical techniques

Ultrapure (Optima grade) reagents and water (18.2 MΩ Milli-pore) were used in this study, and all procedures were carried out in acid-washed laboratory ware to minimize contamination. Ca, Mg, U and Ba concentrations in multi-acid digestates of whole rock samples and sequentially extracted fractions, and Mn and U in produced waters, were obtained by analysis on a Perkin Elmer NexION 300X ICP-MS under standard mode and a Spectro EOP ICP-AES at the University of Pittsburgh. Groundwater reference standard ES-L-2, seawater standard NASS-6, and spring water standard NIST-1640a were repeatedly measured for quality control. All laboratory procedures, including dilution with ultrapure 2% nitric acid for elemental analysis, were performed gravimetrically to avoid errors due to density differences. Metal concentrations of produced water samples reported in this study take into account the specific gravity of the sample. Internal standards were used to correct for matrix effects and instrumental intensity drifts.

For the produced waters, potential matrix-induced effects on uranium content due to high TDS levels were minimized by diluting samples 100 fold (TDS < 0.2%) and preparing matrix-matched external standards in 0.2% NaCl + 2% HNO_3. The method detection limit (MDL) is 0.84 ng L^{-1} (Table S1). Measured U concentrations in matrix-matched NIST1640a were always within 5% of certified concentration (Table S2). The analytical procedure for the measurement of uranium concentrations is described in detail in the Supplementary Information.

High levels of chloride and dissolved solids can cause both matrix and spectrally induced interferences on As. Therefore, As in all samples, including whole rock assays, sequential extracts, and produced waters, was measured by ICP-MS under kinetic energy discrimination (KED) mode using helium as collision gas, based on US EPA 200.8 method and a Perkin Elmer application note (Pruszkowski and Bosnak, 2012). This has been demonstrated to successfully remove isobaric interferences on $m/z = 75$ such as $^{40}Ar^{35}Cl^+$, $^{40}Ca^{35}Cl^+$, and $^{37}Cl^2H^+$ (Pereira et al., 2010; Pruszkowski and Bosnak, 2012). External standards and spring water NIST1640a were prepared in a matrix containing 1% HCl and 1% HNO_3. The NIST1640a mixtures were repeatedly monitored every 5–8 samples for quality control on accuracy. During the analysis, the analytical blank (1% HCl + 1%HNO_3) typically gained 1–5 counts s^{-1} at $m/z = 75$, giving a maximum background equivalent concentration (BEC) for $^{75}As^+$ of 0.04 μg L^{-1}. The long-term recoveries of arsenic in NIST1640a ranged from 95% to 104%. The MDL was 0.77 μg L^{-1}, which translates to a calculated detection limit of 77 μg L^{-1} for the undiluted sample. The major elements discussed here (Al, Si, Fe, S) and % total organic content (TOC) for whole rock powders were obtained from Activation Laboratory Ltd. using the sodium peroxide fusion method and analysis by ICP-MS and ICP-OES.

3. Results and discussion

Lithologic units associated with the Marcellus Formation have been classified based on factors such as total organic content (TOC), mineralogy (e.g. carbonate or clay content), and grain size (Wang and Carr, 2012). Units analyzed in this study include the

Tully limestone that caps the Hamilton Group, as well as Hamilton Group shales, the Marcellus Shale, and the underlying Onondaga limestone. We categorized samples based on carbonate mineral content, as this factor tends to play a major role in element distribution and mobility. Group A, which includes most of the high TOC shales, has <10% carbonate; Group B, which encompasses calcareous shales, ranged from 10% to 30% carbonate; Group C samples, which include marls (clay-rich limestone) and limestones, have >30% carbonate mineral content.

3.1. Partitioning of uranium

3.1.1. U in sequentially extracted solids

Whole rock U concentrations in the core and drill cuttings ranged from 2 to 47 mg kg^{-1} (Table 1; Fig. 2a and b), which fall within the range reported for the Marcellus Shale and related lithologies (Swanson, 1961; Leventhal et al., 1981; Wang and Carr, 2012; Chermak and Schreiber, 2014). By comparison, water and ammonium acetate extracted negligible amounts of U (<5%) from all three sample groups. This is consistent with the low concentrations of U (mostly <0.5 μg L^{-1}) in the produced waters analyzed (Table 2). Of note is that even in limestone and calcareous mudstones in Group C (>30% carbonate minerals), acetic acid extracted up to 22 mg kg^{-1} of uranium (17–64%). Even though the acetic acid leach is primarily designed to dissolve carbonate minerals, some phosphate minerals (e.g., apatite) and uranium oxides could be partially dissolved (Quejido et al., 2005). This suggests that acidic dissolution of carbonate minerals and some U oxides could release significant amounts of uranium. In fact, the sample with the highest whole rock U (G7; 47 mg kg^{-1} U) contained 54% carbonate minerals. Even for Group A samples (<10% carbonate; includes most of the black shale samples), up to 20% (5 mg kg^{-1} U) of the total uranium is associated with the acetic acid-soluble fraction.

The hydrogen peroxide extraction results in oxidative dissolution of organic matter and sulfide minerals such as pyrite. This also releases tetravalent uranium (U^{4+}) from oxides such as U$_3$O$_8$ or UO$_2$ (uraninite) associated with or bound to organic matter (Eary et al., 1986; Peper et al., 2004). Previous study showed that uraninite grains (<1 μm) were observed to be proximal to silicate and clay minerals in nine out of ten samples of Marcellus Shale rock (Fortson, 2012). This suggests that the U in this fraction was extracted due to the oxidation of U oxides, rather than leaching of U directly associated with organic matter. This organic and sulfide fraction contained less than 10% (0.1 mg kg^{-1}) of whole rock U from Group C limestone/marls but up to one third (0.1–8 mg kg^{-1}) of whole rock U from Group A and B shales, which are higher in sulfide minerals (based on high whole rock Fe and S content) and organic matter.

Whole rock U and TOC data for all samples in this study display a modest positive correlation (R^2 = 0.37; Fig. 3a). Core-scale positive correlations of TOC content with uranium concentration are reported for North American Devonian black shales (Leventhal, 1981; Lüning and Kolonic, 2003; Wang and Carr, 2012), and Kochenov and Baturin (2002) reported a positive correlation between U content and organic matter (OM) in marine sediments. For all samples, Group A and B shale residues hold 44–95% of total U, and Group C limestone/marl samples 28–78% (Table 1). We note that there is possibility of incomplete oxidation of organic matter for dry drilled cuttings samples, as some grains could be up to 2 mm in diameter, providing a protective mantle for uraninite crystals. However, in the oxidizable extraction step, hydrogen peroxide was repeatedly reacted with the rock powders until no bubbling was observed. In addition, the Greene County core samples were crushed to a fine powder, making it unlikely that any organic matter escaped oxidation. For these samples, less than 6% of total U was extracted in oxidizable fraction of Group A and B shale

whereas 77–95% remained in the residue. Thus, our data suggest that the main reservoir for uranium in Marcellus Shale is insoluble silicate minerals rather than organic matter.

3.1.2. Comparison with uranium in produced water

Although the uranium content of the core and drill cuttings was high, U concentrations in the produced water samples were generally very low (from less than the reporting limit of 0.084 μg L^{-1} to 3.26 μg L^{-1}, Table 2). Uranium contents were higher in the first 5 days (Fig. 4) even though these waters are generally lower in total dissolved solids (TDS) than later produced waters (Hayes, 2009; Chapman et al., 2012; Barbot et al., 2013). The highest U was observed in sample WE-A2 (3.26 μg L^{-1}, day 2) in Westmoreland Co (Well 6) and in sample GR-A002 (1.99 μg L^{-1}, day 2) in Greene Co (Well 9). After day 10, uranium concentrations in all samples were <0.48 μg L^{-1}. After day 30, uranium dropped below the detection limit (0.084 μg L^{-1}) and remained so for samples collected more than two years later (sample GR-A813a).

It is possible that the injected fracturing fluid could contain a measurable amount of U, which is pumped out or reduced to insoluble U oxides within the first week; we did not have access to samples of pre-injection frac fluid for these wells. Alternatively, waters returned in the first week, which contain a greater fraction of oxygenated hydraulic fracturing fluid, could reflect the oxidative dissolution of some U-bearing minerals in the formation. Hydrochloric acid is commonly used in the initial stages of hydraulic fracturing to clean up perforations in the cement well casing. Therefore, limited dissolution of carbonate minerals due to interaction with acidic injected fluid during the early stages of hydraulic fracturing could be responsible for the slightly elevated U in the early returned waters, as has been suggested as well for observed Sr isotope trends (Stewart et al., 2015).

Radium (Ra) is a decay product of uranium; total Ra activites reported for Marcellus produced waters range from 73 to 6540 pCi L^{-1}, with higher activity found in late stage produced waters (Rowan et al., 2011). This inverse relationship between uranium and Ra concentration can be explained by their behavior under the conditions at which the injected fluid interacts with the reducing shale unit. Soluble hexavalent U (as uranyl UO$_2^{2+}$) would be rapidly reduced and precipitated by ferrous iron (Fe^{2+}) and manganese (Mn^{2+}) present in the waters (Fe = 16–123 mg L^{-1}; Chapman et al., 2012; Mn = 0.47–11.2 mg L^{-1}; Table 2). In contrast, Ra liberated from minerals by radiation damage would be easily released into formation water (Rowan et al., 2015), which may be the dominant component of produced water at the later stages of gas production (Capo et al., 2014).

3.2. Partitioning of arsenic

3.2.1. As in sequentially extracted solids

Arsenic in the whole rock in Group A shales ranged from 16 to 90 mg kg^{-1} (Table 1; Fig. 2c and d), similar to other North American marine organic-rich shales such as the New Albany Shale (25–255 mg kg^{-1}; Tuttle et al., 2009) and the Chattanooga Shale (up to 70 mg kg^{-1}; Leventhal, 1991). Calcareous Group B samples contained a lower amount of As (5–28 mg kg^{-1}) whereas carbonate mineral-rich Group C whole rock samples contained the lowest amount of As (5.4–19 mg kg^{-1}). The anomalously high As, Fe, and S concentrations in sample G3 (90 mg kg^{-1}) suggest that, in spite of the use of a powder splitter, the whole-rock split (~150 mg) was disproportionally enriched in sulfide minerals such as arsenopyrite relative to the ~2 g split used for the sequential extractions. Negligible amounts of As were released in the water and ammonium acetate (exchangeable), and acetic acid (carbonate mineral) fractions. A small amount of As was extracted in the acetic

Table 1
TOC, carbonate, major elements, uranium, arsenic, and barium contents in whole rock and selective sequential extractions of shales of the Middle Devonian Marcellus Formation.

Sample ID	Group	Depth (m)	Carbonate[a] (%)	TOC[b] (wt.%)	Al$_2$O$_3$[b] (%)	SiO$_2$[b] (%)	Fe$_T$[b] (%)	S$_T$[b] %	Uranium (mg kg^{-1}) Total	W	E	C	O	R[c]	Arsenic[*] (mg kg^{-1}) Total	W	E	C	O	R[c]	Barium (mg kg^{-1}) Total	W	E	C	O	R[c]
Tioga County, NY, USA																										
T1	C	901	52.4	0.22	7.92	29.1	2.2	0.50	1.9	<0.002	0.02	0.35	0.05	1.44	5.4	<0.01	<0.04	0.32	0.39	4.66	1093	4.8	250	89.8	4.32	744
T2	A	1337	1.45	0.57	17.3	56.9	4.7	1.72	5.3	<0.002	0.03	0.15	0.37	4.79	16	<0.01	<0.04	0.16	4.53	11.3	500	2.6	371	35.7	8.27	82.6
T3	A	1358	1.12	1.25	15.9	53.7	4.2	2.90	20	0.021	0.35	0.80	3.09	15.5	25	<0.01	<0.04	0.17	12.4	12.1	584	3.9	426	36.7	9.60	108
T4	A	1370	8.72	1.47	12.9	54.6	4.1	3.78	18	0.065	0.85	3.70	1.98	11.8	35	0.026	0.10	0.91	10.4	23.5	348	4.1	213	34.7	3.75	92.6
T5	B	1389	18.4	1.06	6.54	51.6	2.3	2.30	23	0.010	0.75	4.33	7.81	9.91	28	<0.01	<0.04	0.66	19.3	8.28	670	4.6	125	30.5	6.17	504
T6	B	1410	15.7	0.36	8.24	55.6	2.5	0.76	2.4	<0.002	0.05	0.23	0.10	2.06	4.9	<0.01	<0.04	0.21	<0.22	4.47	568	17	162	35.2	4.77	349
T7	C	1434	43.1	<0.05	3.38	46.6	1.2	0.46	1.9	<0.002	0.04	0.32	0.13	1.36	8.3	<0.01	<0.04	0.34	1.23	6.68	185	2.4	57.5	20.7	4.16	100
Greene County, PA, USA																										
G1	B	2374	17.9	<0.05	13.7	44.1	5.8	3.90	3.6	<0.002	0.02	0.17	0.18	3.23	12	<0.01	<0.04	0.55	5.85	5.53	514.2	1.4	89.0	29.0	5.48	389.3
G2	C	2376	78.2	ND	2.97	9.37	1.3	0.76	3.0	0.003	0.06	1.20	0.09	1.68	11	<0.01	<0.04	0.25	2.66	7.81	1938	5.6	492	252	10.8	1177
G3	A	2380	6.57	1.07	15.8	45.4	8.1	7.37	35	0.048	1.21	4.97	2.02	27.0	90	<0.01	<0.04	0.34	24.0	65.5	467.3	1.4	71.8	15.1	0.28	378.7
G4	A	2386	1.02	1.08	17.1	58.8	3.9	2.19	8.2	0.003	0.02	0.10	0.25	7.81	21	<0.01	<0.04	0.08	6.47	14.4	765.8	1.5	102	3.78	2.97	655.8
G5	A	2389	0.39	1.11	17.7	56.3	4.3	3.05	15	<0.002	0.04	0.18	0.53	14.2	26	<0.01	<0.04	0.12	12.1	13.8	898.4	1.2	275	9.29	53.4	559.5
G6	A	2398	3.93	2.47	15.0	52.8	3.6	3.50	17	0.007	0.04	0.24	0.73	15.6	26	<0.01	<0.04	0.33	20.3	5.76	603.7	2.2	55.1	31.0	8.06	507.4
G7	C	2404	53.8	1.55	2.57	31.4	1.6	2.01	47	0.048	1.05	21.6	11.3	13.1	19	0.01	0.15	0.68	13.6	4.85	251.7	3.0	55.4	39.2	5.43	148.7
G8	C	2407	79.7	ND	0.45	5.67	1.2	3.03	9.7	0.006	0.16	6.20	0.22	3.07	7.4	<0.01	<0.04	0.22	4.20	2.89	3333	2.8	483	261	82.1	2505
Data quality control: Measured mean value ± SD[d]/Certified value																										
SGR-1									4.90 ± 0.02/5.40 ± 0.40												288 ± 2/290 ± 40					
AGV-1			8.6 ± 0.1/8.8 ± 0.2[e]						1.92 ± 0.01/1.92 ± 0.15												1210 ± 4/1230 ± 16					
NIST1640a									23.17 ± 0.34/25.35 ± 0.27						7.99 ± 0.36/8.075 ± 0.070						142 ± 13/151 ± 1					

ND: no data.
[a] Calculated from [Ca] and [Mg] in 1.0 N acetic acid extraction.
[b] Analyzed by Actlabs.
[c] Calculated by subtracting total of concentrations in extracted fractions from the total concentration of whole rock.
[d] Standard deviation of either 3 separate digestions of reference samples SGR-1 (shale), AGV-1 (andesite), or measurements of aliquot replicates of NIST-1640a (spring water) in different days.
[e] Measured and certified value of Ca concentration W, E, C, O, R: water soluble, exchangeable, carbonate, oxidizable, and residue fractions, respectively.
[*] Arsenic in all samples were measured by ICP-MS under KED mode.
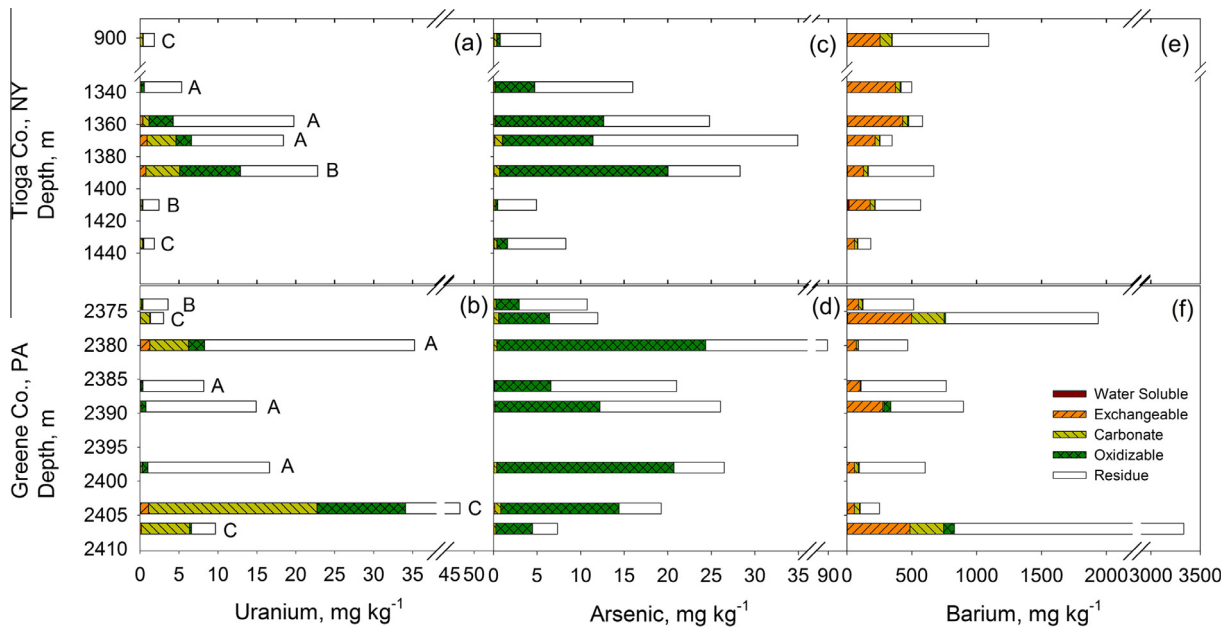
Fig. 2. Distribution of uranium (a, b), arsenic (c, d) and barium (e, f) in sequentially extracted fractions of Tioga County NY dry-drilled cutting samples (top) and Greene County, PA core samples (bottom). Sample group names A (<10% carbonate), B (10–30% carbonate), and C (>30% carbonate) are shown in (a) and (b).

acid fraction of the carbonate mineral-rich Group C samples (0.2–0.7 mg kg^{-1}; 2–6%). A poor correlation of whole rock As with TOC ($R^2 = 0.14$), combined with the good correlation between As and S contents ($R^2 = 0.75$; Fig. 3b) in all samples indicates that As in the shale and related calcareous shales of Marcellus Formation is primarily associated with sulfide minerals such as pyrite (possibly with small amounts of arsenopyrite, FeAsS), consistent with observations from other black shales (Smedley and Kinniburgh, 2002; Zhu et al., 2008).

In contrast to uranium, more than 97% of the whole rock arsenic in Group A samples was present in the combined oxidizable fraction (5–24 mg kg^{-1}; 27–77%) and residue (6–66 mg kg^{-1}; 22–73%). Based on calculated pyrite contents (8.2–11.6%) and assuming that the As extracted in the oxidizable fraction is wholly attributed to pyrite, the maximum concentration of As in pyrite from Marcellus drill cuttings could be expected to average about 270 mg kg^{-1} (median = 250 mg kg^{-1}) which falls at the lower end of typical As contents (100–77,000 mg kg^{-1}) in common rock-forming pyrite (Smedley and Kinniburgh, 2002). Because As is mainly associated with sulfide minerals, the effective primary strategy to prevent release of As at disposal sites would be to minimize oxidative conditions in high-S samples. Group B samples show a similar trend, with up to 19 mg kg^{-1} present in the oxidizable fraction and 8 mg kg^{-1} in the residual fraction. Even though carbonate mineral-rich Group C samples contain the lowest amount of sulfide minerals (Fe and S), up to 14 mg kg^{-1} (70% of total As) was extracted in the oxidizable fraction.

3.2.2. Arsenic in produced water

The concentrations of As in all produced water samples were <77 μg L^{-1} (based on the MDL of 0.77 μg L^{-1} on 100X diluted samples). This relatively low concentration relative to the Group A organic rich shale (up to 90 mg kg^{-1}) is consistent with our results that As in the organic-rich Group A shales is held mainly in the oxidizing fraction, and not mobilized during hydraulic fracturing partly because microbial sulfate reduction helps maintain low-Eh conditions (Engle and Rowan, 2014).

3.3. Partitioning of barium

Barium concentrations in Group A whole rock samples range from 348 to 898 mg kg^{-1} with an average value of 595 mg kg^{-1} (Table 1). Weight % CaCO$_3$, Al$_2$O$_3$, and SiO$_2$ do not show significant relationships with total Ba in Group A, indicating that carbonate and silicate minerals are not direct carriers of Ba during shale deposition. Barium concentrations in Group C limestone/marl samples range from 185 to 3333 mg kg^{-1} and are generally higher than in shales. The water soluble and oxidizable fractions of all samples contain small amounts of Ba (1.2–16 mg kg^{-1} and 0.3–82 mg kg^{-1}, respectively) that in total contribute less than 6% of total Ba.

Generally <10% of total Ba (4–37 mg kg^{-1}) in shale samples was extracted by acetic acid, indicating that the amount of barium associated with carbonate cement and in filling was relatively low. The bulk of whole rock Ba was retained in the residue of both limestone/marl (54–75% of total Ba; 100–2505 mg kg^{-1}) and shale (17–86% of total Ba; 83–656 mg kg^{-1}).

A significant proportion of extractable Ba is contained in the cation exchangeable fractions of both shale and calcareous lithologies (Fig. 2e and f), consistent with the findings of Stewart et al. (2015). Barium concentrations in Group C limestone/marl samples range from 55 to 493 mg kg^{-1}, contributing 15% to 31% of the total Ba. In shales, we observed a wide range of exchangeable Ba (9–74% of total Ba) that was related to geographic location; Group A shale samples from Tioga County, NY contained more exchangeable Ba (61–74% of total Ba) than those from Greene County, PA (9–31% of total Ba). Exchangeable Ba is most likely held in clay minerals or organic matter. Barium remaining in the residues of sequentially extracted rocks is most likely held in barite (BaSO$_4$), which is not expected to dissolve in the extraction procedure (Gonneea and Paytan, 2006).

Barium in Appalachian brines from conventional oil and gas wells ranges from a few mg L^{-1} to 4370 mg L^{-1} (Dresel and Rose, 2010). Produced water from Marcellus Shale gas wells tend to be high (range = 76–13,600; Hayes, 2009; Blauch et al., 2009; Chapman et al., 2012; Haluszczak et al., 2013). Our finding of relatively high Ba concentrations in the exchangeable extractions suggests that interaction of injected water with exchange sites

Table 2
Concentrations of uranium, barium, and manganese in 43 Marcellus produced water samples from 10 unconventional wells.

Sample/Location	Description	Uranium[a] (±2SD) ($\mu g\,L^{-1}$)	Barium[b] ($mg\,L^{-1}$)	Manganese[c] (±2SD) ($mg\,L^{-1}$)	Specific gravity ($g\,mL^{-1}$)
Bradford County, PA (Well 1–5)					
BR-A1	Produced water	<0.084	5490	3.26 ± 0.07	1.042
BR-A2	Produced water	<0.084	12,000	6.03 ± 0.14	1.060
BR-A3	Recycled prod. water	<0.084	7820	ND	1.047
BR-A4	Recycled prod. water	<0.084	6470	2.97 ± 0.17	1.048
BR-A5	Recycled prod. water	<0.084	5860	2.51 ± 0.09	1.038
Westmoreland County, PA (Well 6 (WE-A-) and Well 7 (WE-B-))					
WE-A1.5	Prod. water, day 1.5	0.98 ± 0.10	70	0.67 ± 0.03	1.036
WE-A2	Prod. water, day 2	3.26 ± 0.42	179	0.47 ± 0.03	1.027
WE-A4	Prod. water, day 4	1.81 ± 0.16	740	1.69 ± 0.08	1.073
WE-A5	Prod. Water, day 5	2.09 ± 0.26	888	1.73 ± 0.11	1.088
WE-A7	Prod. water, day 7	1.07 ± 0.26	1405	2.60 ± 0.15	1.083
WE-A12	Prod. water, day 12	0.22 ± 0.14	2193	3.59 ± 0.10	1.090
WE-A15	Prod. water, day 15	0.19 ± 0.09	2687	4.48 ± 0.24	1.096
WE-A29	Prod. water, day 29	<0.084	2987	7.58 ± 0.52	1.108
WE-B3	Prod. water, day 3	1.76 ± 0.15	333	1.04 ± 0.02	1.065
WE-B5	Prod. water, day 5	1.42 ± 0.13	1058	1.84 ± 0.06	1.066
WE-B7	Prod. water, day 7	0.96 ± 0.31	1490	2.05 ± 0.14	1.087
WE-B9	Prod. water, day 9	0.91 ± 0.42	1892	2.37 ± 0.07	1.072
WE-B13	Prod. water, day 13	0.62 ± 0.32	2306	2.99 ± 0.09	1.086
WE-B18	Prod. water, day 18	0.35 ± 0.18	2700	3.29 ± 0.13	1.092
Washington County, PA (Well 8)					
WA-A11	Prod. water, day 11	0.14 ± 0.04	151	7.63 ± 0.20	1.127
WA-A13	Prod. water, day 13	<0.084	194	7.50 ± 0.40	1.120
WA-A15	Prod. water, day 15	<0.084	253	8.92 ± 0.39	1.133
WA-A17	Prod. water, day 17	0.48 ± 0.04	296	9.88 ± 0.45	1.131
WA-A20	Prod. water, day 20	<0.084	328	10.7 ± 0.63	1.146
WA-A25	Prod. water, day 25	0.24 ± 0.03	349	10.4 ± 0.50	1.159
WA-A30	Prod. water, day 30	<0.084	379	11.2 ± 0.60	1.154
Greene Country, PA (Well 9 (GR-A-) and Well 10 (GRN-A1-))					
GR-AF	Frac water	<0.084	393	ND	1.057
GR-A001	Prod. water, day 1	1.13 ± 0.30	1108	2.36 ± 0.18	1.092
GR-A002	Prod. water, day 2	1.99 ± 0.57	1560	2.58 ± 0.09	1.098
GR-A003	Prod. water, day 3	1.54 ± 0.51	1487	2.62 ± 0.07	1.097
GR-A004	Prod. water, day 4	0.96 ± 0.33	1756	2.97 ± 0.14	1.102
GR-A005	Prod. water, day 5	1.11 ± 0.51	1638	3.01 ± 0.10	1.101
GR-A007	Prod. water, day 7	1.00 ± 0.26	962	6.37 ± 0.33	1.099
GR-A015	Prod. water, day 15	0.37 ± 0.15	2273	3.68 ± 0.03	1.089
GR-A020	Prod. water, day 20	0.28 ± 0.15	2525	3.82 ± 0.05	1.108
GR-A027	Prod. water, day 27	<0.084	ND	ND	1.110
GR-A067	Prod. water, day 67	<0.084	ND	ND	1.119
GR-A438	Prod. water, day 438	<0.084	ND	ND	1.111
GR-A813a	Prod. water, day 813	<0.084	ND	ND	1.106
GRN-A1-0001	Prod. water, day 1	1.13 ± 0.07	ND	ND	1.012
GRN-A1-0004	Prod. water, day 4	0.72 ± 0.07	ND	ND	1.097
GRN-A1-0047	Prod. water, day 47	<0.084	ND	ND	1.139
GRN-A1-0080	Prod. water, day 80	<0.084	ND	ND	1.142
GRN-A1-0320	Prod. water, day 320	<0.084	ND	ND	1.136
Reference sample:					
NIST1640a: Mean value ($\mu g\,L^{-1}$) (*n* = 9)		25.62 ± 0.69	–	40.95 ± 8.97	
Certified value ($\mu g\,L^{-1}$)		25.35 ± 0.27	–	40.39 ± 0.36	

ND: no data.
[a] Method detection limit (MDL) = 0.84 ng L^{-1}. Reported concentrations (<0.084 $\mu g\,L^{-1}$) are accounted for 100 fold dilution factor of produced water samples.
[b] Barium concentrations were previously reported in Chapman et al. (2012).
[c] MDL = 0.11 $\mu g\,L^{-1}$.

could contribute to the high Ba concentrations observed in Marcellus Shale produced waters. However, other data suggest that the primary source of Ba in produced water from Marcellus Shale is formation brine that evolved from evaporated paleoseawater (Rowan et al., 2015; Stewart et al., 2015).

3.4. Simulation of interaction of drilling waste with rainwater and landfill leachate

Drill cuttings can be exposed to rainwater when stored on the surface prior to disposal, or to landfill leachates after disposal. Although U in the drill cuttings is primarily held in silicate miner-

als, our results indicate that significant amounts can be released by (1) carbonate mineral dissolution and (2) the oxidation of organic matter and uraninite. Our experiments on drill cuttings, conducted at pH 2.3 and 25 °C, resulted in dissolution of >90% of carbonate minerals within four hours. Hexavalent uranium CO_3^{2-} and HCO_3^- complexes (Tang et al., 2013) would inhibit the chemical and microbial reduction of U into the insoluble tetravalent form (Maher et al., 2012). In order to relate this to disposal conditions, saturation indices (SI) of U, As and Ba-bearing minerals found in cutting waste were determined using Geochemist's Workbench (GWB) v. 10 (Bethke, 2008) for: (1) northeastern US rainwater based on measurements reported in the National Atmospheric
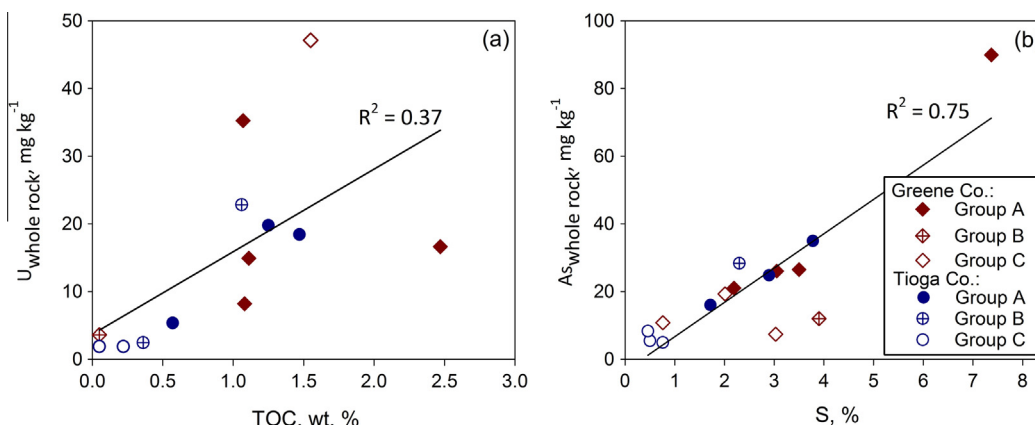
Fig. 3. Plot (a) indicates a weak correlation of uranium in whole rock with TOC content. Plot (b) indicates a good correlation of arsenic in whole rock with sulfur contents suggesting that arsenic is associated with sulfide minerals.
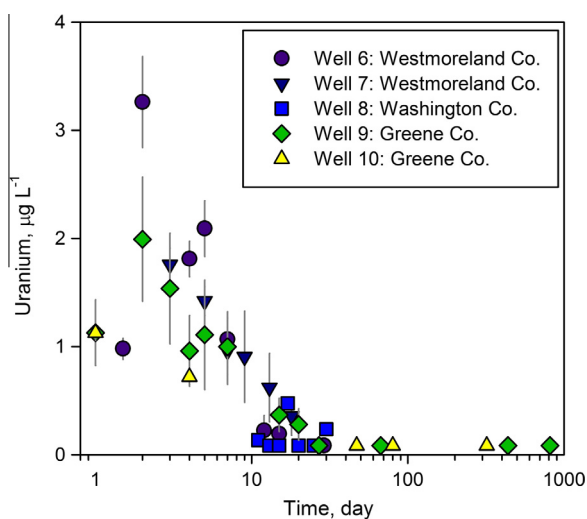

Fig. 4. Variation in concentrations of uranium in Marcellus produced waters in Westmoreland Co., Washington Co., and Greene Co. in Pennsylvania plotted versus time (days after the start of water return from the well). Uranium concentrations of the samples from 5 wells in Bradford Co. were less than the reporting limit (0.084 µg L^{-1}) and are not plotted because the collection times, days after water begins flowing back from the wells, are undefined. Error bars are two analytical standard deviations.

Deposition Program-USA (Willey et al., 2012), with U concentration in rainwater = 6 ng L^{-1} (Muramatsu et al., 1994); and (2) landfill leachates, based on chemistry reported in Christensen et al. (2001), Kjeldsen et al. (2002), and Owen and Manning (1997) under redox conditions approximating both subaerial or shallow oxidizing conditions and the low Eh conditions expected in the deeper portions of landfills (Eh < 0.15 V; Owen and Manning, 1997) (Fig. 5). Model reactions of northeastern US rainwater with U- and As-bearing minerals, including calcite, rutherfordine, uraninite, pyrite, and arsenopyrite, were constructed using React program of GWB.

The thermodynamic database (thermo.comv8.r6+) was further modified with the critically reviewed formation constants of U aqueous species (Guillaumont et al., 2003), alkaline earth uranyl carbonate complexes (Dong and Brooks, 2006; Geipel et al., 2008), and solubility products of major U(VI) minerals compiled in Table S5 in Kanematsu et al. (2014) and from Chen et al. (1999). For As, we incorporated the latest reviewed hydrolysis constants of arsenous and arsenic acids, formation constants of aqueous metal arsenate and arsenite complexes, and stability of

selected minerals at standard state (Nordstrom et al., 2014) (Tables S3 and S4). The limitations of these models, due in part to incomplete mineral stability data, are reviewed in detail by Ewing et al. (1999), Bethke (2008), and Nordstrom and Campbell (2014). For instance, the solubility of uranophane (log K = 10$^{10.82}$) (Shvareva et al., 2011) used in our thermodynamic database is lower than the values reported in Prikryl and Murphy (2001). This is because high solubility reported in Prikryl and Murphy (2001) could be possibly due to incomplete separation of fine-grained uranophane particles from the soluble U.

Fig. 5 shows that the SIs of calcite and dolomite calculated for northeastern US rainwater were both negative under a wide range of Eh (0–0.65 V) (Fig. 5a) suggesting carbonate minerals in cutting waste are not thermodynamically stable in the presence of rainwater (Morse and Arvidson, 2002). However, because landfill leachates are typically supersaturated with calcite and dolomite minerals (Owen and Manning, 1997), also shown in Fig. 5b, dissolution of carbonate minerals is not likely to occur deeper in the landfill. Similarly, landfill leachate is saturated with barite and hematite. It is worth noting that major U and As containing minerals are under-saturated in both rainwater and landfill leachates.

3.4.1. Uranium mobility during interaction of rainwater with drill cuttings

To further understand the weathering of these minerals at surficial conditions (*i.e.*, drilling waste directly exposed to acidic rainwater on site and at uncovered disposal landfills), we generated model reactions of (1) U-bearing carbonate (combined rutherfordine, UO$_2$CO$_3$, plus calcite to make equivalent concentration of U found in carbonate minerals) with northeastern US rainwater at a water:rock mass ratio of 100:1 (Fig. 6a and b), and (2) uraninite and rainwater at a water:rock mass ratio of 1:1 (Fig. 6c and d). While dissolution of carbonate minerals in a closed system should increase solution pH, this model simulates a "wash through" system in which fresh rainwater keeps flushing through and interacting with carbonate minerals. Therefore, pH was fixed instead of leaving it to be controlled by the dissolution reaction. The fine grain sizes of drilling waste (0.025–6.3 mm) (Barry and Klima, 2013) suggest that the reactive surface can be large, enhancing the dissolution of calcite. When drilling waste is freshly exposed to the surface on site, dissolution of carbonate minerals can occur progressively and consistently because acidic rainwater is in excess and the system remains under-saturated with respect to carbonate minerals (Fig. 5a). Modeling result (Fig. 6a and b) show that dissolution of rutherfordine and calcite does not produce U secondary minerals. In fact, U becomes soluble and is present as
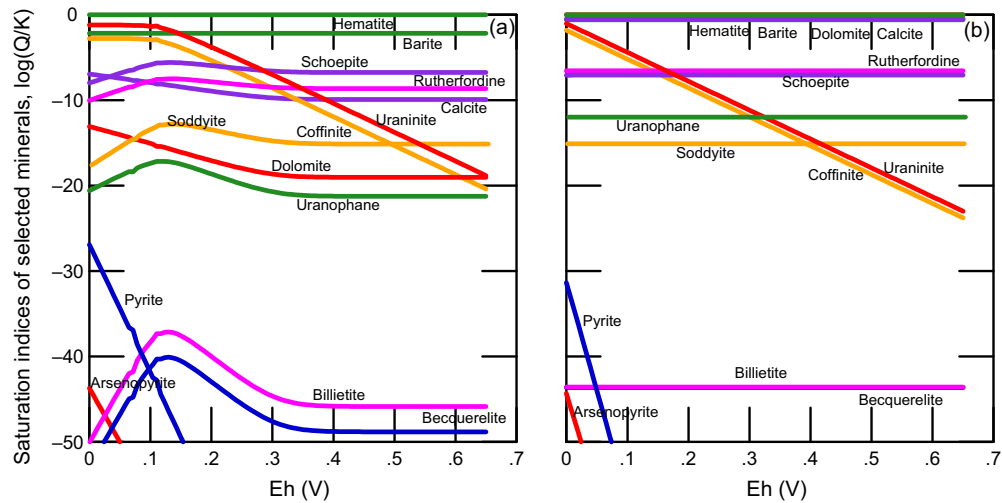
Fig. 5. Variation in saturation indices of selected minerals as a function of redox potential from oxic to suboxic conditions at 25 °C in (a) northeastern US rainwater at pH 5, and (b) typical landfill leachate at pH 8.
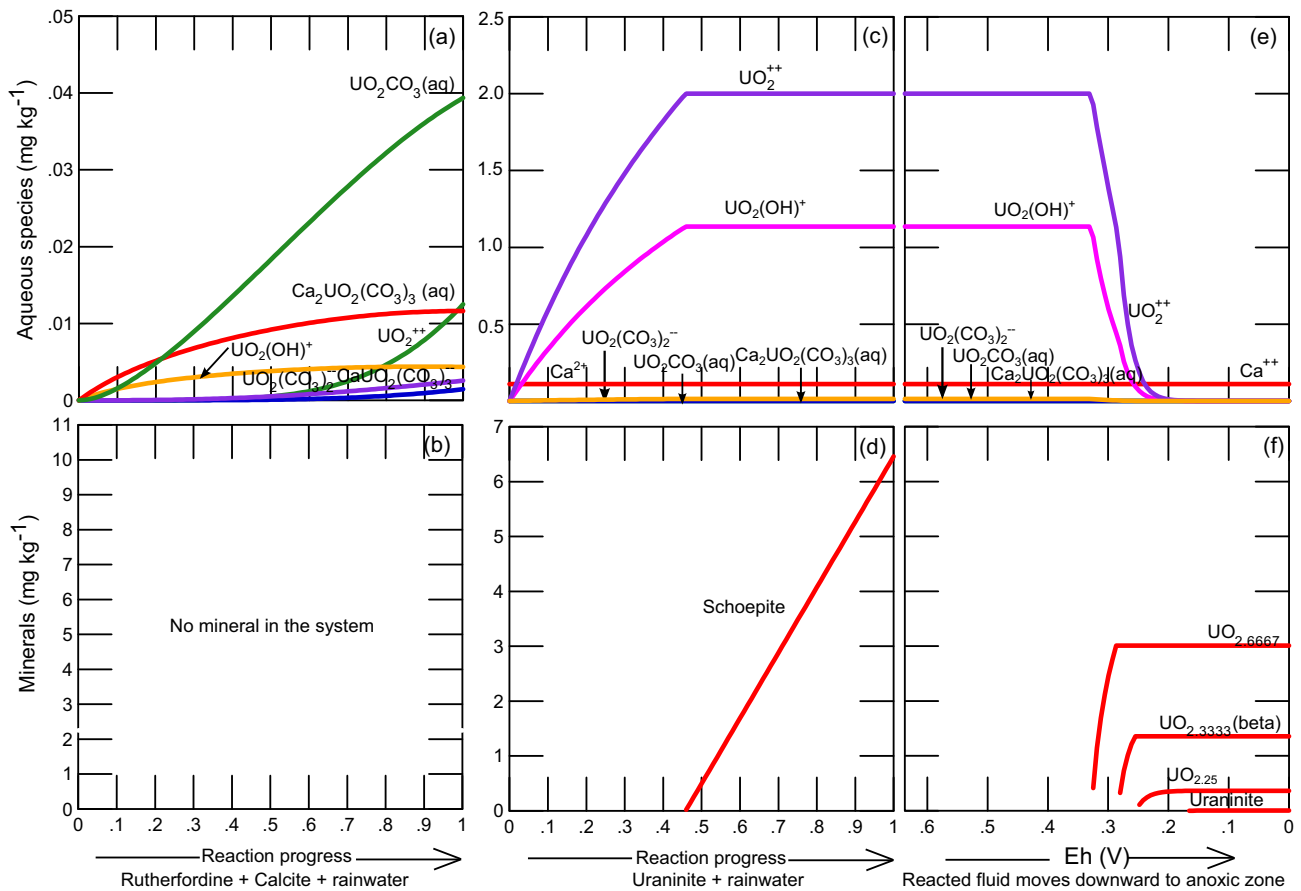

Fig. 6. Plots of model reaction progress, representing the reactions of calcite, rutherfordine (UO_2CO_3), and calcite minerals in the Marcellus drill cuttings with northeastern US rainwater under acidic (pH = 5; fixed) and oxic conditions (Eh = 0.637 V; fixed) at 25 °C. The pH, Eh, and chemistry of rainwater were actual measurements of northeastern US rainwater (Willey et al., 2012; National Atmospheric Deposition Program-USA). (a, b) 1 g of calcite and 0.07 mg of rutherfordine in 1 kg rainwater (water:rock = 100:1). Note that Ca^{2+} increases linearly to 400 mg kg^{-1} as reaction complete; no mineral formed. (c, d) 10 mg of uraninite in 1 kg rainwater (water:rock = 1:1). (e, f) This model simulates a situation in which a fluid contains rainwater after complete reaction with 10 mg of uraninite at the oxic zone and moves downward to the anoxic zone in disposal landfills (typically Eh < 0.15 V). The initial conditions for this simulation were taken from the final stage from the simulation presented in (c) and (d). The Eh is gradually decreased from 0.637 V to 0 V. Reaction progress is explained in the main text.

species such as $UO_2CO_{3(aq)}$, $Ca_2UO_2(CO_3)_{3(aq)}$, and UO_2^{2+}. The Eh–pH diagrams constructed for uranium activity in rainwater at different Ca^{2+} concentrations demonstrate that UO_2^{2+} is dominant under

acidic and oxidizing conditions. On the other hand, in the presence of Ca (activity = 10^{-3}), $Ca_2UO_2(CO_3)_{3(aq)}$ is the most dominant species under alkaline pH conditions (Fig. 7b) which is commonly

observed in surface water (Norrström and Löv, 2014; Nair et al., 2014).

Our experimental data demonstrate that the percentage of U in Marcellus drill cuttings that is susceptible to oxidative dissolution is relatively high (3–34% of the total U). Abiotic oxidation of organic matter and uraninite could occur when drill cuttings are exposed to water under oxidizing conditions; the rate of oxidation can be microbially accelerated (Edwards et al., 1999; Watzlaf and Hammack, 1989). Dissolved oxygen in rainwater is generally greater than 1.0 mg L^{-1} (Gikas and Tsihrintzis, 2012), which is sufficient to oxidize uraninite (Campbell et al., 2011; Moon et al., 2009). This is consistent with the geochemical simulation showing that uraninite is oxidized in acidic (pH 5) northeastern US rainwater under oxic conditions (Eh = 0.637 V) at 25 °C (Fig. 6c and d). The simulations show that dissolved U as UO_2^{2+} and $UO_2(OH)^+$ generated from the oxidation of uraninite, a proxy for U in the oxidizable fraction, are controlled by the solubility of schoepite (Fig. 6d). This suggests that a strategy to minimize release of U from cutting waste at drilling sites is to use lined containment and to cover exposed piles to prevent interactions with acidic rainwater.

3.4.2. Uranium mobility under anaerobic conditions

When drilling waste is covered by soil or other waste layers, decomposition and fermentation of organic matter can produce an acidic leachate (Barlaz et al., 1989) that is chemically destructive and enhances the dissolution of minerals such as carbonates (Kjeldsen et al., 2002). However, modeling shows that the lower Eh conditions in these situations are likely to enhance immobilization of U in uranium oxide minerals (Fig. 6e and f).

When the fluid resulting from the complete reaction of rainwater with uraninite at the oxic zone (Eh = 0.637 V) moves downward to the anoxic zone in disposal landfills (Eh < 0.15 V), UO_2^{2+} reduction occurs at Eh = 0.3 V (Fig. 6e), forming varying uranium oxides and apparently uraninite as Eh is further decreased (Fig. 6f).

In summary, much of the U released from either oxidation of uraninite or dissolution of U-bearing carbonate would be limited by the solubility of schoepite according to geochemical modeling results. In the presence of aqueous SiO_2 and/or Ca^{2+}, soddyite and/or uranophane were observed as secondary minerals that limit the mobility of uranium resulted from the oxidation of uraninite or

other uranium ores (Langmuir, 1997). Any excess soluble U formed under oxidizing conditions is likely to be reduced as it moves to deeper, anoxic portions of the landfill (Eh < 0.15 V), to form insoluble uranium oxides.

In cases where drill cutting waste is in contact with old leachate that is circulated to enhance waste degradation, dissolution of carbonate minerals is not likely to occur because the landfill leachates are supersaturated with calcite and dolomite minerals (Fig. 5b) at pH 8 that is commonly observed in landfill leachate (Owen and Manning, 1997). Therefore, recycling of landfill leachate for enhancing waste decomposition is unlikely to introduce the risk of U being released from calcite dissolution.

3.4.3. Arsenic mobility in landfills

In contrast with uranium, oxidation of As-bearing pyrite (modeled as a mixture of pyrite to arsenopyrite at a 2000:1 ratio) at Eh = 0.637 V does not form As-rich secondary minerals but produces soluble arsenic in arsenate forms including arsenic acid and iron arsenates (Fig. 8a), sulfate, Fe^{2+}, and $FeSO_{4(aq)}$ (Fig. 8b). When Eh is gradually decreased from 0.637 V to 0 V, sulfate reduction takes place at Eh = 0.28 V (Fig. 8e). This produces sulfide, which starts to precipitate with arsenite to form insoluble mineral, orpiment (As_2S_3), and ultimately pyrite is formed again (Fig. 8f). The Eh–pH diagrams (Fig. 9) for arsenic activities equal to or greater than those found in rainwater show that orpiment is formed under reducing conditions, which limits the solubility of arsenic.

Our experimental data suggest that As is primarily associated with pyrite, which is not likely to be released by reductive dissolution processes that act on oxides of Fe and Mn as observed in As-rich groundwater (Clancy et al., 2013; Reza et al., 2010; Smedley and Kinniburgh, 2002). Our simulations (Fig. 8) demonstrate that the oxidation of pyrite and arsenopyrite will be greatest in the top layer of the drill cutting pile where there is direct exposure of cutting waste to acidic and oxic rainwater (Descostes et al., 2004) at Eh values >0.45 V. The dissolved arsenic would be predominantly in arsenate forms (arsenic acid and iron arsenates) under acidic and oxidizing conditions (Eh > 0.55 V) and transition to arsenite form (arsenous acid) at lower Eh values (Fig. 8d).
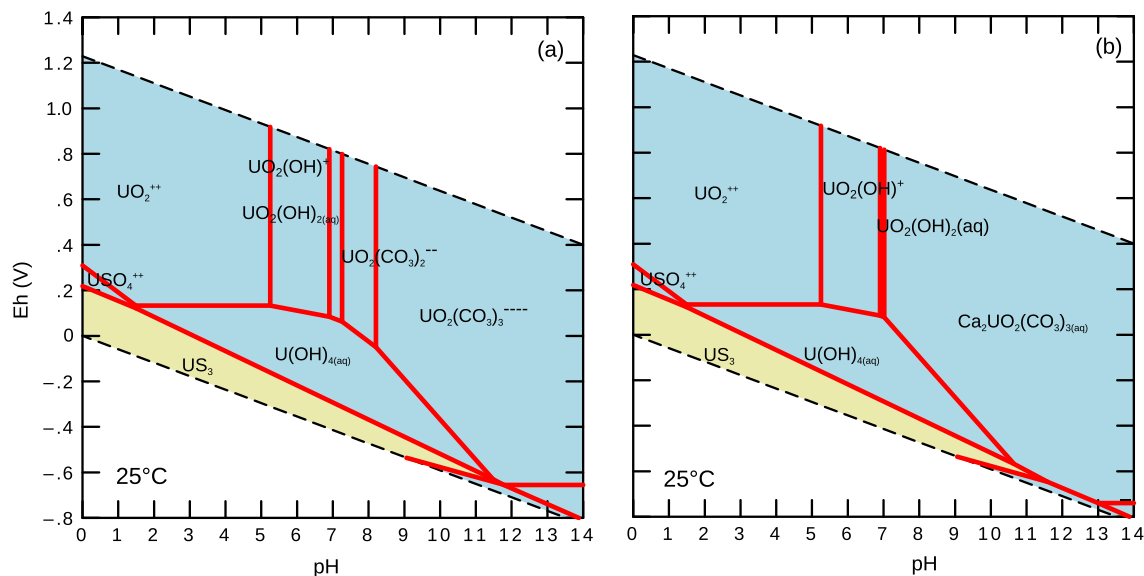

Fig. 7. Eh–pH diagrams for uranium at activity $a_{UO_2^{2+}} = 10^{-10.78}$ in the presence of northeastern US rainwater that is in equilibrium with the atmospheric CO_2 ($P_{CO2} = 10^{-3.5}$) at 25 °C, $P = 1$ bar, with the activities of Ca^{2+} as: (a) concentration of Ca^{2+} found in rainwater, $a_{UO_2^{2+}} = 10^{-10.78}$, $a_{Ca^{2+}} = 10^{-5.58}$; (b) high concentration of Ca^{2+}, $a_{UO_2^{2+}} = 10^{-10.78}$, $a_{Ca^{2+}} = 10^{-3.0}$. The solid lines represent the equilibrium boundaries between two minerals or between a mineral and aqueous species. The tan shaded areas show solid phases.
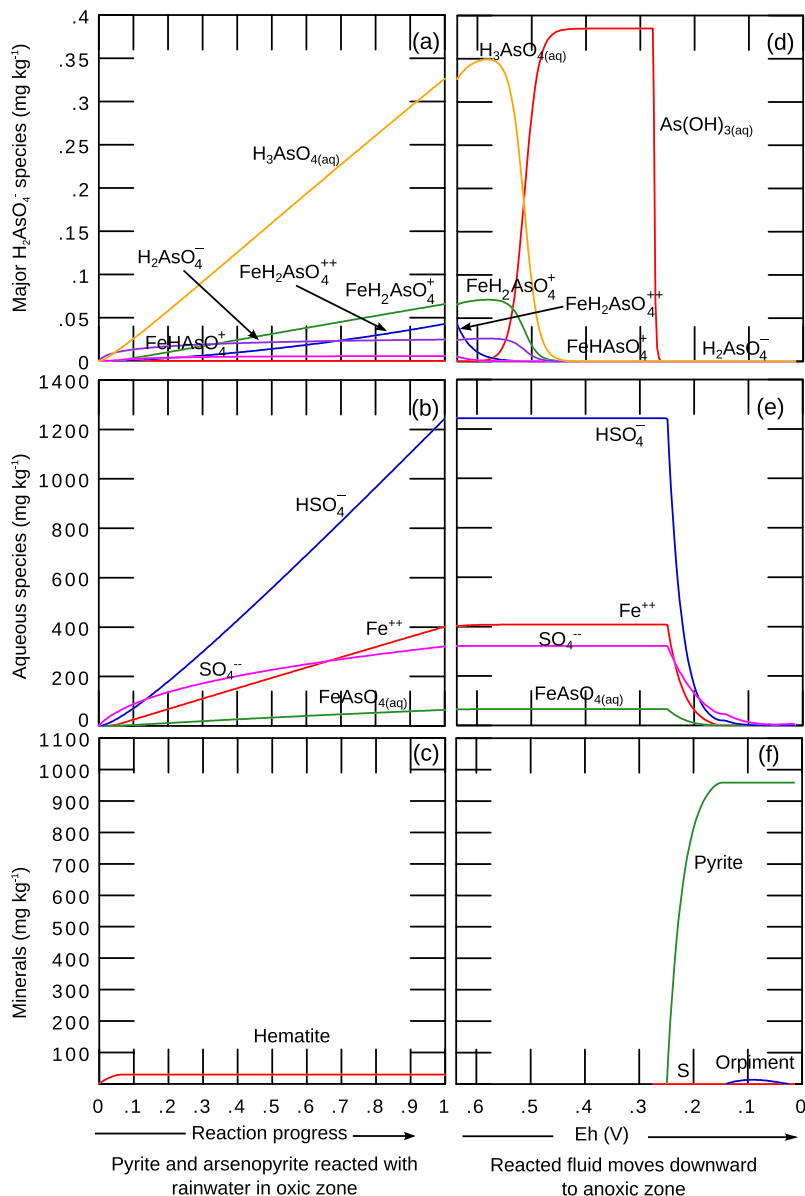
Fig. 8. Plots of model reaction progress, representing the simultaneous reactions of 1 g of pyrite and 0.5 mg of arsenopyrite minerals in the Marcellus drill cuttings with 1 kg of northeastern US rainwater at 25 °C under acidic (pH = 5; allowed to change) and oxic conditions (Eh = 0.637; fixed) (a–c). A drop in pH resulting from the oxidation of pyrite and arsenopyrite enhances carbonate dissolution, which could release more uranium. The model presented in (d–f) simulates a situation in which a fluid contains rainwater after complete reaction with 0.5 mg of arsenopyrite and 1 g of pyrite at the oxic zone and moves downward to the anoxic zone in disposal landfills (Eh < 0.15 V). The initial conditions for this simulation were taken from the final stage from the simulation presented in a, b, and c. Eh is gradually decreased from 0.637 V to 0 V.

Under the reducing conditions commonly observed in landfills (Eh < 0.15 V) (Owen and Manning, 1997), many studies showed that high arsenic water is not expected to be found in the presence of high levels of reduced sulfur, because of arsenic precipitation as secondary minerals such as orpiment and realgar (AsS) (Kirk et al., 2004; Smedley and Kinniburgh, 2002). This is consistent with the result of modeling (Fig. 8f) showing that soluble arsenic in arsenite form will be precipitated out with sulfide at Eh < 0.28 V to form insoluble orpiment.

In short, abiotic arsenopyrite and pyrite oxidation of drilling waste in contact with rainwater could lead to releasing arsenic into the aqueous phase as arsenate form under oxic conditions (Eh > 0.55 V). As the landfill leachate moves downward to the anoxic zone, the arsenate is reduced to soluble arsenite form, and further precipitated out in the presence of sulfide. Many studies have demonstrated that the oxidation of pyrite is significantly enhanced by microbial activity (Baker and Banfield, 2003; Zhu et al., 2008). This study demonstrates that overall oxidative dissolution of sulfide minerals, i.e. pyrite and arsenopyrite, in drilling waste is significant at the top waste layers and could release as much as 27–77% of the total arsenic in shale whole rocks. Therefore, this should be taken into account in planning for shale drill cutting disposal.

3.4.4. Barium mobility in landfills

The exchangeable and potentially bioavailable Ba (54–81% of all Ba released in Tioga drill cuttings, 83–89% for the Greene County core) is significant because ion exchange can rapidly occur when drill cuttings are in contact with landfill leachates or water. In a high ionic strength solution such as landfill leachate (Christensen et al., 2001), barium adsorbed on the surfaces of clay minerals and organic matter could be displaced by divalent cations
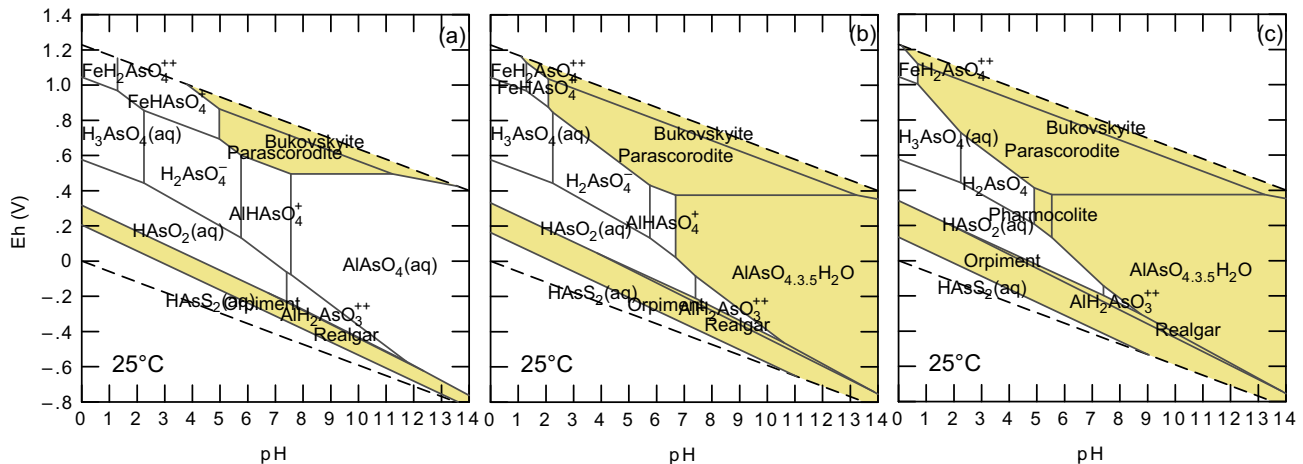
Fig. 9. Eh–pH diagrams for arsenic in the presence of northeastern US rainwater that is in equilibrium with the atmospheric CO_2 ($P_{CO2} = 10^{-3.5}$) at 25 °C, $P = 1$ bar at different activities: (a) activity found in rainwater $a_{H_2AsO_4^-} = 10^{-8.878}$; (b) activity $a_{H_2AsO_4^-} = 10^{-6}$; (c) activity $a_{H_2AsO_4^-} = 10^{-4}$. The solid lines represent the equilibrium boundaries between two minerals or between a mineral and aqueous species. The tan shaded areas show solid phases.

(Sugiyama et al., 2000), followed by formation of a soluble acetate, chloride, perchlorate, or nitrate complexes (Lamb et al., 2013). Our results indicate that this could occur relatively rapidly; an average of 40% of total Ba was extracted by 1 N ammonium acetate within four hours. Thus drill cuttings stored in contact with soil could result in Ba accumulation (with potentially phytotoxic effects) (Lamb et al., 2013) and/or subsequent migration of Ba to ground water. At disposal sites, recycling of landfill leachates to enhance waste degradation increases the risk of releasing Ba into the aqueous phase due to cation exchange of barium adsorbed on clay minerals with high ionic strength leachate. Subsequently, the released Ba would be further precipitated out as secondary minerals such as witherite ($BaCO_3$) and barite ($BaSO_4$) as predicted by a separate geochemical model (data not shown).

4. Conclusions

The rise in unconventional shale gas extraction from the Marcellus Shale and other black shales with its concomitant increase in rock waste production necessitates a greater understanding of the mineral reservoirs and processes that govern fate and transport of trace metals in these high surface area materials, as well as the role that fluid-rock interaction plays in the generation of the high TDS fluids produced from these wells, Better understanding of these processes is essential both for the development of industry best practices, and for potential resource recovery and beneficial reuse of drill cuttings and produced waters.

In this study, multi-acid digestion and sequential extraction experiments were employed to determine the partitioning of U, As, and Ba in unweathered rock samples of the Marcellus Formation and adjacent units. Uranium concentrations in whole rock ranged from 2 to 47 mg kg^{-1}. Although a core-scale positive correlation between U and OM in shale has been observed in some studies, our data indicate that U in the Marcellus Shale and associated rocks is primarily held in silicate and carbonate minerals. In contrast, up to 77% of total As in shales (16–90 mg kg^{-1}) is associated with sulfide minerals such as arsenopyrite. Barium concentrations extracted from the exchange sites in shale samples are greater than all other extractable fractions combined, and vary geographically (61–74% in Tioga County, NY whereas 9–31% in Greene County, PA). This suggests that Ba released from exchange sites could contribute to the high Ba content observed in produced water. On the other hand, the risk associated with the release of Ba in landfills is not a great concern if the landfill leachate collection system is properly constructed.

Geochemical simulations of the interaction of black shale drill cuttings with rainwater and/or landfill leachates under typical storage environments suggest that carbonate or sulfide mineral dissolution could mobilize arsenic and uranium. Landfills and temporary storage pits of fresh cutting waste at drilling sites should be adequately covered and lined to prevent interaction with rainwater or other low pH waters such as acid mine drainage under oxic (Eh > 0.3) conditions in order to minimize carbonate dissolution and the oxidation of uraninite. Recycling of landfill leachate could reduce the extent of carbonate dissolution. The presence of aqueous silica, calcium, and phosphate in interacting fluids can also mitigate this risk by enhancing the formation of insoluble minerals such as uranophane and soddyite. Arsenic released from the oxidation of pyrite and arsenopyrite by rainwater under similar conditions remains soluble as either arsenate or arsenite. However, under the conditions commonly generated during the methanogenic/sulfate reducing stage in disposal landfills, arsenic is incorporated into insoluble sulfide minerals (e.g. orpiment) and soluble hexavalent uranium is reduced to form insoluble uranium oxides. The actual rate of the processes discussed above would vary depending on the water:rock ratio and grain size/surface area of the drill cuttings, as well as on the environmental conditions of the storage area.

To prevent migration of U, As and Ba into soil or groundwater systems, landfill leachates should be regularly monitored to account for changes in chemistry (e.g., Eh, pH, dissolved load) that could portend release of these elements. Leachate from the landfills that accept Marcellus drill cuttings should be properly treated. Beneficial reuse of drill cuttings as roadside base or as part of wetland restoration should also account for potential pyrite oxidation and carbonate dissolution. Prior to disturbance or relocation of landfill material in which U and As may be immobilized in secondary minerals, consideration should be given to changes in chemical conditions that could result in remobilization of these elements.

Disclaimer

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apgeochem.2015.01.013.

References

Baker, B.J., Banfield, J.F., 2003. Microbial communities in acid mine drainage. FEMS Microbiol. Ecol. 44, 139–152.

Ball, A.S., Stewart, R.J., Schliephake, K., 2012. A review of the current options for the treatment and safe disposal of drill cuttings. Waste Manage. Res. 30, 457–473.

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.

Barlaz, M., Schaefer, D., Ham, R., 1989. Bacterial population development and chemical characteristics of refuse decomposition in a simulated sanitary landfill. Appl. Environ. Microbiol. 55, 55–65.

Barry, B., Klima, M.S., 2013. Characterization of Marcellus Shale natural gas well drill cuttings. J. Unconv. Oil Gas Resour. 1–2, 9–17.

Bethke, C., 2008. Geochemical and Biogeochemical Reaction Modeling. Cambridge University Press, Cambridge.

Blauch, M., Myers, R., Moore, T., Lipinski, B., Houston, N., 2009. Marcellus Shale Post-frac Flowback Waters – Where is all the Salt Coming from and what are the Implications?, SPE Eastern Regional Meeting.

Campbell, K.M., Veeramani, H., Ulrich, K.-U., Blue, L.Y., Giammar, D.E., Bernier-Latmani, R., Stubbs, J.E., Suvorova, E., Yabusaki, S., Lezama-Pacheco, J.S., Mehta, A., Long, P.E., Bargar, J.R., 2011. Oxidative dissolution of biogenic uraninite in groundwater at Old Rifle, CO. Environ. Sci. Technol. 45, 8748–8754.

Capo, R.C., Stewart, B.W., Rowan, E., Kolesar, C.A., Wall, A.J., Chapman, E.C., Hammack, R.W., Schroeder, K.T., 2014. The strontium isotope evolution of Marcellus Formation produced waters, Southwestern Pennsylvania. Int. J. Coal Geol. 126, 57–63.

Cathles, L.M., 2012. Assessing the greenhouse impact of natural gas. Geochem. Geophys. Geosyst. 13. http://dx.doi.org/10.1029/2012GC004032.

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.

Chen, F., Ewing, R.C., Clark, S.B., 1999. The Gibbs free energies and enthalpies of formation of U^{6+} phases: an empirical method of prediction. Am. Mineral. 84, 650–664.

Chermak, J.A., Schreiber, M.E., 2014. Mineralogy and trace element geochemistry of gas shales in the United States: environmental implications. Int. J. Coal Geol. 126, 32–44.

Christensen, T.H., Kjeldsen, P., Bjerg, P.L., Jensen, D.L., Christensen, J.B., Baun, A., Albrechtsen, H.-J., Heron, G., 2001. Biogeochemistry of landfill leachate plumes. Appl. Geochem. 16, 659–718.

Clancy, T.M., Hayes, K.F., Raskin, L., 2013. Arsenic waste management: a critical review of testing and disposal of arsenic-bearing solid wastes generated during arsenic removal from drinking water. Environ. Sci. Technol. 47, 10799–10812.

Dale, A.T., Khanna, V., Vidic, R.D., Bilec, M.M., 2013. Process based life-cycle assessment of natural gas from the Marcellus Shale. Environ. Sci. Technol. 47, 5459–5466.

Descostes, M., Vitorge, P., Beaucaire, C., 2004. Pyrite dissolution in acidic media. Geochim. Cosmochim. Acta 68, 4559–4569.

Dong, W., Brooks, S.C., 2006. Determination of the formation constants of ternary complexes of uranyl and carbonate with alkaline Earth metals (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) using anion exchange method. Environ. Sci. Technol. 40, 4689–4695.

Dresel, P.E., Rose, A.W., 2010. Chemistry and origin of oil and gas well brines in western Pennsylvania: Pennsylvania Geological Survey, 4th ser., Open-File Report OFOG 10–01.0, p. 48.

Duan, Y., Severmann, S., Anbar, A.D., Lyons, T.W., Gordon, G.W., Sageman, B.B., 2010. Isotopic evidence for Fe cycling and repartitioning in ancient oxygen-deficient settings: examples from black shales of the mid-to-late Devonian Appalachian Basin. Earth Planet. Sci. Lett. 290, 244–253.

Eary, L.E., Barnes, H.L., Cathles, L.M., 1986. Acidic rate-controlled and flow-controlled dissolution of uraninite ores. Metall. Trans. B, Process. Metall. 17, 405–413.

Edwards, K.J., Goebel, B.M., Rodgers, T.M., Schrenk, M.O., Gihring, T.M., Cardona, M.M., Mcguire, M.M., Hamers, R.J., Pace, N.R., Banfield, J.F., 1999. Geomicrobiology of pyrite (FeS_2) dissolution: case study at Iron Mountain, California. Geomicrobiol. J. 16, 155–179.

Engelder, T., Lash, G.G., 2008. Marcellus Shale Play's Vast Resource Potential Creating Stir in Appalachia. The American Oil & Gas Reporter.

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.

Ewing, R., Tierney, M., Konikow, L., Rechard, R., 1999. Performance assessments of nuclear waste repositories: a dialogue on their value and limitations. Risk Anal. 19, 933–958.

Ferrar, K.J., Michanowicz, D.R., Christen, C.L., Mulcahy, N., Malone, S.L., Sharma, R.K., 2013. Assessment of effluent contaminants from three facilities discharging Marcellus Shale wastewater to surface waters in Pennsylvania. Environ. Sci. Technol. 47, 3472–3481.

Fortson, L., 2012. Geochemical and Spatial Investigation of Uranium in the Marcellus Shale. M.Sc. Thesis, State University of New York at Buffalo.

Geipel, G., Amayri, S., Bernhard, G., 2008. Mixed complexes of alkaline earth uranyl carbonates: a laser-induced time-resolved fluorescence spectroscopic study. Spectrochim. Acta, Part A: Mol. Biomol. Spectrosc. 71, 53–58.

Gikas, G.D., Tsihrintzis, V.A., 2012. Assessment of water quality of first-flush roof runoff and harvested rainwater. J. Hydrol. 466–467, 115–126.

Gonneea, M.E., Paytan, A., 2006. Phase associations of barium in marine sediments. Mar. Chem. 100, 12.

Gregory, K.B., Vidic, R.D., Dzombak, D.A., 2011. Water management challenges associated with the production of shale gas by hydraulic fracturing. Elements 7, 181–186.

Guillaumont, R., Fanghänel, T., Fuger, J., Grenthe, I., Neck, V., Palmer, D., Rand, M.H., 2003. Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium. Elsevier, Amsterdam.

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.

Hayes, T., 2009. Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas. Marcellus Shale Coalition, Gas Technology Institute, Des Plaines, IL.

Howarth, R.W., Ingraffea, A., Engelder, T., 2011. Natural gas: should fracking stop? Nature 477, 271–275.

Jin, L., Mathur, R., Rother, G., Cole, D., Bazilevskaya, E., Williams, J., Carone, A., Brantley, S., 2013. Evolution of porosity and geochemistry in Marcellus Formation black shale during weathering. Chem. Geol. 356, 50–63.

Johnson, J.D., Graney, J.R., 2011. Coupling Lead Isotope Ratios and Element Concentrations to Track Processes Involved in Resource Extraction from the Marcellus Shale. Geological Society of America, p. 566.

Johnson, J.D., Graney, J.R., 2015. Fingerprinting Marcellus Shale waste products from Pb isotope and trace metal perspectives. Appl. Geochem. 60, 104–115.

Kanematsu, M., Perdrial, N., Um, W., Chorover, J., O'Day, P.A., 2014. Influence of phosphate and silica on U(VI) precipitation from acidic and neutralized wastewaters. Environ. Sci. Technol. 48, 6097–6106.

Kargbo, D.M., Wilhelm, R.G., Campbell, D.J., 2010. Natural gas plays in the Marcellus Shale: challenges and potential opportunities. Environ. Sci. Technol. 44, 5679–5684.

Kirk, M.F., Holm, T.R., Park, J., Jin, Q., Sanford, R.A., Fouke, B.W., Bethke, C.M., 2004. Bacterial sulfate reduction limits natural arsenic contamination in groundwater. Geology 32, 953–956.

Kjeldsen, P., Barlaz, M.A., Rooker, A.P., Baun, A., Ledin, A., Christensen, T.H., 2002. Present and long-term composition of MSW landfill leachate: a review. Crit. Rev. Environ. Sci. Technol. 32, 297–336.

Kochenov, A.V., Baturin, G.N., 2002. The paragenesis of organic matter, phosphorus, and uranium in marine sediments. Lithol. Min. Resour. 37, 107–120.

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. Petrol. Geol. Bull. 98, 483–513.

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.

Lamb, D.T., Matanitobua, V.P., Palanisami, T., Megharaj, M., Naidu, R., 2013. Bioavailability of barium to plants and invertebrates in soils contaminated by barite. Environ. Sci. Technol. 47, 4670–4676.

Langmuir, D., 1997. Aqueous Environmental Geochemistry. Prentice Hall, Upper Saddle River, New Jersey.

Lavergren, U., Astrom, M.E., Bergbäck, B., Holmström, H., 2009. Mobility of trace elements in black shale assessed by leaching tests and sequential chemical extraction. Geochem.: Explor. Environ., Anal. 9, 71–79.

Leventhal, J.S., 1981. Pyrolysis-gas chromatography to characterize organic matter and its relationship to uranium in Appalachian Devonian shales. Geochim. Cosmochim. Acta 45, 883–889.

Leventhal, J.S., 1991. Comparison of organic geochemistry and metal enrichment in two black shales: Cambrian Alum Shale of Sweden and Devonian Chattanooga Shale of United States. Miner. Depos. 26, 104–112.

Leventhal, J.S., Crock, J.G., Malcolm, M.J., 1981. Geochemistry of Trace Elements and Uranium in Devonian Shales of the Appalachian Basin. Open File Report 81-778. United States Department of the Interior Geological Survey.

Lüning, S., Kolonic, S., 2003. Uranium spectral gamma-ray response as a proxy for organic richness in black shales: applicability and limitations. J. Petrol. Geol. 26, 153–174.

Lutz, B.D., Lewis, A.N., Doyle, M.W., 2013. Generation, transport, and disposal of wastewater associated with Marcellus Shale gas development. Water Resour. Res. 49, 647–656.

Maher, K., Bargar, J.R., Brown, G.E., 2012. Environmental speciation of actinides. Inorg. Chem. 52, 3510–3532.

Maloney, K.O., Yoxtheimer, D.A., 2012. Production and disposal of waste materials from gas and oil extraction from the Marcellus Shale play in Pennsylvania. Environ. Pract. 14, 278–287.

Molofsky, L.J., Connor, J.A., Wylie, A.S., Wagner, T., Farhat, S.K., 2013. Evaluation of methane sources in groundwater in Northeastern Pennsylvania. Ground Water 51, 333–349.

Moon, H.S., Komlos, J., Jaffé, P.R., 2009. Biogenic U(IV) oxidation by dissolved oxygen and nitrate in sediment after prolonged U(VI)/Fe(III)/SO$_4^{2-}$ reduction. J. Contam. Hydrol. 105, 18–27.

Morse, J.W., Arvidson, R.S., 2002. The dissolution kinetics of major sedimentary carbonate minerals. Earth-Sci. Rev. 58, 51–84.

Muramatsu, Y., Tagami, K., Uchida, S., 1994. Levels of artificial radionuclides and uranium in rain water collected from Ibaraki (Japan) following the Tomsk-7 accident in Russia. J. Radioanal. Nucl. Chem. 188, 305–311.

Nair, S., Karimzadeh, L., Merkel, B., 2014. Surface complexation modeling of uranium(VI) sorption on quartz in the presence and absence of alkaline earth metals. Environ. Earth Sci. 71, 1737–1745.

Nordstrom, D.K., Campbell, K.M., 2014. Modeling low-temperature geochemical processes. In: Holland, H.D., Turekian, K.K. (Eds.), Treatise on Geochemistry, second ed., vol. 7. Elsevier, Oxford, pp. 27–68.

Nordstrom, D.K., Majzlan, J., Königsberger, E., 2014. Thermodynamic properties for arsenic minerals and aqueous species. Rev. Mineral. Geochem. 79, 217–255.

Norrström, A.C., Löv, Å., 2014. Uranium theoretical speciation for drinking water from private drilled wells in Sweden – implications for choice of removal method. Appl. Geochem. 51, 148–154.

Ohio Department of Natural Resources. Fact Sheet: Drill Cuttings from Oil and Gas Exploration in the Marcellus and Utica Shale Regions of Ohio. <http://oilandgas. ohiodnr.gov/portals/oilgas/pdf/Fact%20Sheet%20on%20Drilling%20Muds.pdf> (accessed 10.07.14).

Osborn, S.G., Vengosh, A., Warner, N.R., Jackson, R.B., 2011. Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. Proc. Natl. Acad. Sci. USA 108, 8172–8176.

Owen, J., Manning, D., 1997. Silica in landfill leachates: implications for clay mineral stabilities. Appl. Geochem. 12, 267–280.

Pennsylvania Department of Environmental Protection, 2011. Marcellus Shale. <http://www.portal.state.pa.us/portal/server.pt/community/marcellus_shale/ 20296> (accessed 10.07.14).

Pennsylvania Department of Environmental Protection, 2012. DEP Announces Comprehensive Oil and Gas Development Radiation Study. <http://www.portal. state.pa.us/portal/server.pt/community/newsroom/14287?id=19827&typeid= 1> (accessed 10.07.14).

Pennsylvania Department of Environmental Protection, 2014. PA DEP Oil & Gas Reporting Website. <https://www.paoilandgasreporting.state.pa.us/ publicreports/Modules/Welcome/Welcome.aspx> (accessed 29.09.14).

Peper, S.M., Brodnax, L.F., Field, S.E., Zehnder, R.A., Valdez, S.N., Runde, W.H., 2004. Kinetic study of the oxidative dissolution of UO$_2$ in aqueous carbonate media. Ind. Eng. Chem. Res. 43, 8188–8193.

Pereira, C.D., Garcia, E.E., Silva, F.V., Nogueira, A.R.A., Nóbrega, J.A., 2010. Behaviour of arsenic and selenium in an ICP-QMS with collision and reaction interface. J. Anal. At. Spectrom. 25, 1763–1768.

Prikryl, J.D., Murphy, W.M., 2001. The solubility of uranophane under oxidizing conditions in CaCl$_2$ and SiO$_2$(aq) test solutions. In: 8th International Conference on the Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere, Migration '01, Bregenz, Austria, September 16–21, 2001.

Pruszkowski, E., Bosnak, C.P., 2012. The Analysis of Drinking Waters by U.S. EPA Method 200.8 Using the NexION 300D ICP-MS in Standard, Collision and Reaction Modes. Perkin Elmer Application Note.

Quejido, A.J., Pérez del Villar, L., Cózar, J.S., Fernández-Díaz, M., Crespo, M.T., 2005. Distribution of trace elements in fracture fillings from the "Mina Fe" uranium deposit (Spain) by sequential leaching: implications for the retention processes. Appl. Geochem. 20, 487–506.

Reza, A.H.M.S., Jean, J.-S., Lee, M.-K., Yang, H.-J., Liu, C.-C., 2010. Arsenic enrichment and mobilization in the Holocene alluvial aquifers of the Chapai-Nawabganj district, Bangladesh: a geochemical and statistical study. Appl. Geochem. 25, 1280–1289.

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. US Department of the Interior, US Geological Survey, Reston, Virginia.

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, 10.1306/07071413146.

Schmidt, C.W., 2013. Estimating wastewater impacts from fracking. Environ. Health Perspect. 121, A117.

Shaffer, D.L., Arias Chavez, L.H., Ben-Sasson, M., Romero-Vargas Castrillón, S., Yip, N.Y., Elimelech, M., 2013. Desalination and reuse of high-salinity shale gas produced water: drivers, technologies, and future directions. Environ. Sci. Technol. 47, 9569–9583.

Shvareva, T.Y., Mazeina, L., Gorman-Lewis, D., Burns, P.C., Szymanowski, J.E., Fein, J.B., Navrotsky, A., 2011. Thermodynamic characterization of boltwoodite and uranophane: enthalpy of formation and aqueous solubility. Geochim. Cosmochim. Acta 75, 5269–5282.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Appl. Geochem. 17, 517–568.

Soeder, D.J., 2012. Shale gas development in the United States. In: Al-Megren, H. (Ed.), Advances in Natural Gas Technology.

Soeder, D.J., Sharma, S., Pekney, N., Hopkinson, L., Dilmore, 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.

Souther, S., 2013. Drawbacks to natural gas. Science 340, 141.

Spivak-Birndorf, L.J., 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.

States, S., Cyprych, G., Stoner, M., Wydra, F., Kuchta, J., Monnell, J., Casson, L., 2013. Marcellus Shale drilling and brominated THMs in Pittsburgh, Pa., drinking water. J. Am. Water Works Assoc. 105, E432–E448.

Stewart, B.W., Chapman, E.C., Capo, R.C., Johnson, J.D., Graney, J.R., Kirby, C.S., Schroeder, K.T., 2015. Origin of brines, salts and carbonate from shales of the Marcellus Formation: evidence from geochemical and Sr isotope study of sequentially extracted fluids. Appl. Geochem. 60, 78–88.

Sugiyama, S., Matsumoto, H., Hayashi, H., Moffat, J.B., 2000. Sorption and ion-exchange properties of barium hydroxyapatite with divalent cations. Colloids Surf., Physicochem. Eng. Aspects 169, 17–26.

Swanson, V.E., 1961. Geology and Geochemistry of Uranium in Marine Black Shales: A Review. US Government Printing Office, Washington, DC.

Tang, G., Luo, W., Brooks, S.C., Watson, D.B., Gu, B., 2013. Prediction of aluminum, uranium and co-contaminants precipitation and adsorption during titration of acidic sediments. Environ. Sci. Technol. 47, 5787–5793.

Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace-metals. Anal. Chem. 51, 844–851.

Tuttle, M.L.W., Breit, G.N., Goldhaber, M.B., 2009. Weathering of the New Albany Shale, Kentucky: II. Redistribution of minor and trace elements. Appl. Geochem. 24, 1565–1578.

United States Department of Environmental Conservation New York State, 2011. Supplemental Generic Environmental Impact Statement (SGEIS) On the Oil, Gas and Solution Mining Regulatory Program, New York State.

United States Environmental Protection Agency, 2002. Exemption of Oil and Gas Exploration and Production Wastes from Federal Hazardous Waste Regulations.

Vengosh, A., Jackson, R.B., Warner, N., 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. http://dx.doi.org/10.1021/es405118y.

Vidic, R.D., Brantley, S.L., Vanderbossche, J.M., Yoxtheimer, D., Abad, J.D., 2013. Impact of shale gas development on regional water quality. Science 340. http://dx.doi.org/10.1126/science.1235009.

Vine, J.D., 1969. Element Distribution in Some Paleozoic Black Shales and Associated Rocks. US Government Printing Office.

Wang, G., Carr, T.R., 2012. Methodology of organic-rich shale lithofacies identification and prediction: a case study from Marcellus Shale in the Appalachian Basin. Comput. Geosci. 49, 151–163.

Wang, G., Carr, Timothy.R., 2013. Organic-rich Marcellus Shale lithofacies modeling and distribution pattern analysis in the Appalachian Basin. AAPG Bull. 97, 2173–2205.

Warner, N.R., Jackson, R.B., Darrah, T.H., Osborn, S.G., Down, A., Zhao, K., White, A., Vengosh, A., 2012. Geochemical evidence for possible natural migration of Marcellus Formation brine to shallow aquifers in Pennsylvania. Proc. Natl. Acad. Sci. USA 109, 11961–11966.

Watzlaf, G.R., Hammack, R.W., 1989. The effect of oxygen, iron-oxidizing bacteria, and leaching frequency on pyrite oxidation. In: Proc. 9th Annual West Virginia Surface Mine Drainage Task Force Symp., Morgantown, WV.

Whitacre, J.V., 2014. Carnegie Museum of Natural History Pennsylvania Unconventional Natural Gas Wells Geodatabase (v.2014-Q4) [Computer File]. Carnegie Museum of Natural History, Pittsburgh, PA. <http://www.carnegiemnh.org/science/default.aspx?id=18716> (accessed 13.07.14).

Willey, J.D., Mullaugh, K.M., Kieber, R.J., Avery, G.B., Mead, R.N., 2012. Controls on the redox potential of rainwater. Environ. Sci. Technol. 46, 13103–13111.

Willis, S.S., Johannesson, K.H., 2011. Controls on the geochemistry of rare earth elements in sediments and groundwaters of the Aquia aquifer, Maryland, USA. Chem. Geol. 285, 32–49.

Wilson, J.M., VanBriesen, J.M., 2013. Source water changes and energy extraction activities in the Monongahela River, 2009–2012. Environ. Sci. Technol. 47, 12575–12582.

Yokoyama, T., Makishima, A., Nakamura, E., 1999. Evaluation of the coprecipitation of incompatible trace elements with fluoride during silicate rock dissolution by acid digestion. Chem. Geol. 157, 175–187.

Zhu, W., Young, L.Y., Yee, N., Serfes, M., Rhine, E.D., Reinfelder, J.R., 2008. Sulfide-driven arsenic mobilization from arsenopyrite and black shale pyrite. Geochim. Cosmochim. Acta 72, 5243–5250.